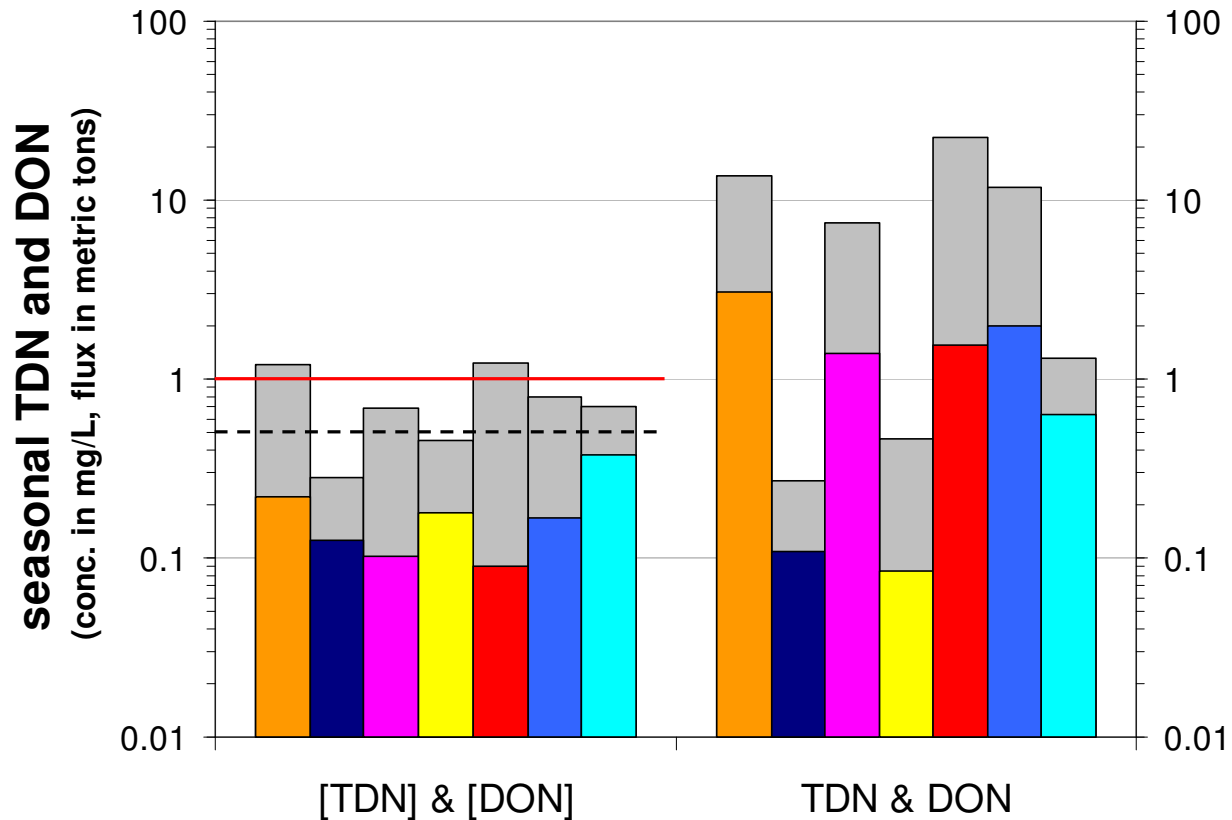


This is a graph of seasonal TDN and DON (well almost, it's really TDN minus nitrate which yields DON plus ammonium (TKN); however ammonium concentrations are almost always negligible) for all Ventura locations that usually have dry-season flow (eliminating VR04, 05, 11 & 12). By seasonal, I mean average concentrations from May through September. The colors sequentially represent seasonal DON concentrations for 2005, 06 and 07, the grey background bars seasonal TDN for the same years. (I have a similar graph showing data from 2001 but the added complexity makes it harder to describe and understand.)

