This is a piece on what happens with nutrients (and some other parameters) during storms on the Ventura River. I promised something on this subject to Scott for inclusion in the UCSB Algae Report, but afterwards realized it was too complicated a subject to be anything but superficially treated in that venue. Instead, I've decided to present and discuss, as fully as possible, the data I have available in this report and allow him to pick and chose.

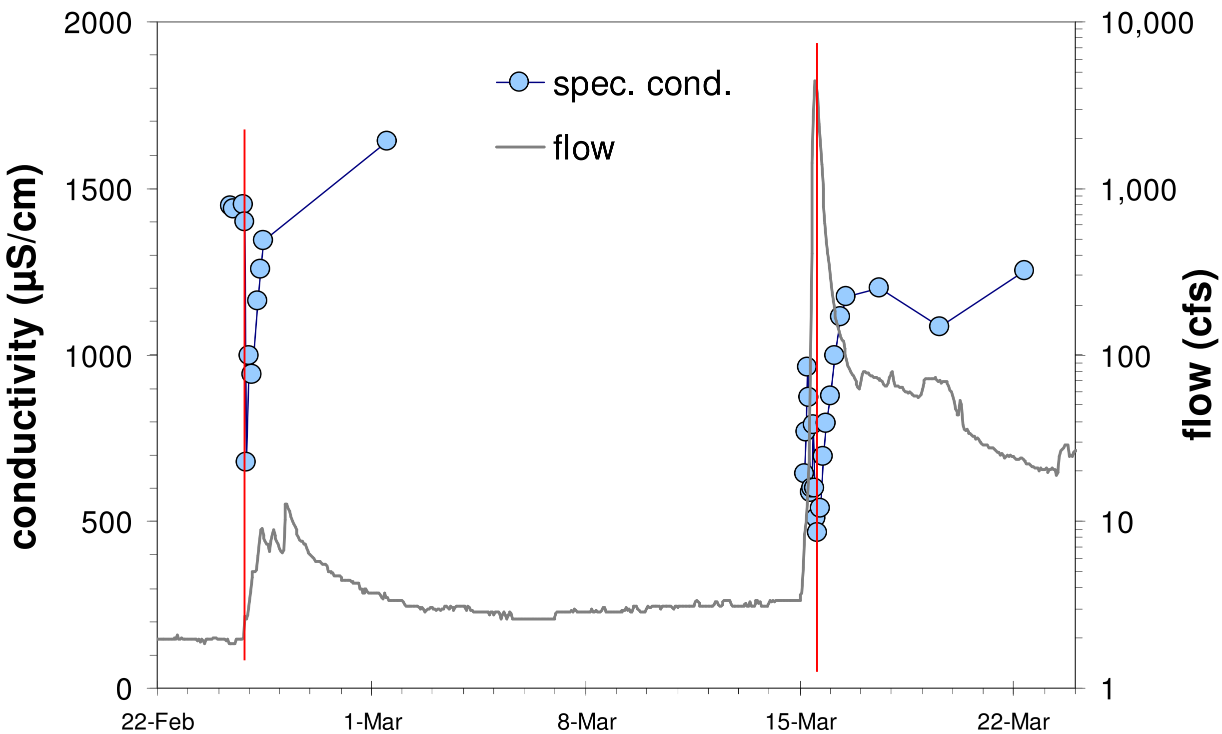
In 2003 I sampled the river at Main Street during two separate storms, a small event in February and a relatively large one in March. The 2003 March storm was the largest storm that occurred between a big rainfall early in March 2001 and the impressive rainfalls of January 2005.

Small storms have very different runoff characteristics than big storms, especially small storms during the first half of the rainy season. At the end of a long dry-season watershed soils act like a dehydrated sponge; and it takes appreciable amounts of rainfall to satisfy the accumulated water deficit – something on the order of four or more inches. Until this deficit is made up (a continual accounting process with rainfall on one side of the ledger and intervals of between-storm drying on the other) little runoff is contributed from watershed soils. Instead, almost all storm runoff originates off of impervious areas. At the beginning of the rainy season these surfaces are loaded with accumulated deposition (dry atmospheric deposition; auto emission residues; fecal matter from birds, dogs and whatever; and all sorts of misc. pollutants) and runoff is usually highly contaminated (the initial storm is appropriately termed "first flush"). Later, especially in a season with continual rainfall, runoff from impervious surfaces becomes far less contaminated and, as far as nutrients are concerned, may contribute only low concentrations.

As the rainy season progresses, and as soil moisture deficits are filled, all portions of the catchment begin to contribute soil water runoff to the nutrient flux. This soil water contribution is usually high in nitrogen, presumably from atmospheric deposition and leakage from chaparral environments in the upper catchment, from horticultural and agricultural use of fertilizer and urban wastes in the lower. As mentioned, impervious surfaces, after the first flushing rainfall, generate lower nutrient concentrations during subsequent storms, concentrations lower than those typically seen in baseflow. During the course of a rainy season, dissolved nitrogen concentrations generally decline with subsequent storms indicating the gradual depletion of whatever catchment reservoirs are responsible for N-export.

Phosphate typically shows a similar decline as the rainy season progresses. Phosphate concentrations in stormflow are highly correlated with sediment load and typically exhibit a pattern of: (1) high concentrations during the first storm due to dry-season deposition and the sediment load associated with stream bank erosion from initial flood-flows in typically dry channels; (2) lower concentrations during following storms unless the subsequent flood crest is of substantially higher magnitude, high enough to recruit new sediment sources; or unless (3) the rain-free period between storms long enough to both dry out the stream channel and appreciably increase the amount of accumulated deposition.

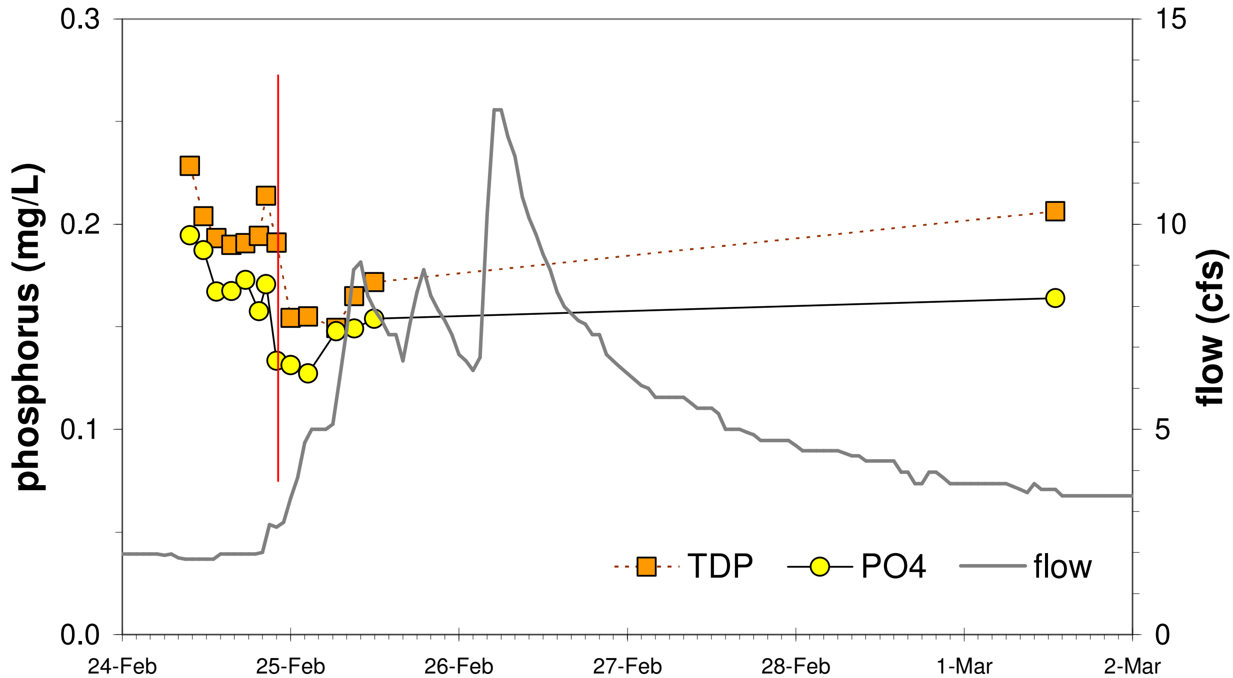
As a general rule, constituents normally found in low concentrations (e.g. suspended sediment, phosphate) are increased during stormflow, while those normally found in high concentrations are decreased (e.g. nitrate on the lower river, conductivity). During large storms, urban areas export fewer nutrients than other developed areas, but the situation is reversed during smaller rainfalls. In the very largest storms (e.g. January 2005) nutrient export from the undeveloped upper catchment dominates any contribution from developed land uses lower down.

