San Diego River Nitrate and Phosphate Trend Development by Analysis of Statistically Significant Peak Events.

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Author Note

This study is the final project of this student for fulfilment of graduation criteria for the award of Master of Science in Soil and Water Science at the University of Florida.

Abstract

The goal of this study is to develop a better understanding of water quality issues and trends in the San Diego River. The San Diego River is little known to many in its surrounding community, despite its essentiality as a water resource and important aquatic/riparian habitat. The river's history of fish kills caused by algal blooms point to the need for deeper understanding of the processes and trends regulating water quality. In general, water quality is deeply dependent on chemical processes and transformations. For this reason, this student chose to focus on two important nutrients in the San Diego River: nitrates and phosphates. Nitrate and phosphate data are analyzed independently to identify any site dependent or seasonal trends with limited success. In response, statistically significant peaks in nitrates and phosphates were analyzed for trend development with three important discoveries: nitrate peak events most often occur in the winter, phosphate peak events frequently occur from summer to fall, and the occurrence of nitrate and phosphate peak events qualitatively correlate negatively.

San Diego River Nitrate and Phosphate Trend Development by Analysis of Statistically Significant Peak Events.

The San Diego River stretches 52 miles from its source in Santa Ysabel to its mouth in the Pacific Ocean at Ocean Beach. The San Diego River played a paramount role in the development of the City of San Diego, as its water source has historically determined the settlement of the area. Early settlement is marked by Kumeyaay culture, followed by the Spanish who created its first aqueducts and dams. The remainder of the river's history has been largely dependent on sediment and flood mitigation. The most drastic change to the river came in 1953, when a rock lined channel was created. The channel drained the river directly into the Pacific Ocean, preventing sediment from entering either of San Diego's two bays (Pryde, 2011) This event began an era of development along the river, or a transition from agriculture to urbanization, and an end to pristine riparian habitat and a vital water resource. Now, local river lovers fight to keep the river flowing, free of pollutants, and habitable.

What are the known water quality problems in the San Diego River? The City of San Diego Draft General Plan (2007) lists the following problems: "fecal coliform, dissolved oxygen, phosphorus, and TDS". The San Diego Coast Keeper scored the water quality as fair, with an index of 72 in 2016. The San Diego Coast Keeper's (2016) water quality index scored turbidity, dissolved oxygen, pH, nitrate, ammonia, phosphate, E. coli, and Enterococcus: rating dissolved oxygen, E. coli, and turbidity as yellow, Enterococcus and Ammonia as orange, and phosphate as red. The 2018 Water Quality Status Report also finds phosphorus to be of concern in the San Diego Region; reporting a mean of total phosphorus at 1.81 mg/L, with a maximum of 1,500 mg/L. It is clear that phosphates are an emerging concern.

In addition to the previously listed water quality problems, there is a history of algal blooms in the San Diego River. A report in the San Diego Union Tribune (2010), October 6, explains the cause of large-scale fish kills in the San Diego River are algal blooms that cause hypoxia during decay. While the phenomenon is generally limited to the urban areas of the San Diego River, harmful algae blooms have also been reported in the estuary. In response, California began Harmful Algal Bloom (HABs) monitoring in 2017 (NCCOS, NOAA, 2017).

The San Diego Regional Basin Water Quality Objectives, or “The Basin Plan”, defines the water quality criteria of the region, in compliance with the Clean Water Act (Section 303). The 2016 edition defines the objectives for nitrates and phosphates as follows: “Inland surface waters, bays and estuaries and coastal lagoon waters shall not contain biostimulatory substances in concentrations that promote aquatic growth to the extent that such growths cause nuisance or adversely affect beneficial uses. Concentrations of nitrogen and phosphorus, by themselves or in combination with other nutrients, shall be maintained at levels below those which stimulate algae and emergent plant growth. Threshold total phosphorus (P) concentrations shall not exceed 0.05 milligrams per liter (mg/l) in any stream at the point where it enters any standing body of water, nor 0.025 mg/l in any standing body of water. A desired goal in order to prevent plant nuisance in streams and other flowing waters appears to be 0.1 mg/l total P. These values are not to be exceeded more than 10% of the time unless studies of the specific water body in question clearly show that water quality objective changes are permissible and changes are approved by the Regional Board. Analogous threshold values have not been set for nitrogen compounds; however, natural ratios of nitrogen to phosphorus are to be determined by surveillance and monitoring and upheld. If data are lacking, a ratio of N:P = 10:1 , on a weight to weight basis shall be used.” With a history of algae blooms in the San Diego River, it is difficult to determine whether water quality objectives are being met.

As referenced above, there is plenty of documentation of water quality problems in the San Diego River. Some water quality data is available through government websites, but much of it is disseminated through vague reports. To better understand water quality challenges and to better understand water quality trends, I wanted to look at raw nutrient data collected from an impartial source. Algal blooms, dissolved oxygen, turbidity, pH, and a host of other water quality parameters are highly interdependent upon water chemistry, thus, this report will focus on two important aquatic health regulators: nitrates and phosphates.

Methods

Data for this analysis has been generously provided by the San Diego River Park Foundation. The data comes from the RiverWatch water quality monitoring program. Data is collected by volunteers from several sites spanning the urbanized lower portion of the San Diego River. The volunteer pool may change over time, but volunteer leaders consist of a pool of trained and highly diverse scientists ranging from chemists to engineers. Data is collected every month, generally on a Friday and subsequent Sunday morning. Location is dependent on the sampling team; however, the team generally focuses one morning on the Santee (or Eastern) portion of the river and the other morning on the Mission Valley (also, Western) portion.