TDN measures nitrogen availability for biological productivity and I'm going to consider DON a measure of that productivity since its principle origin is in dead cells and exuded organic matter (primarily from within the stream itself during the dry season). My first point is that TDN varies considerably between sites (2 orders-of-magnitude) while DON does not (less than an order-of-magnitude at most, and it was markedly consistent between sites in 2007). Second, nitrogen is under-utilized at almost all sites except VR08, VR13-15 and, occasionally (2007), VR01 (most nitrogen remains in the form of nitrate – keep in mind that using a log scale minimizes differences between TDN and DON). Third, the general pattern has been an *increase* in DON concentrations from 2005 to 2007, and the *relative amount* of DON (as a percentage of TDN) has also increased in each subsequent year (the exceptions being VR08 and 10).

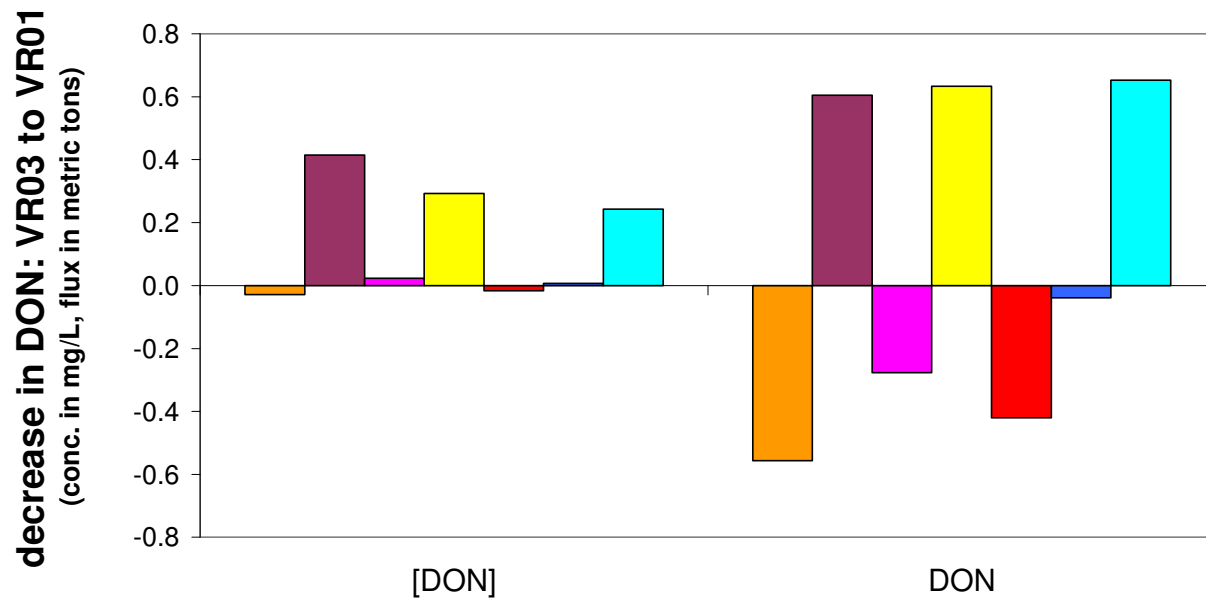
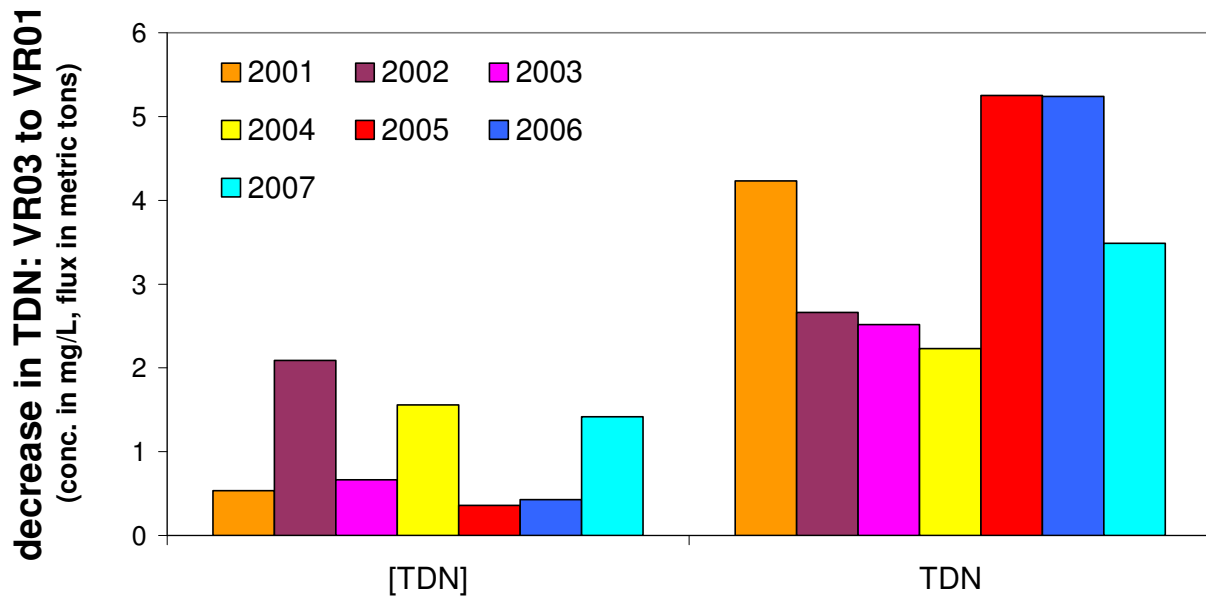
Can we then conclude that productivity (with algal growth a major contributor) has increased since 2005, and that, especially in 2007, most of the sites were more-or-less equally productive? *No*, or at least not yet, because the influence of biological productivity on in-stream concentrations is also highly dependent on the volume of stream flow. As flow decreases the same amount of productivity will have an increasing influence on nutrient concentrations and other stream parameters (such as dissolved oxygen).