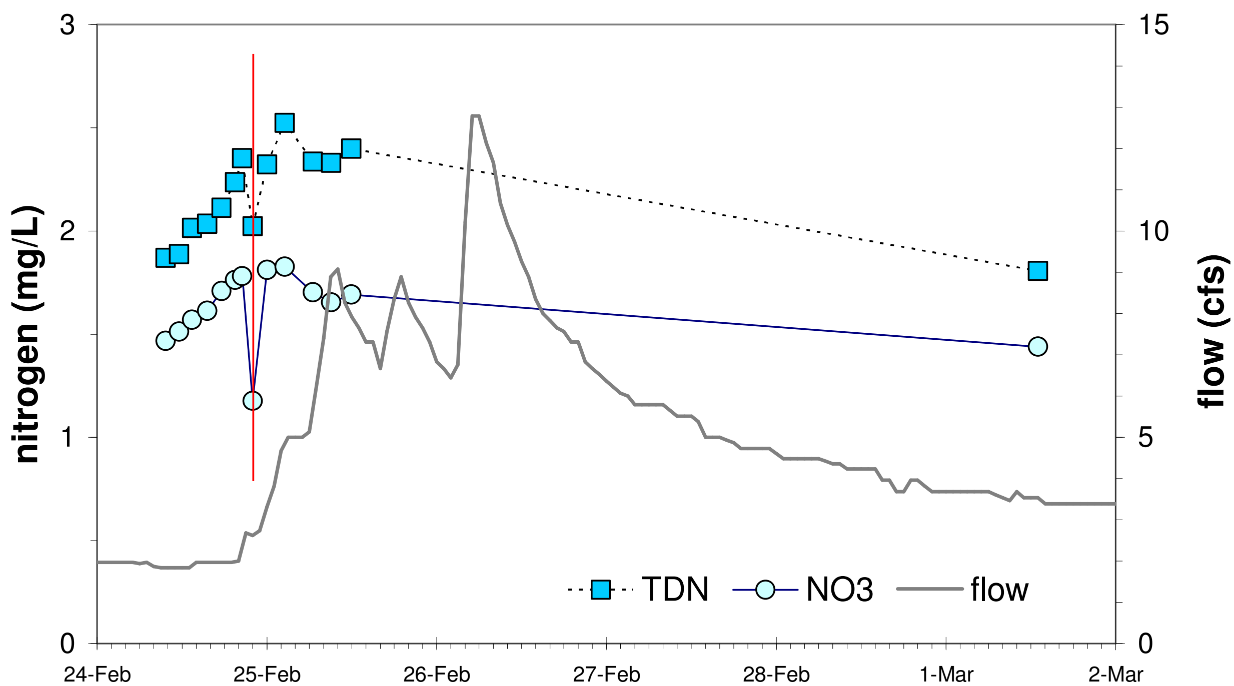


Having said all that by way of introduction, here's the basic data on the two storms: flow in cfs and conductivity in µS/cm. I've shown flow on a log scale since the two storm were vastly different in size (a peak Foster Park flow of 12 cfs on Feb. 26 vs. 4,300 cfs on March 15). I've also added a red line to indicate the time of peak flow at Main Street (the point of lowest conductivity can, almost by definition, be considered the point at which the amount of surface and overland runoff reached its maximum). The basic problem in examining this data is that while sampling was conducted at Main Street, just above the tidal limit, the only flow data available is from Foster Park, 5.5 miles upstream. Stormflows at Main Street would have been different, somewhat different during relatively large storms like the one on March 15, but very different during the small event of Feb. 24-25. I will show similar red lines in all subsequent hydrographs so that the point of peak flow at Main Street can be easily identified.

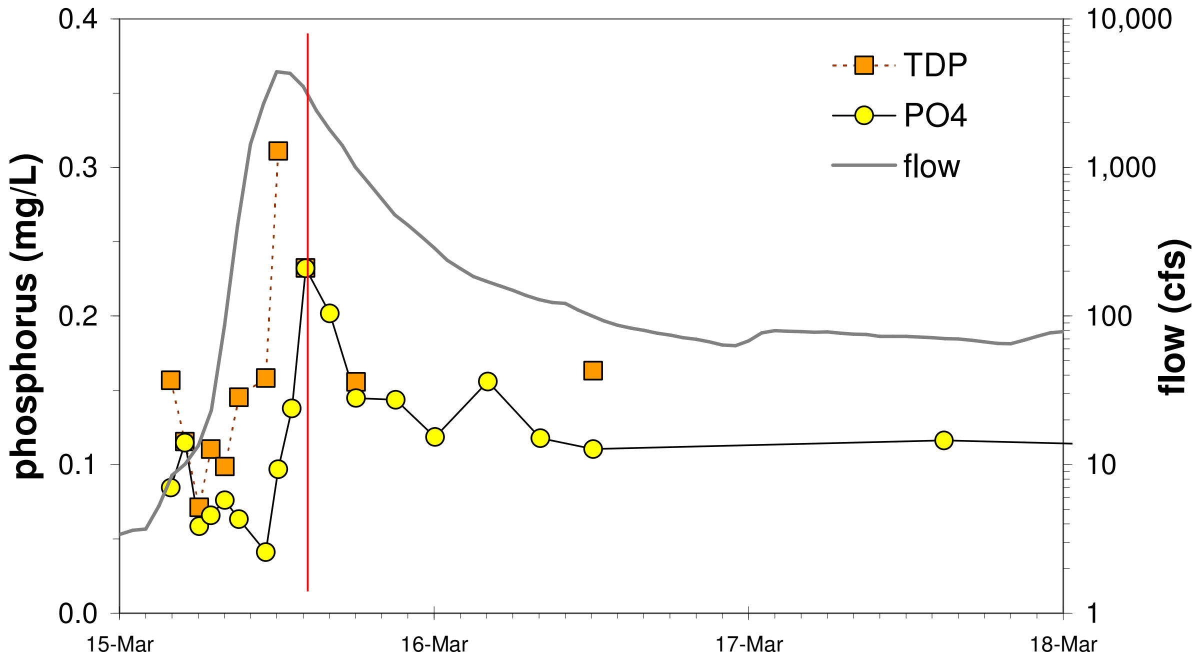
However, note the very large delay between the point of minimum conductivity and the Foster Park hydrograph peak for the Feb. storm – and the high conductivity values seen at Main Street at the time of this peak. Any peak seen at Foster Park will later appear at Main Street, and the March storm offers a reasonable estimate of this delay. The Foster peak occurred around 13:00 hours and the conductivity minimum was measured at 14:12. (None of these times is exact since both flow and conductivity sampling were not continuous.) A delay of about an hour and 12 minutes for locations 5.5 miles apart gives an average stream velocity of 6.7 fps (feet per second), which sound quite reasonable for a flow in excess of 4 thousand cfs. So call it a delay of about an hour.