Volunteers carpool from one location to another at designated sampling locations: Santee segments include sites RW-009 to RW-016, see “Figure 1” and Mission Valley segments include sites RW-001 to RW-008, see “Figure 2”. Sampling sites were selected according to access, permissions, hydrology, representativeness, and historical data (SDRPF QAPP, 2014).

Santee Sampling Locations

Figure 1: Sampling locations in Eastern segment of Lower San Diego River. Red targets indicate sampling locations.

Mission Valley Sampling Locations

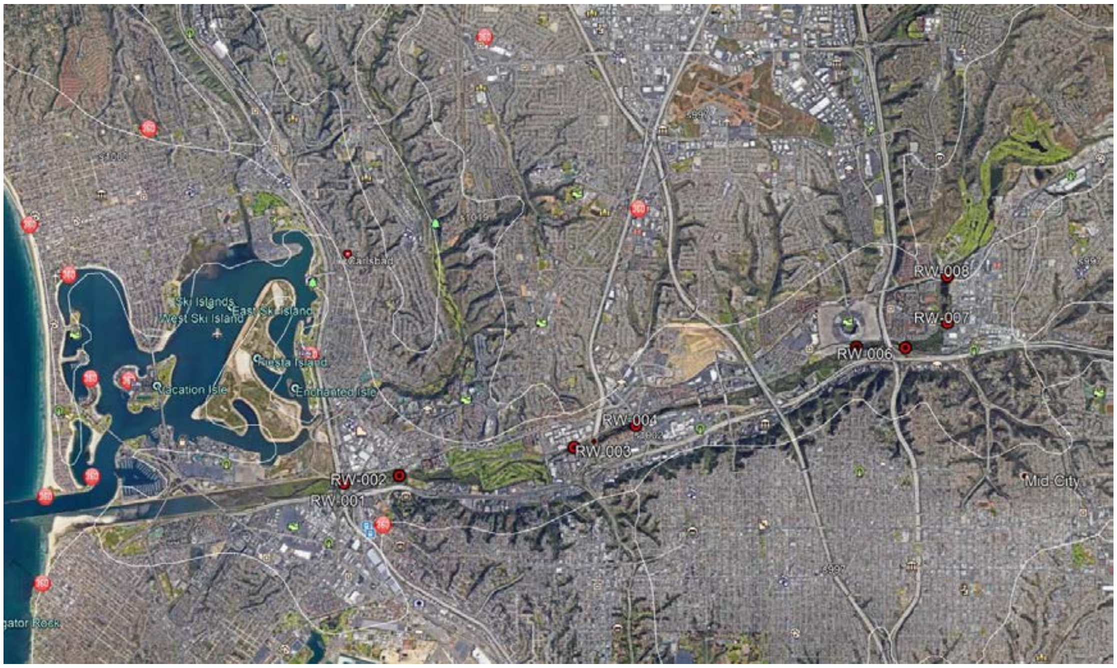

Figure 2: Sampling locations in Western segment of Lower San Diego River. Red targets indicate sampling locations.

Sampling Method

Volunteers use a YSI Pro Plus probe to sample temperature, percent dissolved oxygen, dissolved oxygen, specific conductivity, pH, and barometric pressure; the date and time are recorded. Water samples are taken at two to three locations within the Santee or Mission Valley segments and chilled on ice until nitrate and phosphate chemistry is conducted. In general, probe sampling and water chemistry occurs within a three hour window from 9am to 12pm each time and at the same location with few exceptions.

For nitrate and phosphate chemistry, sites RW-002E and RW-008 in Mission Valley and sites RW-012, RW-013, and RW-016 in Santee are primary sampling locations. Sites RW-012b and RW-016b are occasionally substituted, most likely when there is an inconvenience with access to the primary sampling location. The Zinc reduction method is used for nitrates and the Stannous Chloride method is used for phosphates via CHEMTest kits in the field. For more information on sampling methods or Quality Assurance/Quality Control, consult the SDRPF QAPP (2014). The table below indicates the limitations of the sampling methods for nitrates and phosphates per the SDRPF QAPP “Table 7.2”.

Nitrate and Phosphate Data Quality Objectives

Parameter	**Method/range**	**Units**	**Detection Limit**	**Sensitivity**	**Precision**	**Accuracy**	**Completeness**	**Bias**
Nitrate	Zinc reduction	mg/l	0.1	0.2	±10%	±10%	80%	102% Recovery
Phosphate	Stannous Chloride	mg/l	0.1	0.2	±10%	±10%	80%	95% Recovery

Table 1: Nitrate and Phosphate Data Quality Objectives. (SDRPF QAPP, Table 7.2, 2014)

Analytical Method

Data from the RiverWatch database was provided by the San Diego River Park Foundation with permission for data analysis. The data was sorted to enable reference to nitrate and phosphate levels over time at each site in an Excel spreadsheet. Nitrates and phosphates were analyzed for all sites together and independently for sites of interest. Non-primary sample sites were excluded from independent analysis as a result of small sample size.

Sites of interest, or primary sampling sites, are defined as sites having a greater sample size and that are sampled consistently over time. Sites of interest include: RW-002, RW-008, RW-012, RW-013, and RW-016. Data collected from sites RW-002E and RW-002W, RW-012 and RW-012b, and RW-016 and RW-016b may be pooled when data for a particular month is not available at the primary site but is at the secondary site because of proximity of sampling sites. Sites of interest were graphed annually to visualize seasonal trends.

Next, data for sites of interest are analyzed for mean and standard deviation. The standard deviation is calculated separately for each site. A standard deviation of three is used to define statistically significant events within sites of interest. Lastly, the frequency of statistically significant events are graphed to determine whether a trend in nitrates and phosphates are seasonally correlated.