To illustrate the importance of flux (the product of concentration multiplied by flow) the above graph shows seasonal (May-September) TDN and DON concentrations (in brackets, i.e., [TDN]) and fluxes at Foster Park (VR06). The different colors again indicate DON in sequential years since 2001 and the background grey bars TDN concentrations and fluxes. Note that seasonal TDN and DON concentrations at Foster Park are relatively consistent from year to year, but the seasonal flux can vary by almost 2 orders-of-magnitude (i.e., 100-fold). At this location there is always enough nitrogen – TDN *always* exceeds DON concentrations and nitrate is *always* present (the average monthly nitrate concentration during the season is 0.6 mg/L). At this site other factors, sunlight, wetted area, stream velocity, etc., control algal growth, not nutrient availability.

While DON concentrations steadily increased from 2005 through 2007, the DON flux shows a more complicated picture. If the DON flux is considered a measure of biological productivity, seasonal productivity slightly increased from 2005 to 2006 (1.6 to 2.0 metric tons of DON exported), and then appreciably decreased in 2007 (0.6 tons – again, log scales can fool the eye). While total productivity in 2007 (measured by the DON flux) dropped to almost a third of what it was in 2005 and 2006, *relative productivity* (relative to the amount of available nitrogen and flow) increased over the three years from 7 to 21 to 53 %, respectively, as measured by the percent of DON to TDN.

Years of low productivity, 2002 and 2004, were years of low flow, even though the proportions of the seasonal DON to TDN ratio were relatively high: 45 and 39 %, respectively. In contrast, high flow years, 2003 (the year of Julie’s study) and 2005 had low percentages of DON: 14 and 7 %, respectively.