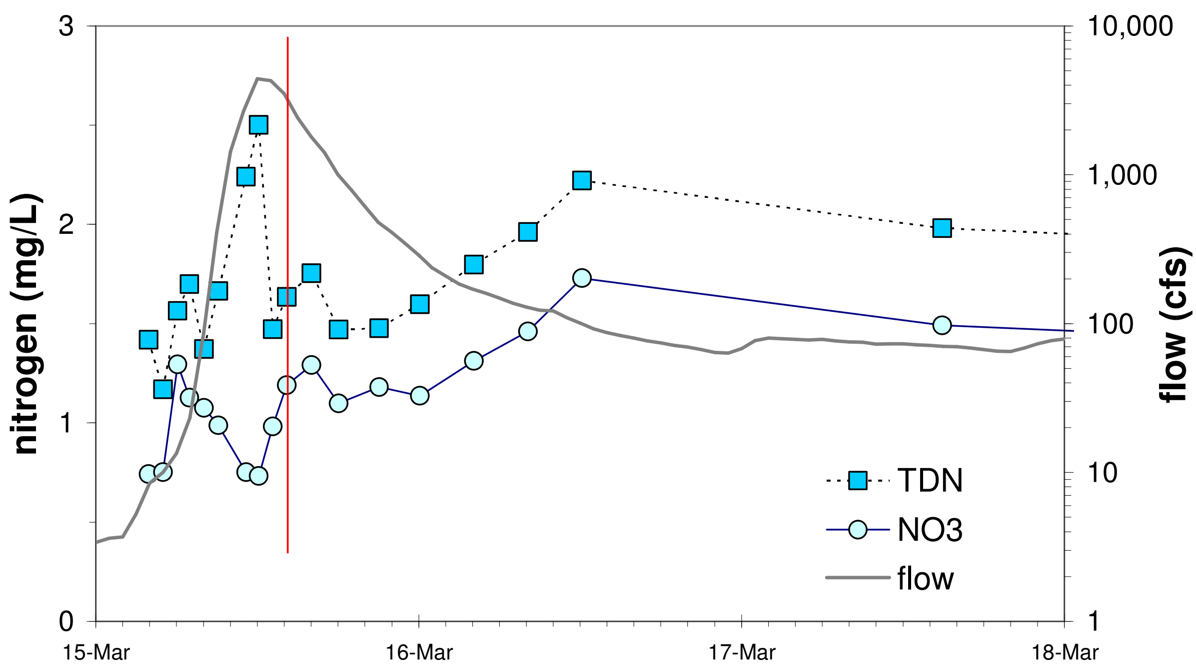
Returning to the small storm, the very long delay, and high conductivity at the time of the Foster Park peak, indicates that this later water represents slowly entering soil and groundwater contributions from relatively far up the catchment – most probably from areas adjacent to San Antonio Creek.





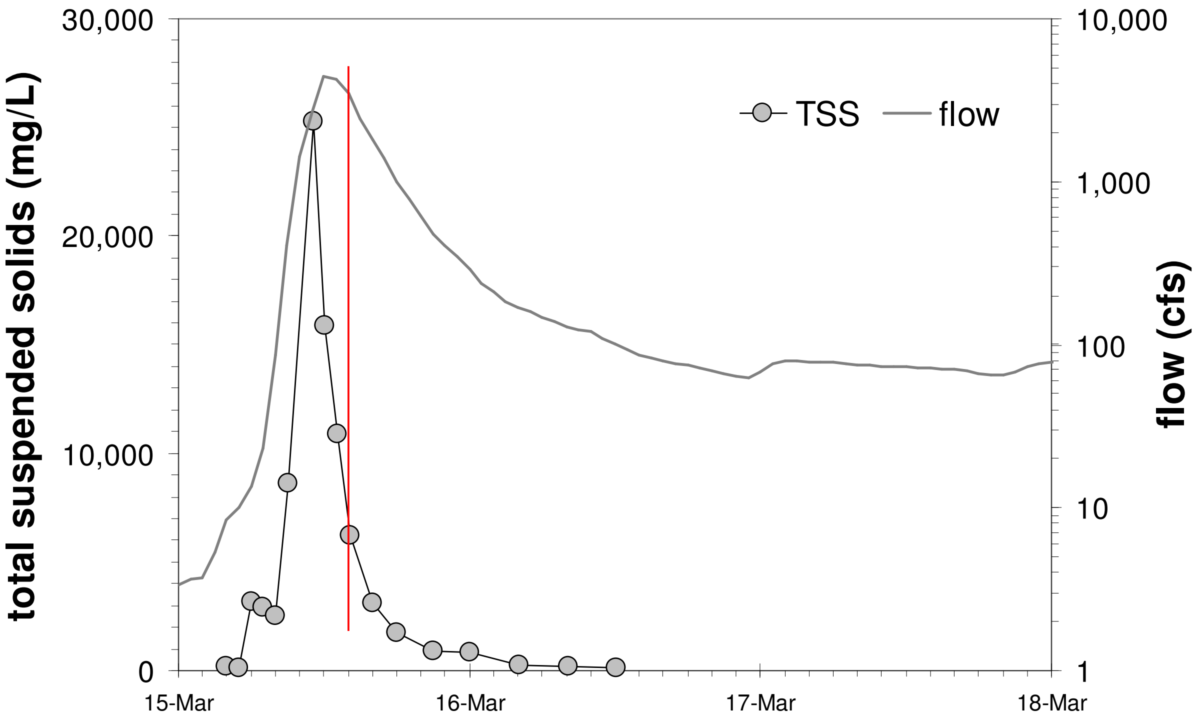
The small February storm: At Main Street this storm was characterized by a long slow drizzle interrupted by a single strong pulse of rainfall around the time of the conductivity minimum. During the event, phosphorus generally declined while nitrogen slowly increased, until the sharp surface runoff pulse abruptly lowered concentrations of both nutrients.