Results

Average nitrates vary per section, with a range of 0.01 mg/L to 3.15 mg/L. The range of average nitrates at primary locations is 0.15 mg/L to 2.00 mg/L. Average phosphates per section range from 0.0 mg/L to 0.8 mg/L. Phosphates at primary locations range from 0.21 mg/L to 0.42 mg/L. Site RW-016 has the highest nitrate levels on average; while site RW-013 has the highest average phosphates. “Figure3” and “Figure 4”, depict the variability in nitrates and phosphates over time; a 10% error bar indicates limitations in the precision and accuracy of the sampling method. “Table 2” and “Table 3” summarize the findings of nitrates and phosphates at sites of interest, including site averages and standard deviations.

San Diego River Nitrates from 2005 to 2018

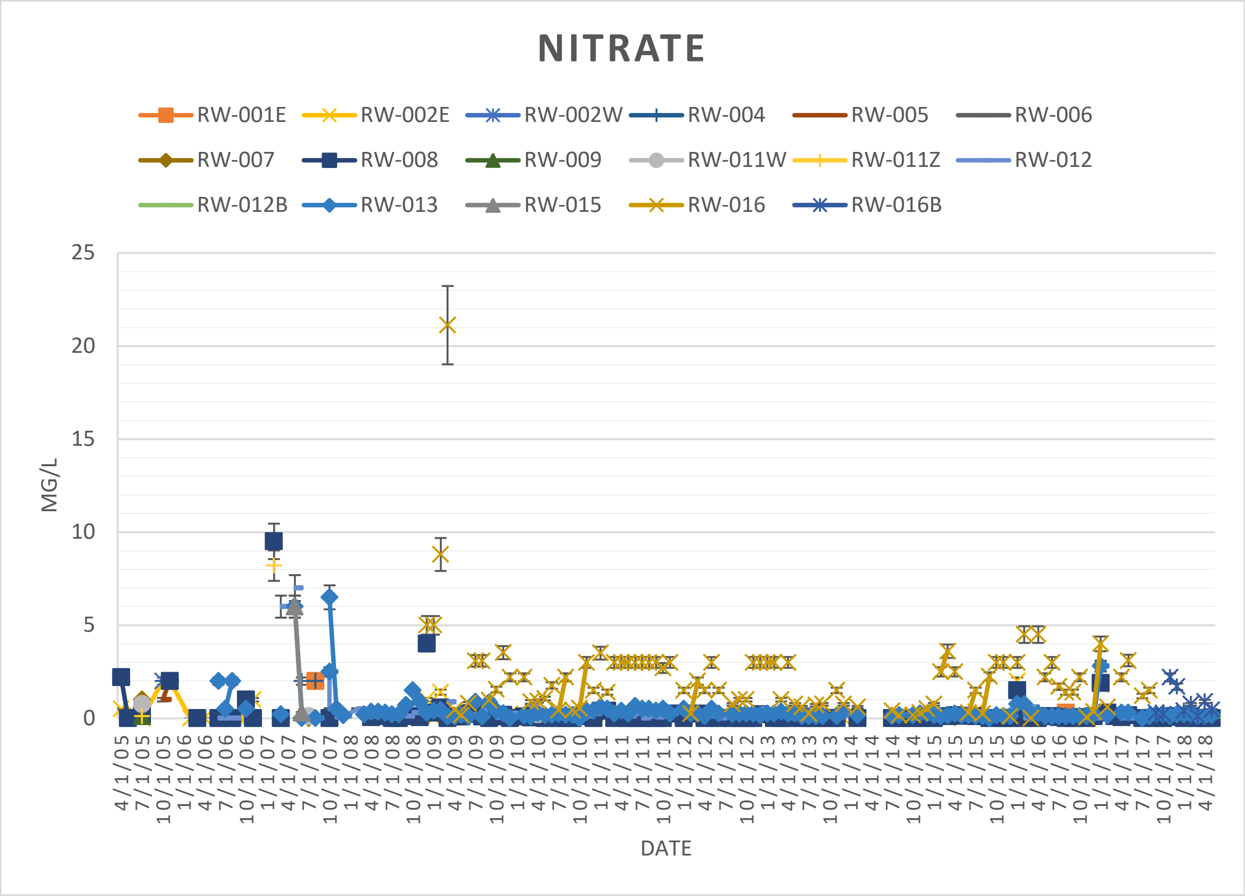

Figure 3: All nitrate samples for all sections, from April 2005 to April 2018.