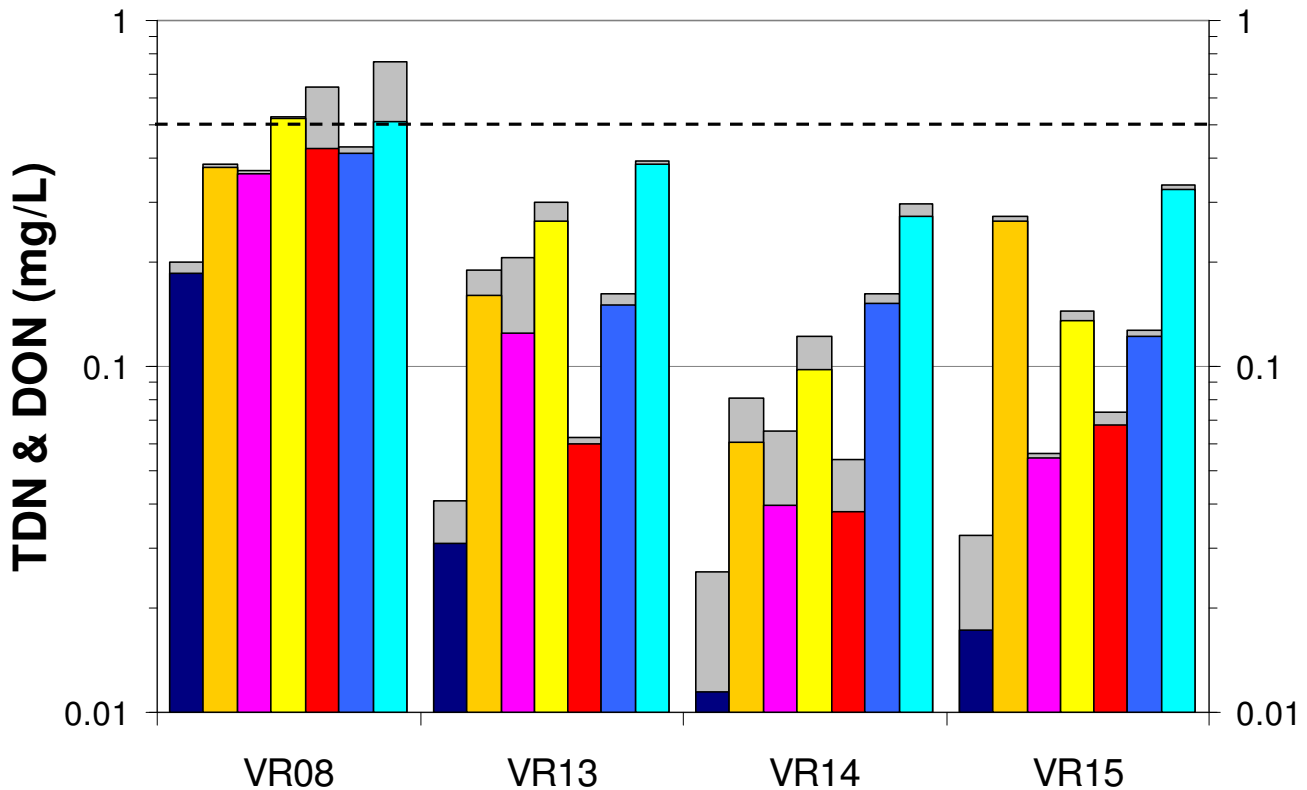
Of course, the flux at a specific site doesn't mean that it was produced at that location. Rather, it represents the culmination of a multitude of upstream processes – how far upstream remains an open question. The answer being dependent on the parameter being measured and the magnitude of the dominating process. At VR06 (the previous slide) the dominating reach is relatively short since during the dry season the main stem of the river is dry and contributions from San Antonio Creek are usually non-existent or minor. Since dry season flow below the Ojai treatment plant is relatively constant, the change in nitrogen concentrations between VR03 and VR01 (tidal limit) gives us a defined reach where we can measure the flux changes between two points and speculate as to the reasons for inter-annual differences. The upper panel in the figure shows the decrease in TDN concentration and flux in this reach – nitrate and TDN *always* decrease due to uptake and (possibly) denitrification. The decrease in TDN concentration was greater in dry years (2002, 04, 07) than in wet (2001, 03, 05, 06).