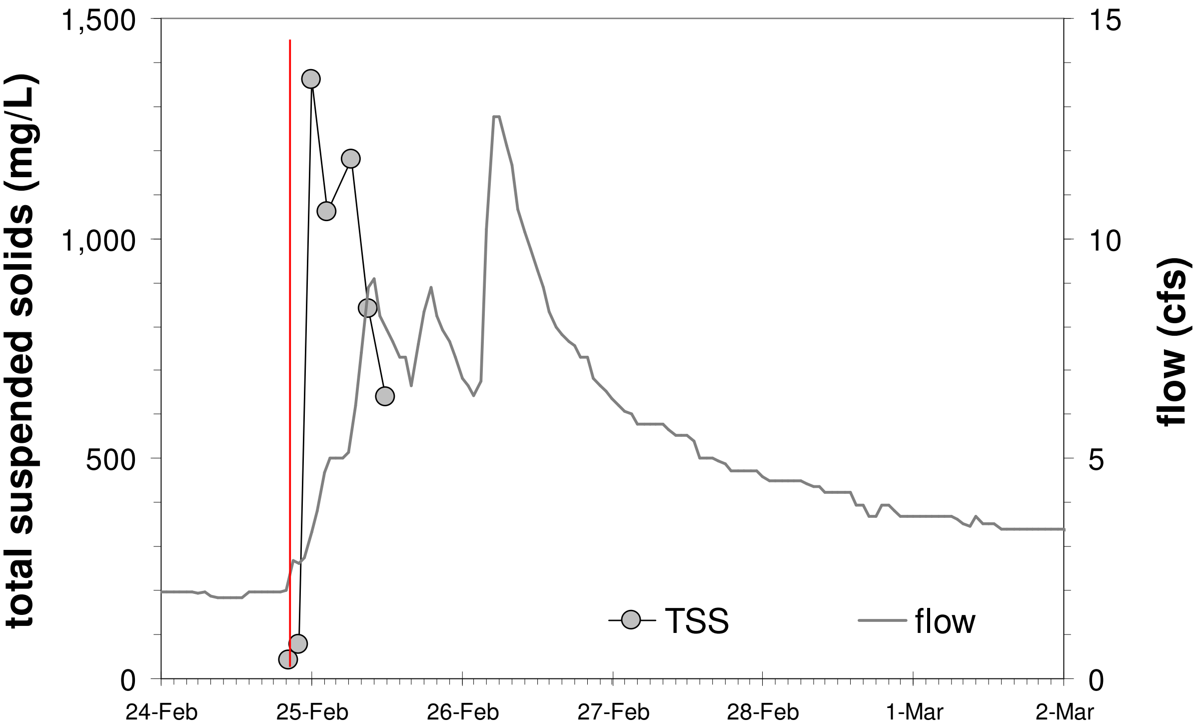


The large March storm: Large pulses of rain had already fallen by the time sampling began. The early samples mostly record contributions heavily influenced by runoff from impervious areas circa Main Street: nitrate and phosphate dipping to low concentrations when rainfall intensity increased, rebounding when it slowed to a drizzle. Note that concentrations prior to the conductivity minimum (the red line representing peak flow at Main Street) are lower than during the small Feb. storm (then nitrate ranged circa 1.5 to 2 and phosphate 0.15 to 0.2 mg/L). Phosphorus and total nitrogen (in contrast to nitrate) reached a maximum just prior to peak flow. These high values are associated with peak sediment flows which I'll show next.

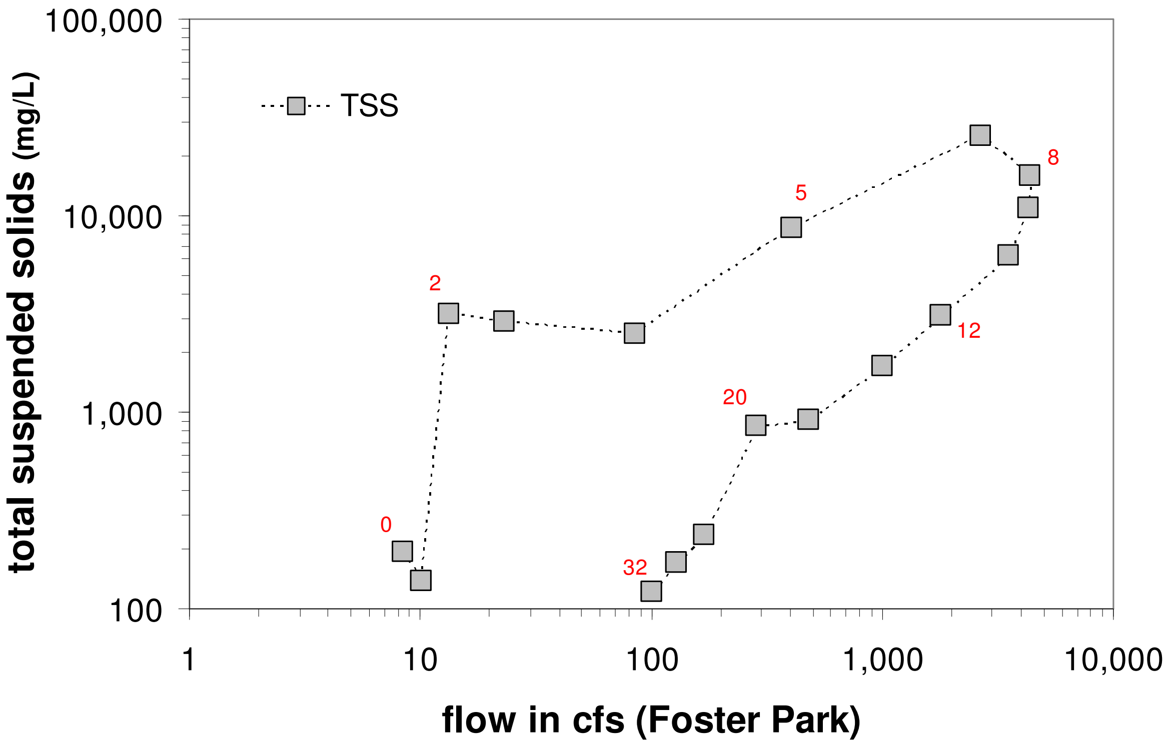
Following the hydrograph peak, phosphorus concentrations decline, but nitrate continually increases indicating that the major sources are further up the catchment and probably consist of delayed soil and groundwater inflows. This probably represents contributions from around Ojai and perhaps some of the upper catchment, big-storm, contribution I mentioned in the introduction.



This is a plot of suspended sediment at Main Street. Note that the sediment peak (and a very high sediment peak it is, the local mountains produce some of the highest suspended sediment loads seen in the world) occurs before peak flow at either Main Street (red line) or Foster Park (hydrograph peak) indicating that the probable source areas are from the middle reaches of the watershed: above urban development, but below the relatively pristine upper catchment – agricultural areas above Ventura and along lower San Antonio would seem to be indicated). Note also that sediment levels had dramatically decreased by the time nitrate concentrations began to rise. In other words, there is little correlation between sediment concentrations and nitrate, but, in contrast, a reasonably good relationship between sediment and phosphorus (as there should be, the phosphate tri-valent anion being preferably and easily captured by soil particle exchange sites; these particles being subsequently broken apart in the flood steam and phosphate dissolved via equilibrium reactions). Nitrate, on the other hand, highly water-soluble and rarely retained on soil particles, is surprisingly well correlated with conductivity for reasons I'll touch on later.