San Diego River Phosphates from 2005-2018

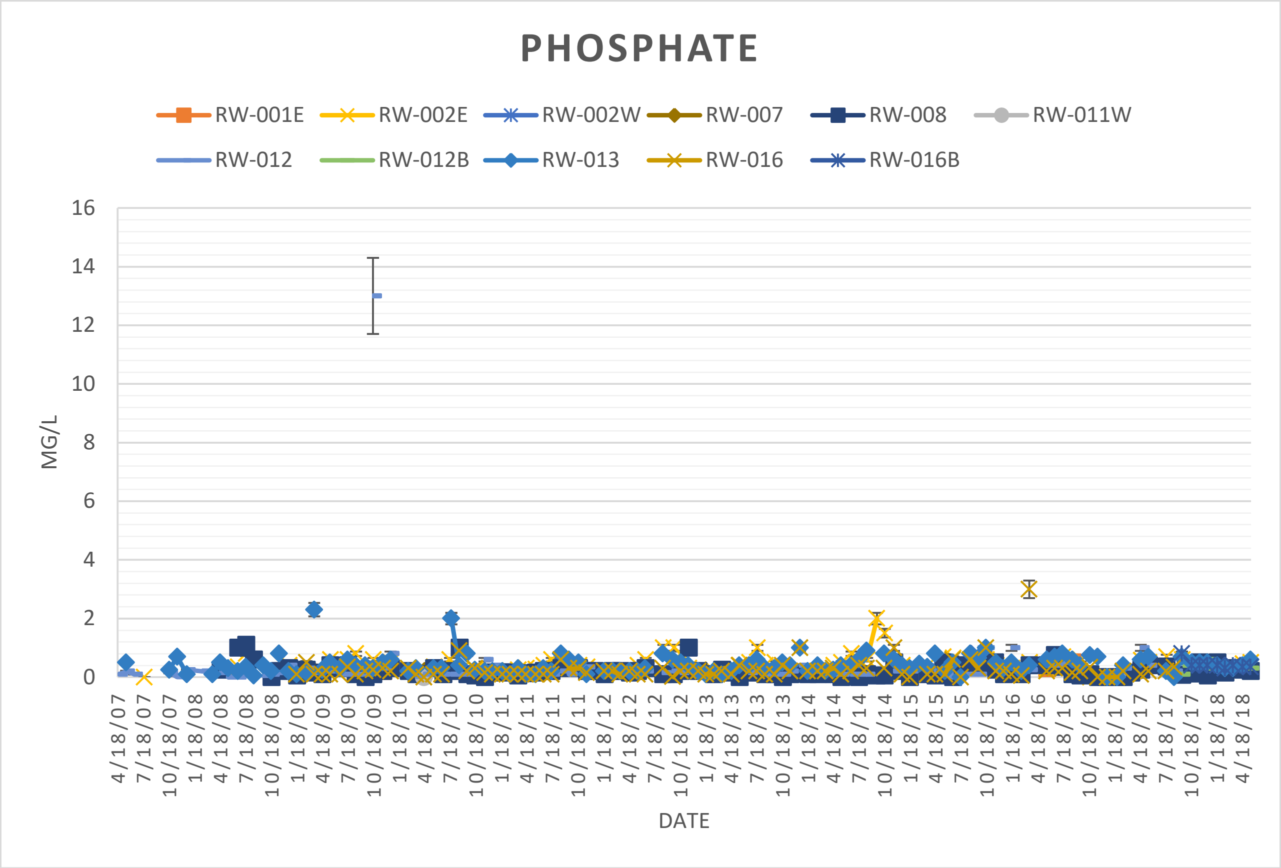

Figure 4: All phosphate samples for all sections, from April 2005 to April 2018.

Nitrates

Section ID	Sample Size	Average Nitrates (mg/L)	Standard Deviation	3 Standard Deviations
RW-002	117	0.15	0.39	1.18
RW-008	115	0.24	1.00	2.99
RW-012	112	0.34	0.92	2.75
RW-013	122	0.41	0.85	2.55
RW-016	102	2.00	2.40	7.20

Table 2: Nitrate averages and standard deviations at sites of interest.

Phosphates

Section ID	Sample Size	Average Nitrates (mg/L)	Standard Deviation	3 Standard Deviations
RW-002	106	0.39	0.30	0.91
RW-008	109	0.21	0.22	0.65
RW-012	117	0.34	1.19	3.58
RW-013	119	0.42	0.32	0.97
RW-016	104	0.27	0.34	1.02

Table 3: Phosphate averages and standard deviations at sites of interest.

From the annual nitrate trend graphs, it is possible to speculate about nitrate peak trends. Site RW-012 peaks in nitrates during March, July, and October of 2007. There is an additional peak in nitrates in January of 2017. See “Figure 5”. Site RW-013 peaks in June, August, and October of 2006; May and October of 2007; October of 2008; and January of 2017. See “Figure 6”. Site RW-016 does not show a seasonally high trend, but rather a consistently higher than average year-round trend. There are notable peaks January through March of 2009; February and April of 2016, and December of 2008. See “Figure 7”. Site RW-008 peaks in nitrates during April and November of 2005; October of 2006; February of 2007; and December of 2008. See “Figure 8”. Site RW-002 peaks in nitrates during October and November of 2005; November of 2006; December of 2008; February and November through December of 2009; January of 2016; and January of 2017. See “Figure 9”.

Annual Nitrate Trend: RW-012

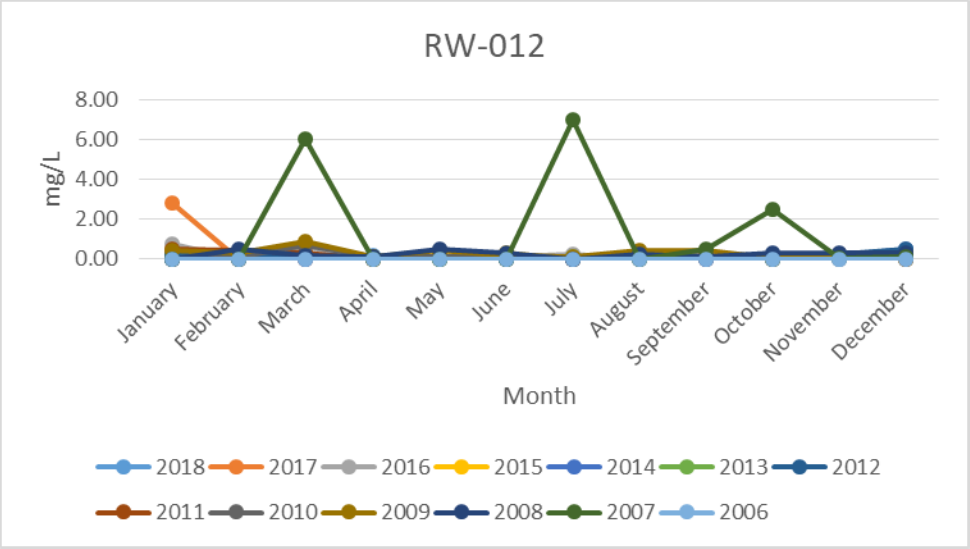

Figure 5: Nitrates for site RW-012, graphed annually to show seasonal trends.