The cause of greater dry-year decreases in TDN is primarily due to the principal mentioned earlier: it's easier for biological processes (indeed, any process) to change the characteristics of a smaller volume (or flow) of water than a larger. The average seasonal flow (at Foster Park) during the 3 dry-years was 3 cfs compared with 28 cfs during the 4 wet-years. However, inter-annual variations in the seasonal TDN flux decrease presents a more complicated picture than the changes in concentration. The decrease in TDN during the 2002 and 2004 dry years was, as could be expected, smaller than during the 2001, 2005 and 2006 wet years. But the flux during relatively wet-year of 2003 was lower than that of the 2007 dry-year. That 2003 was a relatively "low" wet-year (average seasonal flow of 15 cfs) and 2007 a relatively "high" dry-year (5 cfs) is part of the explanation. However, looking more closely at the data, it also appears that the decrease in TDN concentrations between the two locations is noticeably lower in algal dominated years in contrast with years that are plant dominated. Aquatic plants were more prevalent on the lower river in 2007. The reduced differences in flow, combined with a greater 2007 concentration decrease, create the anomaly.

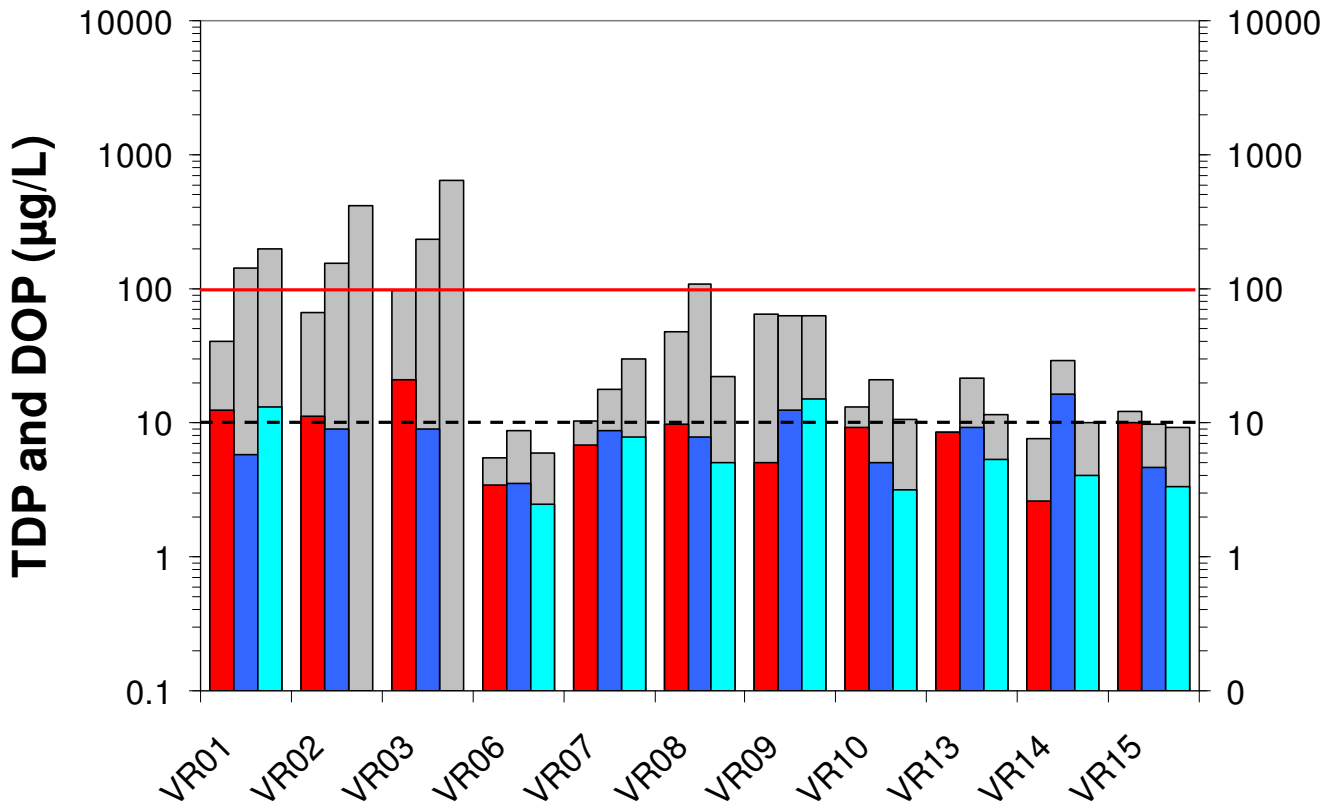