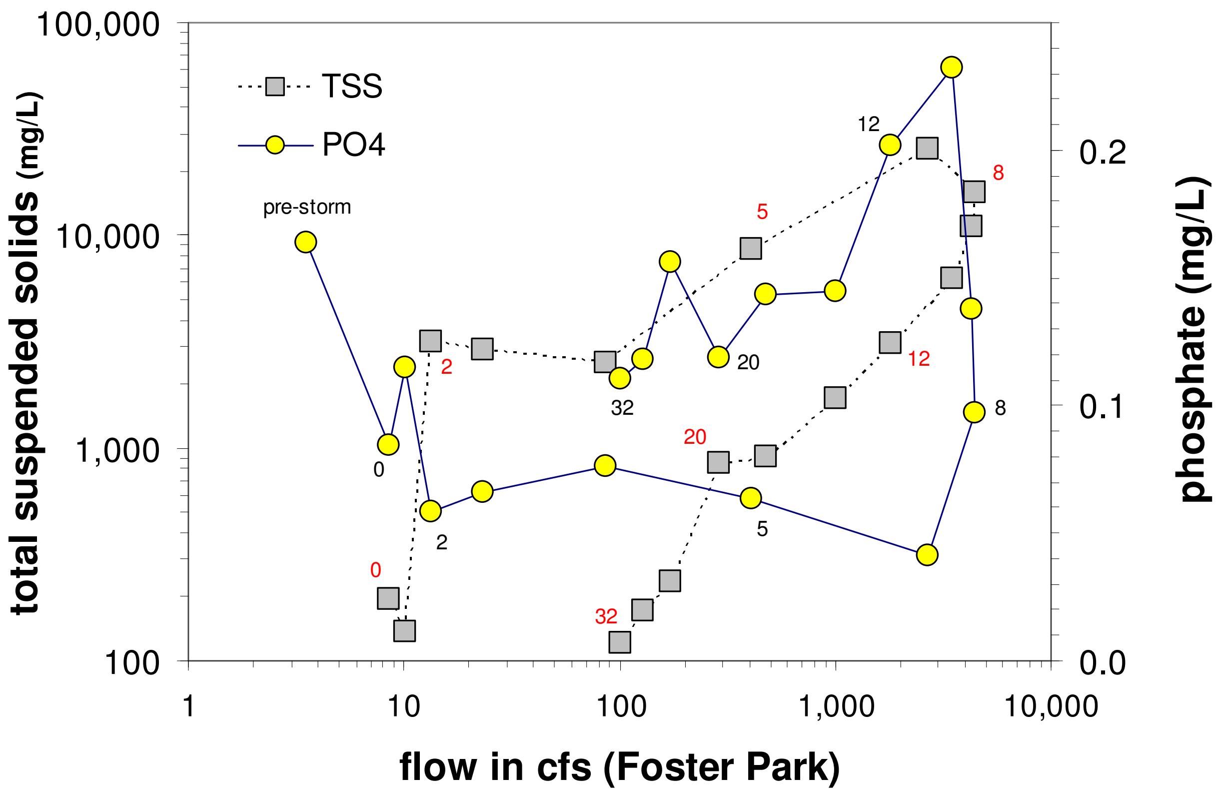
This is a another plot of suspended sediment, again at Main Street but for the first storm. During this small storm the sediment peak occurred soon after peak flow at Main Street indicating a relatively close source – most probably the agricultural areas just above this location. Note that the peak concentration is very much lower than seen in the larger storm that followed: 1,400 vs. 25,000 mg/L, a difference of more than an order of magnitude. That the higher flows later seen at Foster Park were not associated with high sediment concentrations is evidence that they consisted mostly of soil and groundwater contributions.



This is a concentration-discharge curve (C/D), a plot of concentration vs. flow constructed for a specific stream location that is often useful in interpreting what types of processes may be taking place. This one is for total suspended solids (TSS) sampled at Main Street during the big March storm of 2003. As before, I'm forced to use flow at Foster Park which makes this analysis less than ideal, but more on that later. I'm starting with suspended solids because it's easy to understand and explain. From here we'll go on to the harder, and more complicated, constituents. The numbers in red represent hours since the start of sampling: 0 indicates the first sample (taken after the storm had already begun), 32 the last sample, taken 32 hours after the first. (To keep the diagram uncluttered I have not assigned a number to each sample.)

The plot shows pronounced "hysteresis," i.e. the path taken to the highest value is different than the path followed on the return. In this case the hysteresis is clockwise, indicating that concentrations increased early on the rising hydrograph limb and then declined more rapidly after the flood peak had passed. For example, at 500 cfs on the rising limb TSS was 9,000 mg/L, but only 900 mg/L at the same flow on the return path – it's a rising flood that moves sediment into the stream and not simply a question of flow. The simple rule is that things that occur later in time either *happened further away* (thus taking more time to get to the sampling point) or resulted from processes that *took place more slowly*. We can classify runoff into a steam during a storm as coming from (1) surface runoff, (2) soilwater inflows, and (3) groundwater contributions. The first is rapid, the second slower, and the third, an increase in groundwater contributions, even slower. That two factors separate factors might have similar effects can make analysis somewhat subjective in the absence of other evidence.

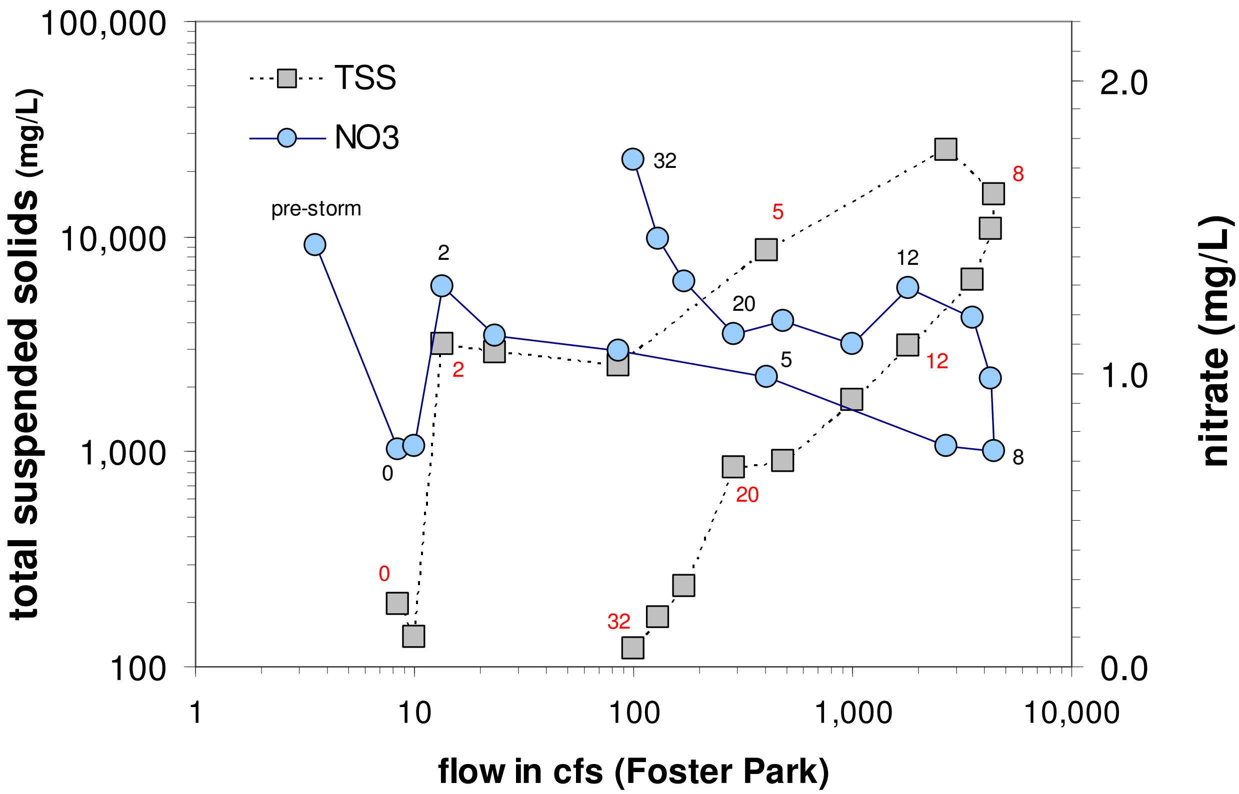
In this case it's simple; only surface flows generate sediment and since peak TSS occurred prior to peak flow the source was neither nearby nor at the furthest reaches of the watershed, but, as stated earlier, most probably in the middle Ventura and/or lower San Antonio Creek drainages.