Annual Nitrate Trend: RW-013

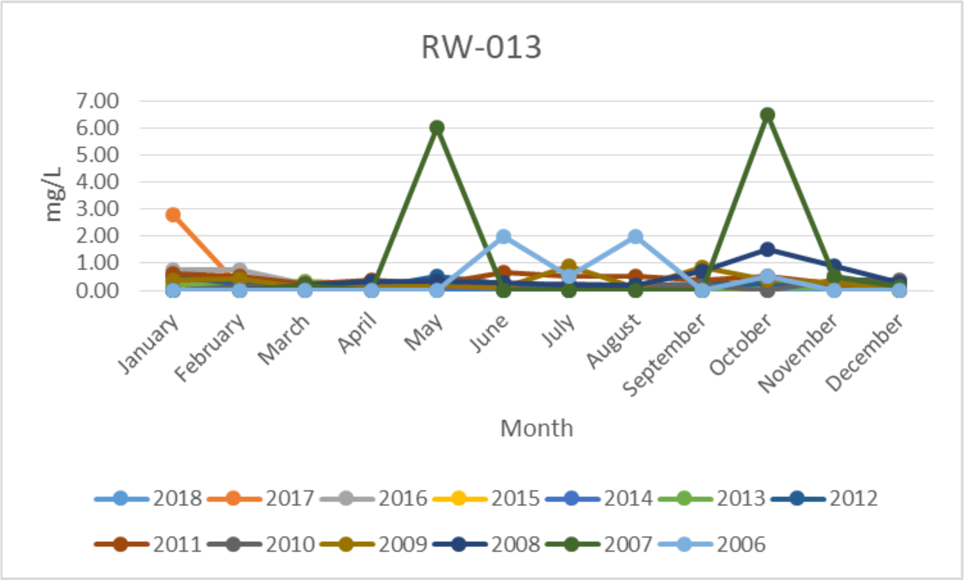

Figure 6: Nitrates for site RW-013, graphed annually to show seasonal trends.

Annual Nitrate Trend: RW-016

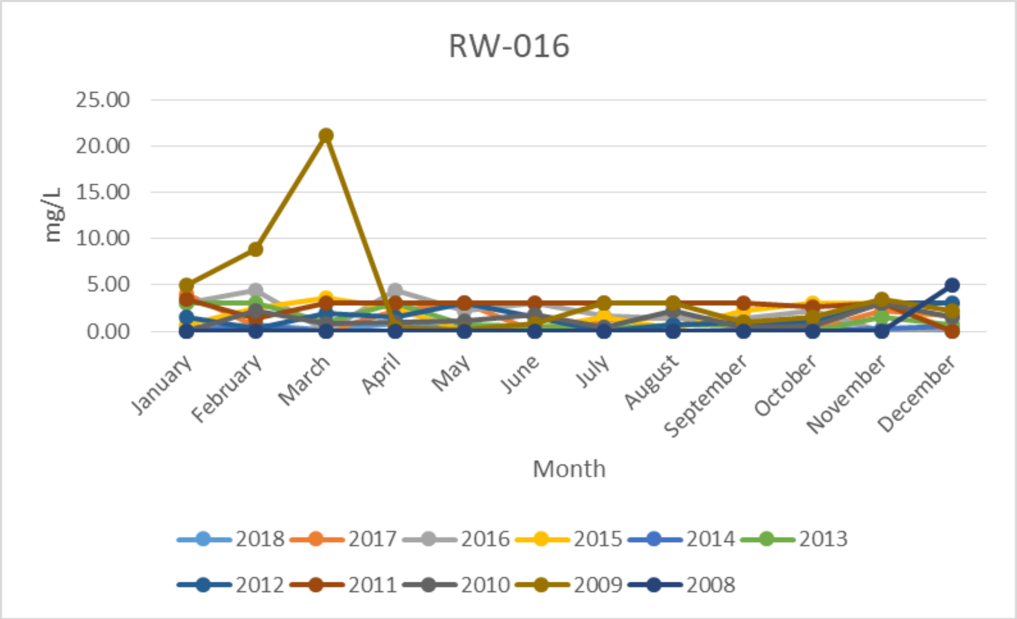

Figure 7: Nitrates for Site RW-016, graphed annually to show seasonal trends.