Turning to the change in seasonal (May through September) DON concentrations and fluxes between VR03 and VR01, the picture (lower panel) changes completely. No longer is there a reliable decrease with flow downstream (as seen for nitrate and TDN), instead, concentrations, and the flux, can either increase or decrease. DON concentrations appreciably decreased during dry-years and either increased (negative bars in 2001, 05) or decreased only slightly (2003, 06) during wet years. The pattern in seasonal flux changes is even clearer: an increase in the DON flux during wet-years (negative bars), a decrease during dry. Considering that wet-years are always years of algal dominance, and dry-years are usually dominated by plants, suggests that this is the explanation. Algae, with their much shorter life cycles, simply leak greater amounts of DON into the stream. Plants endure – usually until washed out in flood flows as particulate matter.

Unfortunately, this rather elegant and satisfying explanation (to me at least) reduces the utility of using differences in the DON flux as a measure of biological productivity. I believe it to still be useful when looking at algal productivity, or any sort of biological productivity characterized by short life cycles of growth, senescence and death, where the seasonal flux approximately captures the entire cycle from beginning to end and most of the transport of organic nitrogen is in dissolved rather than particulate forms.

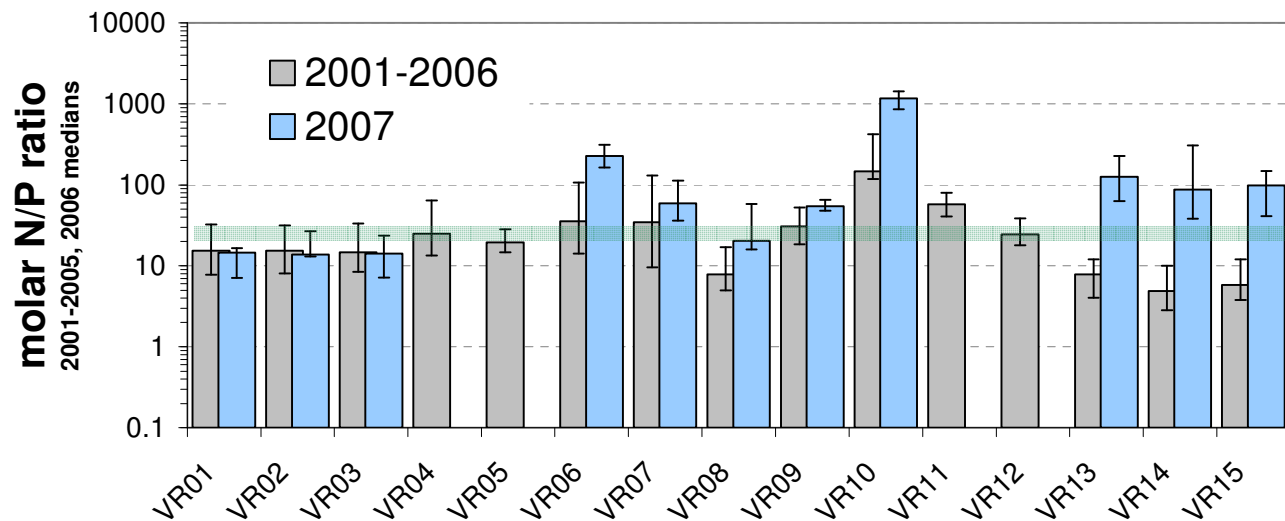
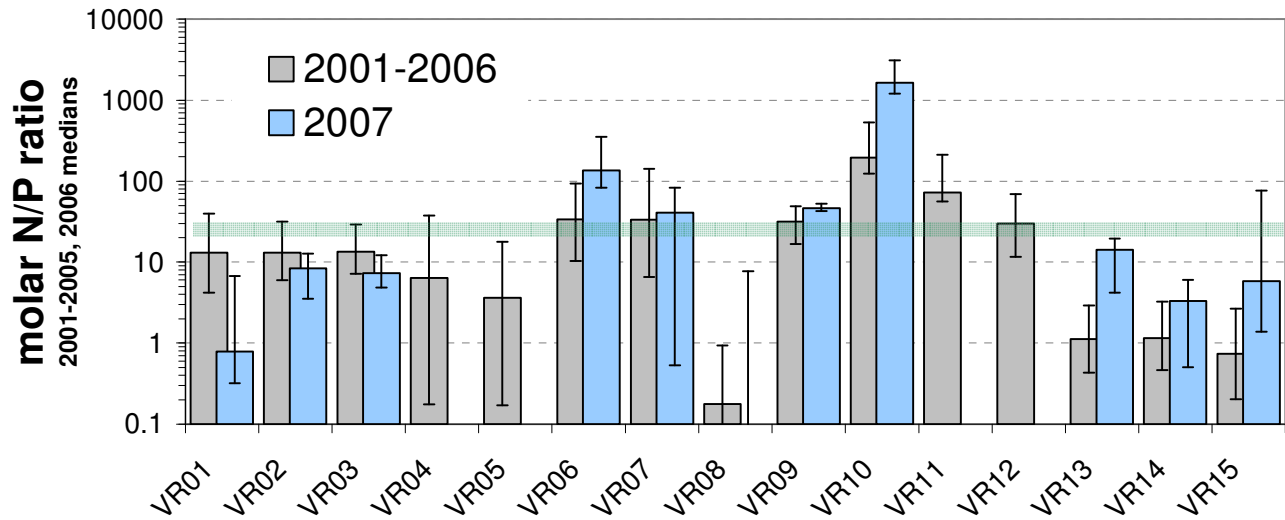
A word about standards. The heavy red and black-dashed lines shown on the previous and following figures represent nutrient criteria from the State of California Water Resources Board SWAMP 305b Report: TN >1 mg/L (as nitrogen) for poor quality waters; <0.5 mg/L for good; with values in between representing waters of fair quality. The 0.50 mg/L criterion is higher than the EPA's recommendation for Ecoregion III, the xeric west, which proposed a TN limit of 0.38 mg/L. It is however, roughly the same as that for sub-region 6 (within the xeric west), the California coast. The 25 percentile concentrations for this sub region are TN = 0.52 mg/L, nitrate + nitrite = 0.16 mg/L, TKN = 0.36 mg/L (all as N). (The recommended criteria were, by definition, the 25 percentile concentrations, i.e., 1/4 of the streams in a region had values lower, ¾ higher, than the criterion.) For phosphorus, the SWAMP 305b Report used criteria of TP > 0.1 mg/L for poor quality; <0.01 mg/L for good; and values in between for fair quality. The EPA Ecoregion III proposed limit for TP was 21.88 µg/L, and for sub-region 6, 0.030 mg/L (all expressed as phosphorus).