I've taken the previous C/D plot and added phosphate. Phosphate also has pronounced hysteresis, but it's counter-clockwise, i.e. early rising limb values tend to be of much lower concentrations than corresponding values on the falling hydrograph limb. Low initial values are due to low phosphate concentrations in runoff from urban impervious surfaces. Rapid surface runoff causes the initial rise in the flood hydrograph and is responsible for much of the flow on the rising hydrograph limb. Note that phosphate concentrations during the initial 8 hours of the storm are all below the pre-storm values.

The phosphate pattern is also rather strange in that the transition between low and high values occurs rather abruptly, around the period of very high flows. The 4 points that form the rapid rise in phosphate are the same 4 high TSS samples – this is the expected sediment/phosphorus correlation. But it is interesting that beginning with hour 7 (not marked), as TSS concentrations decrease, phosphate concentrations rapidly rise. In other words, higher phosphate values are associated with the trailing, and not the leading, edge of the sediment plume. Expressed another way, sediment flows from further up the catchment are the ones higher in phosphorus. Based on other work I've done, I would place these high-phosphorus sediment sources as originating in suburban developments around Ojai. In this region high phosphate usually indicates urban/suburban landscaping and domestic animals.

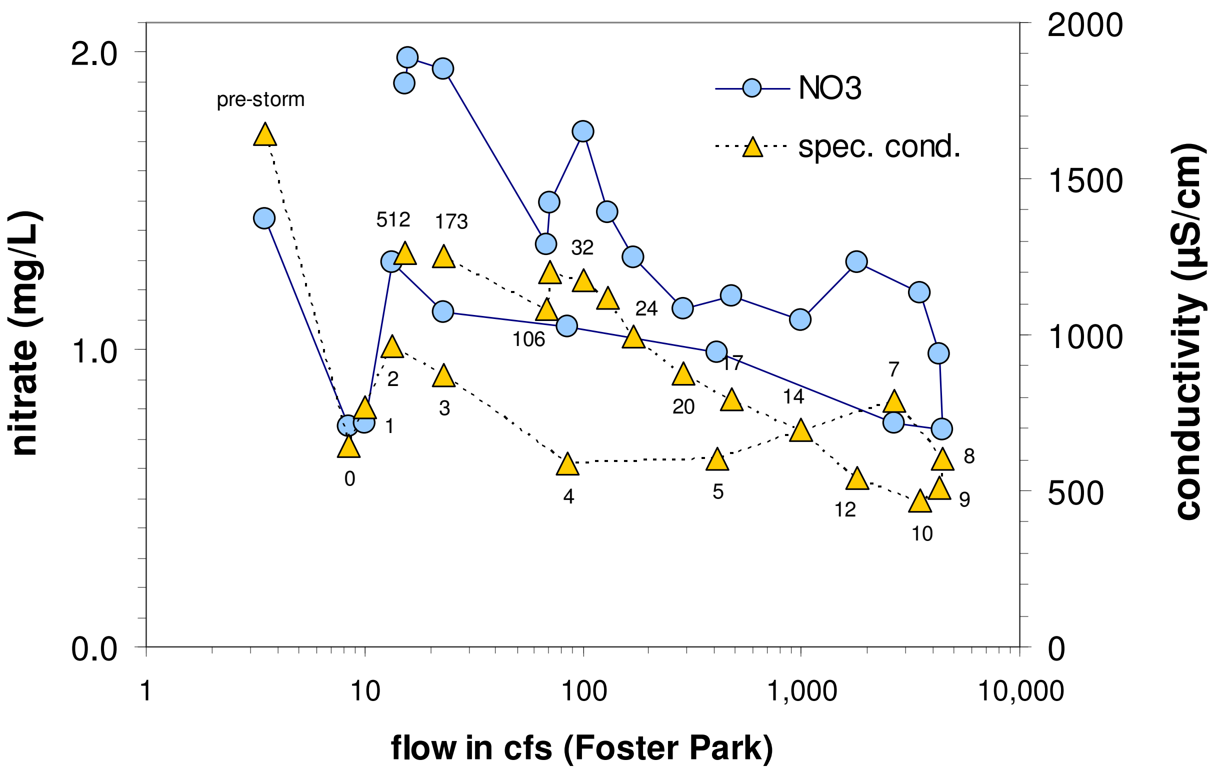
During the remainder of the storm's recessional limb phosphate concentrations remained higher than on the rising hydrograph, but were still lower than pre-storm values indicating that storm-enhanced soil and groundwater flows (rain had long since stopped) were lower in phosphate than the original flows supplying the stream.



On to nitrate: Nitrate, like phosphate, shows counter-clockwise hysteresis, and partially for the same reason. The initial samples (0 and 1), collected after the start of the storm, have very low concentrations; this is rapid, and relatively clean, runoff from impervious surfaces near Main Street. The runoff is clean because it's now relatively late in the rainy season and streets, roofs and paved areas have been washed on many previous occasions by rainfall. Nitrate then moves up and back down as higher nearby nitrate sources and then those from further up-catchment contribute (surface runoff from soils; agricultural soils especially can be high in nitrate – note that the abrupt nitrate increase at hour 2 is accompanied by an even more abrupt increase in sediment load.