Annual Nitrate Trend: RW-008

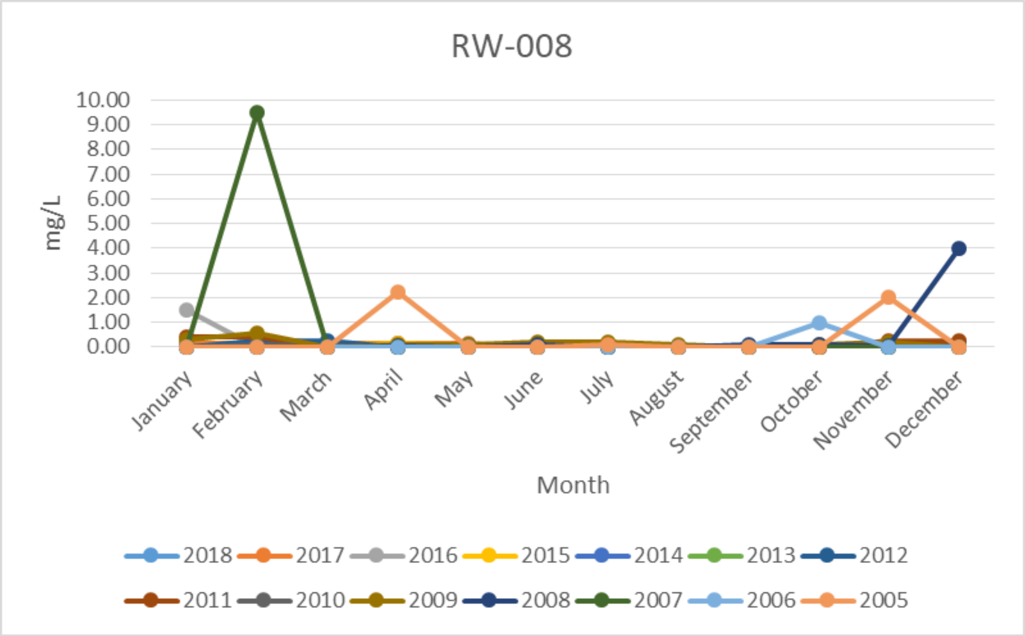

Figure 8: Nitrates for Site RW-008, graphed annually to show seasonal trends.

Annual Nitrate Trend: RW-002

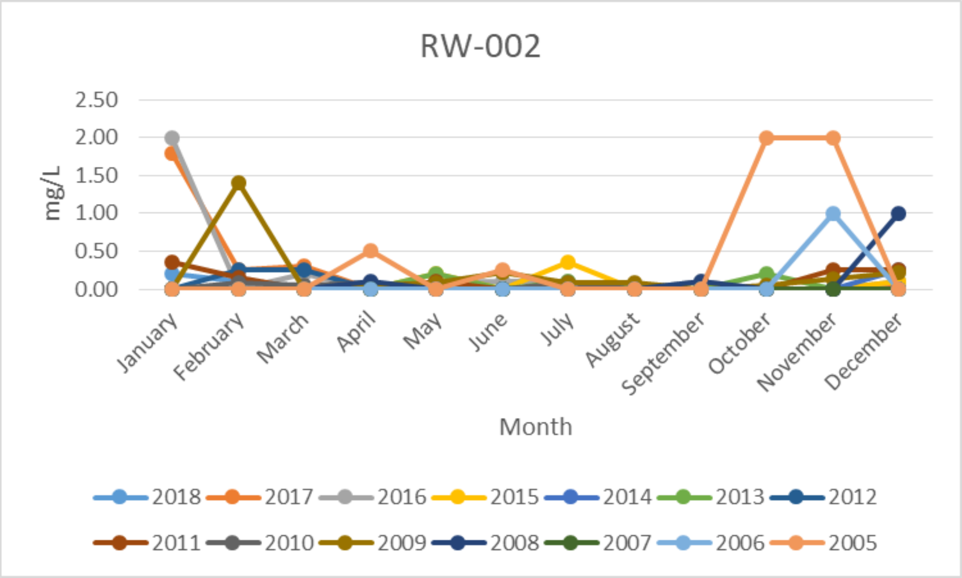

Figure 9: Nitrates for Site RW-002, graphed annually to show seasonal trends.

Similarly, phosphate peak trends are depicted by the annual phosphate trend graphs. Site RW-012 peaks in October of 2009. There are small peaks in October 2015, January 2016, and April 2017 but the site remains fairly consistently low in phosphates compared with other locations. See “Figure 10”. Site RW-016 displays peaks in phosphates in August 2010; December 2013; November 2014; June and October 2015; March of 2016; and September of 2017. See “Figure 11”.Site RW-013 peaks in March 2009 and July of 2010. See Figure “12”. Site RW-008 peaks June through July of 2008, August of 2010, and November of 2012. See “Figure 13”. Site RW-002 peaks from September to October 2014. See “Figure 14”.

Annual Phosphate Trend: RW-012

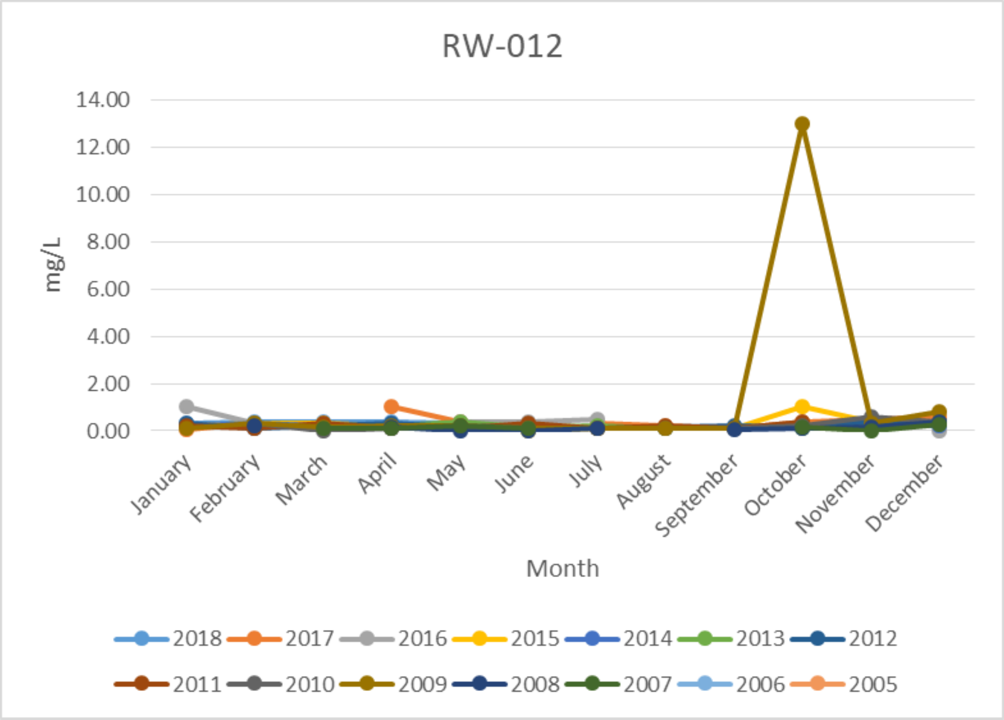

Figure 10: Phosphates for site RW-012, graphed annually to show seasonal trends.