Finally, I wanted to take a look at sampling locations with very low, or below detection limit, nitrate concentrations. Seasonal TDN and DON concentrations for the four Ventura sites that fall within this category are shown in the figure: VR08 (Lion Canyon), VR13 and 15 (Matilija Creek, below and above the dam, respectively), and VR14 (N. Fk. Matilija Creek). The sequential colors represent years from 2001. All four sites express nitrogen primarily as DON and typically, as per the previous discussion, can be expected to, and do, have appreciable algal growth wherever sunlight isn't limiting. I don't believe that aquatic plants play any meaningful role on these reaches (with the exception of some early visits to VR08 I have no personal knowledge; the limited available photos show mostly algae in 2004). There is a quantitative difference between VR08 and the others; TDN concentrations are usually an order-of-magnitude higher and algal growth is typically much denser. The data generally show the trend noted previously, concentrations are usually higher in dry than in wet years. But 2001 appears to be an anomaly, with noticeably lower TDN concentrations and, on the Matilija, lower proportions of DON. The graph seems to exhibit a linear trend from 2001 to 2007 and, indeed, a valid linear regression lines can be drawn through the monthly TDN results: r-squared values for these equations are 0.20, 0.14, 0.10 and 0.07, for sites 14, 13, 15 and 08, respectively. While suggestive, this may simply be a consequence of low 2001 and high 2007 values. 2001 data are suspect as TDN results for August and September of that year were lost in the lab, and my accounting for missing, or erroneous (when nitrate > TDN), TDN values minimizes the seasonal DO concentration. However, it bears watching since, in contrast with other locations, TDN concentrations elsewhere have either remained consistent or decreased (VR08 being a case in point).



I want to take a brief look at phosphorus. The figure shows seasonal (May through September) concentrations of TDP (total dissolved phosphorus) and DOP (dissolved organic phosphorus, calculated as the difference between TDP and phosphate). Sequential colors indicate DOP for the years from 2005 to 2007. I've concentrated on nitrogen as the more important nutrient since, as the figure shows, phosphorus never appears to be limiting (contrast with the earlier nitrogen figure). The figure underestimates the amount of phosphorus available, perhaps appreciably. First, for as yet unknown reasons, only about 50 % of samples analyzed by the LTER return valid TDP results, i.e., where $TDP > \text{phosphate}$. In spite of the question this raises as to the actual, rather than nominal, validity of "good" samples, I've decided to accept them as "real." And to simply assign invalid TDP results a concentration equal to phosphate. In other words, the TDP values shown in the figure are a combination of actual TDP values and others set equal to phosphate ($TDP \geq \text{phosphate}$). This minimizes whatever the true TDP values may be and minimizes actual DOP concentrations (and leads to anomalies like no DOP at VR03 in 2007, i.e., no valid TDP results during that season). LTER results also show a marked decrease in post-2005 phosphate concentrations. I can think of no convincing environmental reason for this and I suspect an analysis problem. I also, based solely on the magnitude of pre-2005 concentrations, suspect that the post-2005 values are the correct ones. If I'm wrong, TDP concentrations shown in the figure could be some 2 to 4-times higher. Either way, two conclusions can be drawn: there appears to be no shortage of phosphorus at any location and site-to-site DOP concentrations are remarkably similar in spite of TDP concentrations varying over 2 orders-of-magnitude.



Lastly, this figure shows molar N/P ratios for all Ventura sampling locations. The bars represent the median ratios, for 2001-2006 data in grey, for 2007 in blue. The error bars indicate the first and third quartiles of the data and the green band marks the general range of the Redfield ratio for freshwater aquatic systems: between 20-30. The upper chart uses the nitrate to phosphate ratio (which heretofore I've assumed to be more indicative because of problems with the TDP results mentioned earlier), while the lower uses TDN to TDP (where missing or obviously incorrect values have been set equal to the nitrate or phosphate concentrations, respectively). Sites falling below the green band are nominally nitrogen limited, above the band, phosphate limited (nominally, because limitation can only occur if the limiting nutrient actually becomes exhausted and, as I've shown, this is rarely the case). In general, most locations would appear to be either nitrogen limited or roughly in balance; only VR10 is convincingly phosphorus limited. Keep in mind that while TDN and nitrate values are accurate, phosphate and, especially, TDP concentrations remain suspect. While all TDP values are likely to be underestimated, those of 2007 incorporate more of the pre- and post-2005 dichotomy than the long-term average. Thus the differences between 2007 results and the broader averages are likely to not be real.