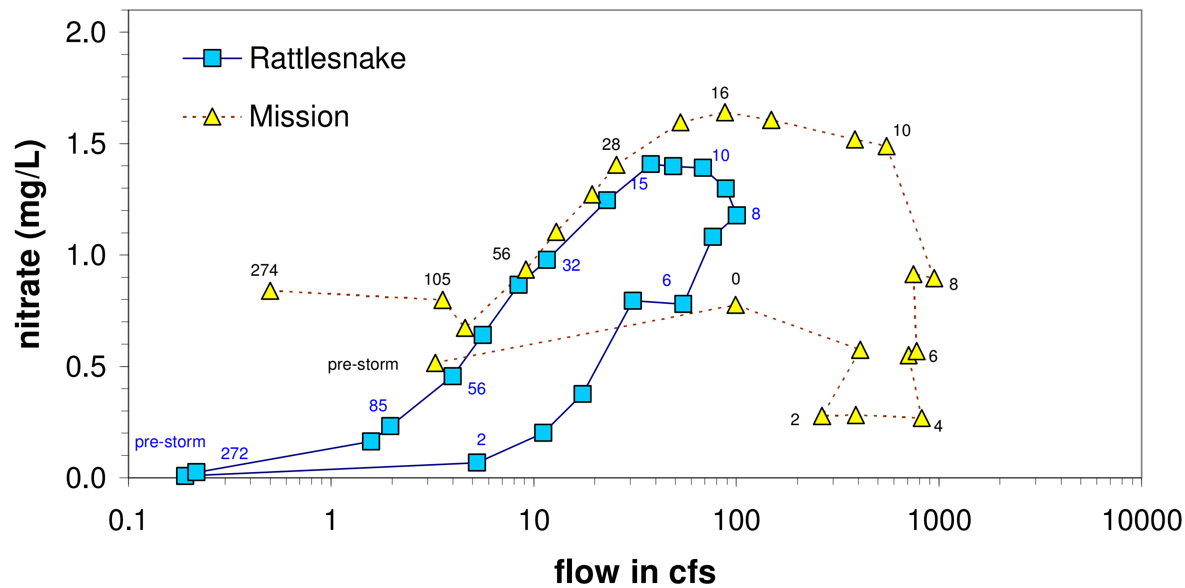
Another low point was reached near peak flow as the sheer mass of water passing under Main Street has significantly diluted nitrate concentrations. After peak flow the amount of surface runoff greatly diminishes and soilwater (and later, groundwater) contributions to flow become dominant. And it's from this point on that nitrate concentrations begin to rise – the highest concentrations occur very late and are most likely associated with high nitrate groundwater being flushed out by recharge that occurred during the storm. Although not shown, nitrate concentrations reached a peak 15 days after the initial rainfall.

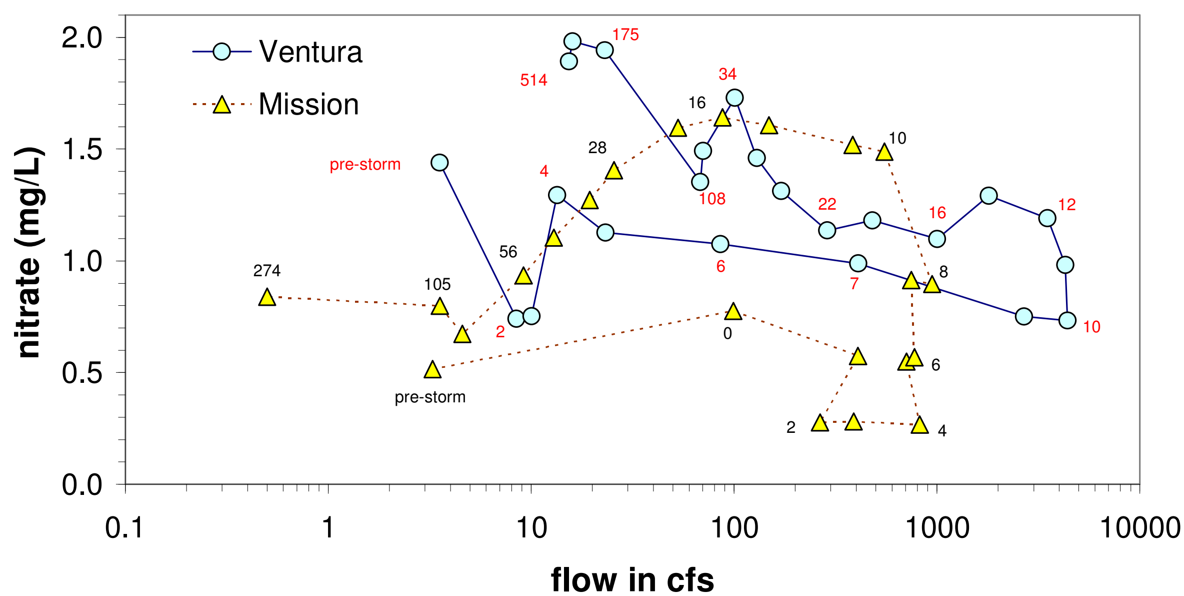
I can say things about the source of these waters (surface runoff, soilwater or groundwater) because other information, to which I'll get to next, is available. It's much harder to say anything definitive about specific locations from which source waters are coming from. This is especially true during the latter part of the event, after the hydrograph peak has been passed. Another caveat might be to mentally insert the word "mainly" or "predominately" before every use of the words describing a water source. Flows, especially circa and after the hydrograph peak, usually represent a mixture of sources, but the dominant source can usually be identified.



This is a the same C/D plot for nitrate shown in the last graph, but I've substituted conductivity for TSS. Conductivity can provide information on the probable source of the flood waters seen at various points along the hydrograph. Before-storm conductivity at Main Street is high since a large percentage of the low flow at this time was treated effluent from the Ojai plant (effluent, originating mainly as Ojai groundwater, has higher conductivity than is generally seen elsewhere in the Ventura watershed). After the start of rainfall (hour 0, 1) conductivity drops abruptly to values circa 500; this is rapid surface runoff from the vicinity of Main Street. Rainfall conductivity in this area generally ranges from 10 to 30 µS/cm and the basic rule-or-thumb is that increases will be roughly proportional to the amount, intensity and time spent in contact with any matrix able to transfer soluble ions to water. Naturally the type of matrix counts, but as a generality surface runoff has low conductivity, soilwater higher, and groundwater higher yet; and runoff from relatively clean impervious surfaces the lowest of all.

Since the increase that followed (2, 3) was also characterized by increased nitrate and sediment load the likely source, as mentioned earlier, was runoff from agricultural fields. Conductivity then dropped back down to the 500 level and sometime around hours 4 and 5 it reached a low point. This represented a crest of the flood wave (and a peak in the hydrograph) caused by surface runoff and rapid soilwater flows from the lower river. The rise in conductivity that followed probably represents increasing amounts of nearby soil and groundwaters. It's interesting that these appear to be low in nitrate as these concentrations continued to fall. The decrease in conductivity after hour 7 was caused by a second flood wave, one from further up the catchment, passed through Main Street. This second wave was associated with the highest concentration sediment flows and also carried increasing concentrations of nitrate and phosphate. This combination of characteristics lead me to assume that it originated on San Antonio Creek, with some possible help from the middle reaches of the Ventura. A double flood peak is relatively common in urban catchments with undeveloped uplands – especially in lengthy catchments. (It happens often in Mission Creek, a catchment we'll examine next.) From this point on conductivity and nitrate are relatively well correlated. I'm tempted to ascribe the prominent rise in both conductivity and nitrate around hours 24 to 32 to increased soil and groundwater flows from the Matilija (given the concomitant decrease in phosphate), but it would be little more than an educated guess.