Annual Phosphate Trend: RW-016

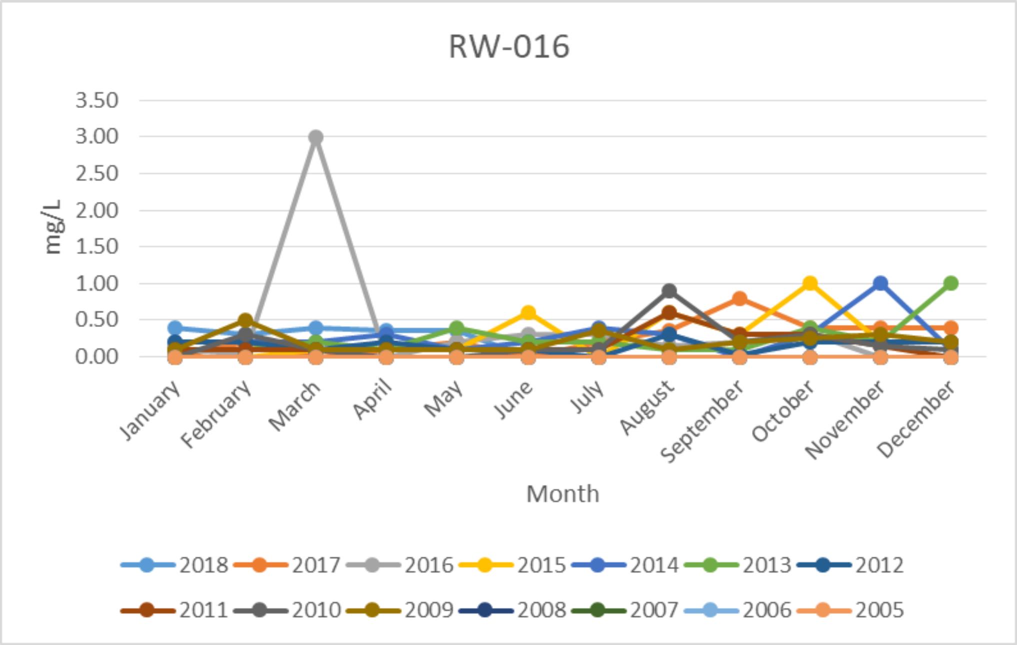

Figure 11: Phosphates for site RW-016, graphed annually to show seasonal trends.

Annual Phosphate Trend: RW-013

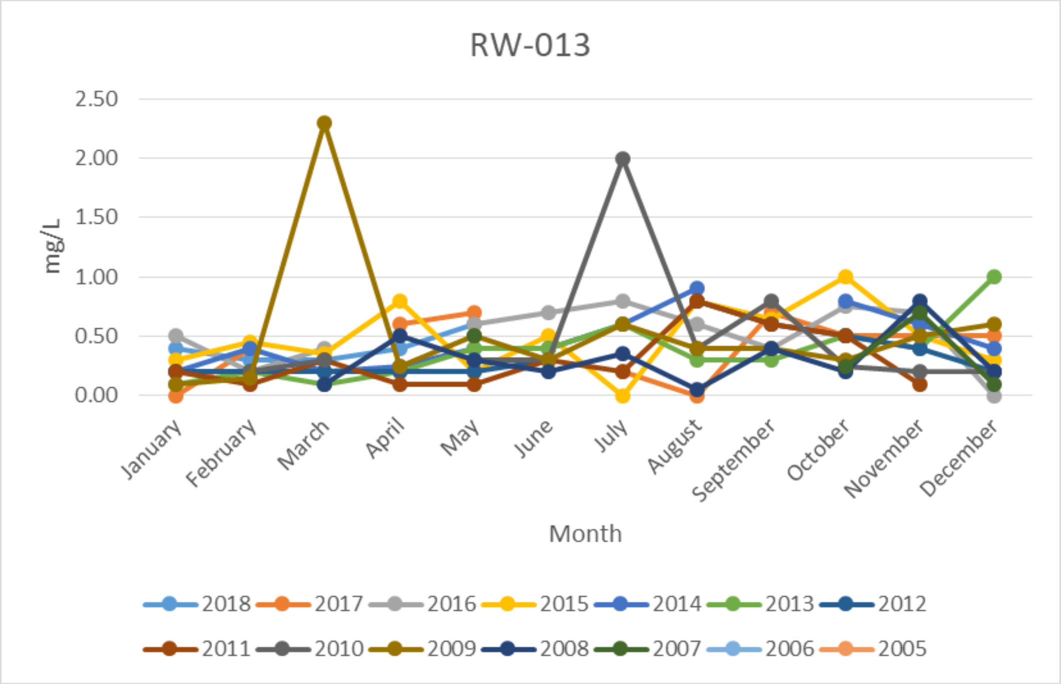

Figure 12: Phosphates for site RW-013, graphed annually to show seasonal trends.