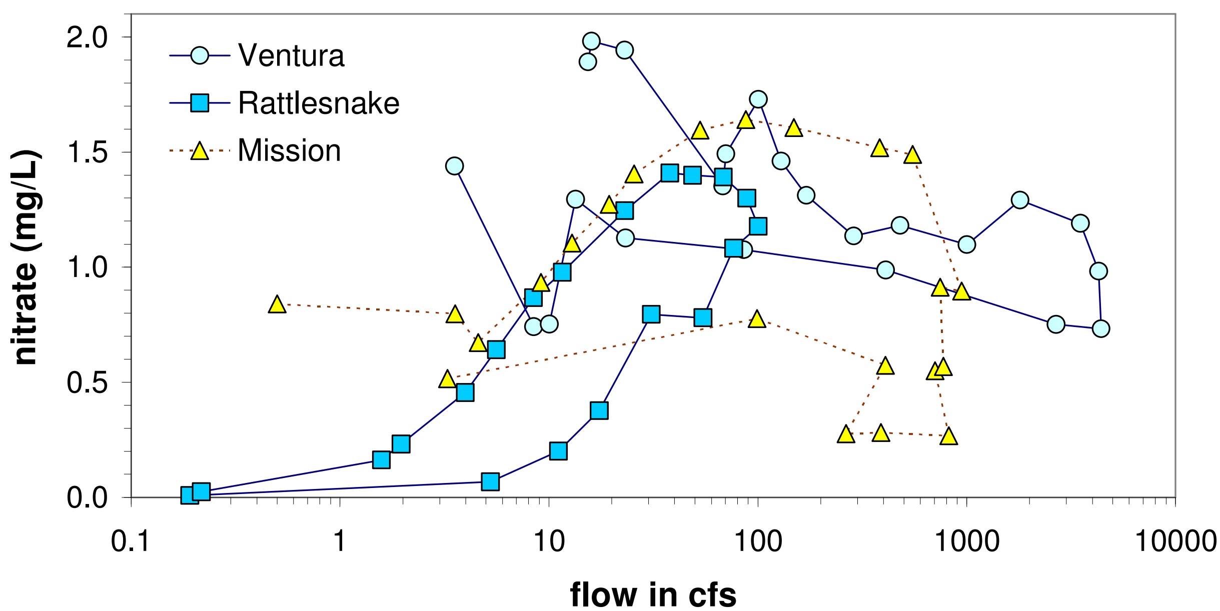


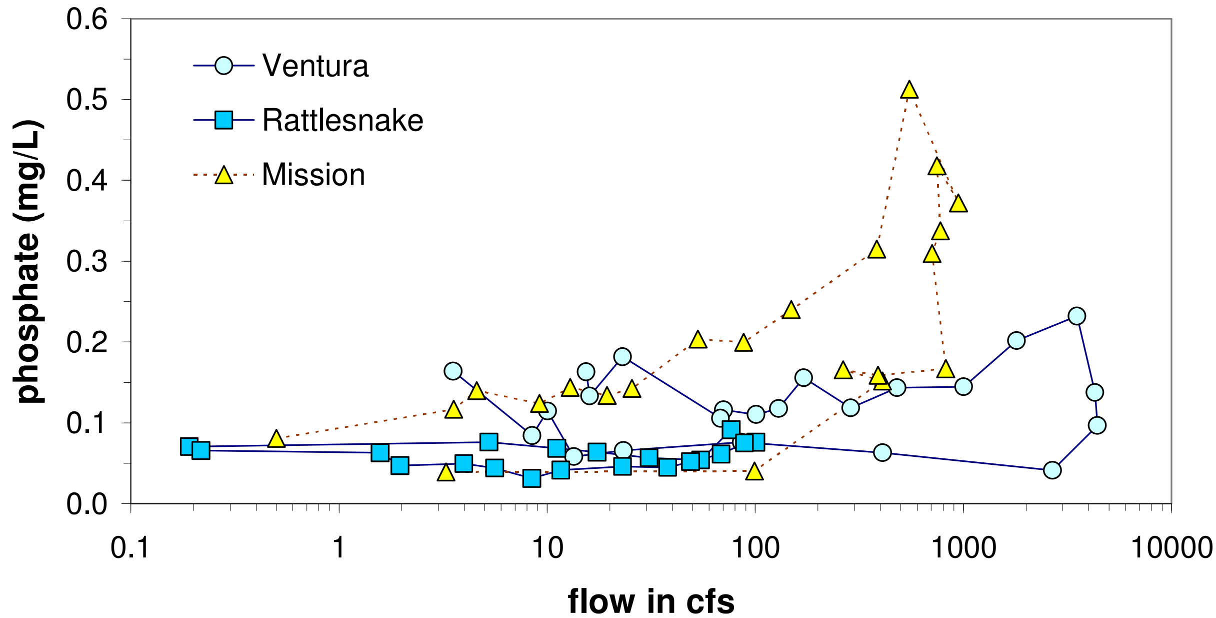
A final technique would be to compare the Ventura C/D relationships with those of other, simpler, catchments for which we have more data. The first graph shown here represents the same storm, March 2003, but the data is from Mission Creek in Santa Barbara and Rattlesnake, its upper tributary. Rattlesnake is a totally undeveloped mountain watershed, while Mission is urban on the plain and suburban with some agriculture in the foothills. Both Mission and Rattlesnake exhibit counter-clockwise hysteresis in their nitrate relationships, like the Ventura. I'll start with the Rattlesnake pattern because of its relatively simplicity.

It starts with very low flow and next to zero nitrate. This is groundwater baseflow since Rattlesnake had almost no storm runoff prior to this point – in fact no storm runoff for almost 2 years. Flow, and nitrate, then started to rise. From about hour 7 through 15 the bulk of the nitrate was flushed out of the system and during this period conductivities remained low and relatively similar (200-250 µS/cm). This probably represents the rapid delivery of soilwater to the creek through organic layers and thin, porous mountain soils on steep slopes. As to the source of this nitrate, think appreciable atmospheric deposition, low nitrogen utilization in a moisture stressed environment, mineralization and nitrification when winter again makes moisture available and, finally, episodic flushing that occurs only during those relatively few years with appreciable rainfall. Past this point (hour 15) flow and nitrate gradually decrease back to the origin. That the starting and finishing points are almost identical implies little change in groundwater as a result of this storm, and that the after-rain decrease in both nitrate and flow may simply have been the decrease of high nitrate soilwater inflows into a sustained zero nitrate baseflow.

Mission begins with a pattern similar to that seen at Main Street on the Ventura: low nitrate surface runoff from the urban area followed by an abrupt increase as high nitrate flows from the middle, or foothill, portion of the watershed began to substantially contribute (high in nitrate due to suburban landscaping, agriculture, domestic animals, etc.). But what is interesting is that starting around hour 8, but definitely by hour 10, flow – and nitrate – from Rattlesnake determined the character of Mission flow (Mission was sampled at the tidal limit on Montecito Street). Most of the nitrate exported from Mission Creek from this point on during this storm came from the undeveloped National Forest above Santa Barbara. In sum, the undeveloped contribution represented a majority of the total nitrate export.

In the lower graph Mission is compared with the Ventura (again, the same storm). And while there are similarities in the nitrate patterns, there are also differences. The "mountain" influence is not as strong, although I believe traces of it can be seen in that late rise around hour 34. But finding differences is not surprising. The Ventura is a much more complicated watershed, with an expanded middle foothill section not to mention many more tributary streams, each of which exerts its own peculiarities.





Finally, I thought I'd finish off this section by trying to convey a visual impression instead of any detailed analysis by showing the patterns for all 3 catchments. As you can se, the "undeveloped" catchment pattern for nitrate (e.g. Rattlesnake) resembles only the latter part of the Mission C/D relationship; Ventura being closer to Mission than Rattlesnake. For phosphate, there is no similarity between Rattlesnake and the others, while Mission and Ventura share a lot of characteristics in common. The inference here is that the upper watersheds, in both Mission and the Ventura, play little role in stormflow phosphate dynamics, while the middle, or foothill, regions of both catchments are the major contributors. For nitrate, while Mission and the Ventura share urban similarities, the relative contributions from mountain and foothill areas, for this storm (and it's unfortunate we have data for no other), were dissimilar and preclude any close comparison.