Annual Phosphate Trend: RW-008

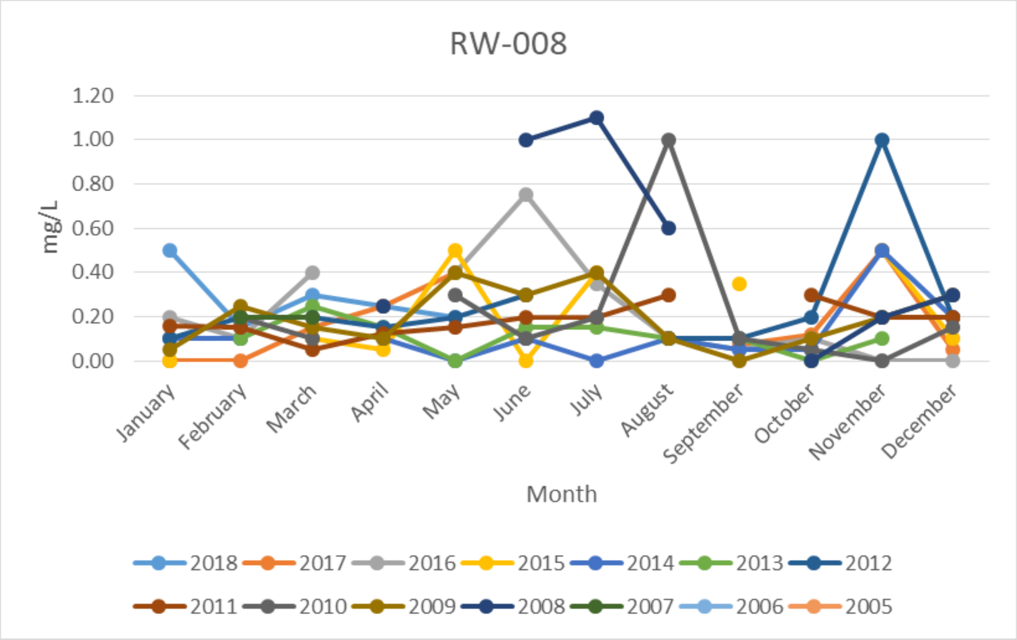

Figure 13: Phosphates for site RW-008, graphed annually to show seasonal trends.

Annual Phosphate Trend: RW-002

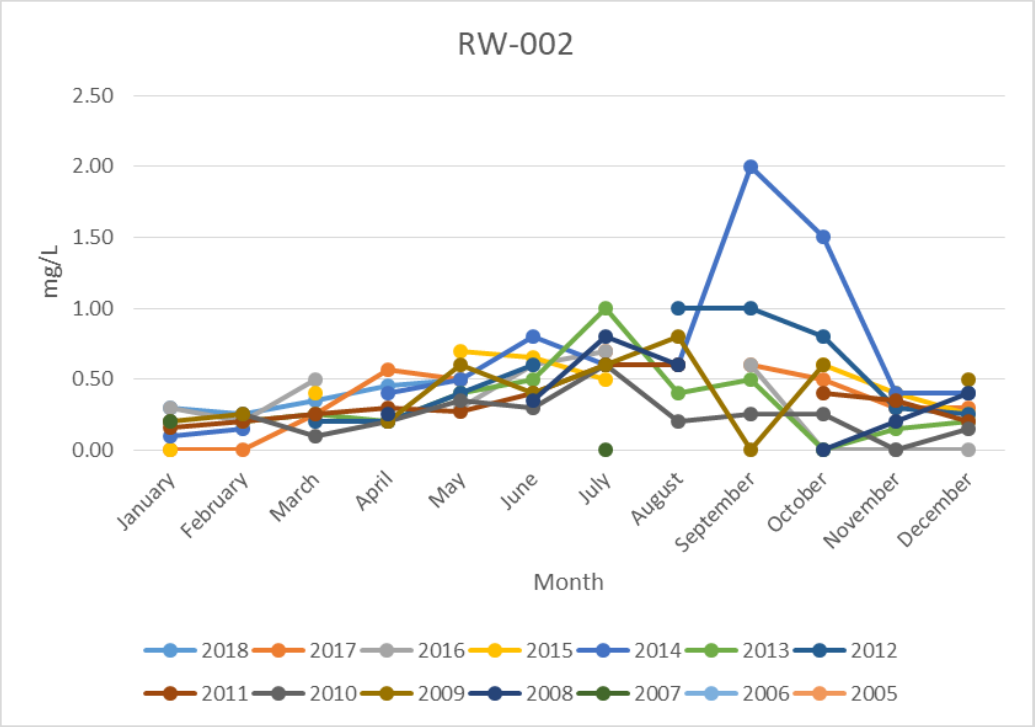

Figure 14: Phosphates for site RW-002, graphed annually to show seasonal trends.

However, some of the preceding nitrate and phosphate trends may not be statistically significant. The graphs also provide poor evidence of correlation. “Table 4” and “Table 5” list the statistically significant peak events for nitrates and phosphates.

Statistically Significant Events (Nitrates)		
Site ID	Date	Significant Events
RW-002	October 2005 November 2005 February 2009 January 2016 January 2017	5

RW-008	February 2007 December 2008	2
RW-012	March 2007 July 2007 January 2017	3
RW-013	May 2007 October 2007 January 2017	3
RW-016	February 2009 March 2009	2

Table 4: Statistically significant nitrate measurement events for each site, defined as events greater than or equal to three standard deviations.

Statistically Significant Events (Phosphates)		
Site ID	Date	Total Significant Events
RW-002	August 2012 September 2012 July 2013 September 2014 October 2014	5

RW-008	June 2008 July 2008 August 2010 November 2012 June 2016	5
RW-012	October 2009	1
RW-013	Mar 2009 July 2010 December 2013 October 2015	4
RW-016	March 2016	1

Table 5: Statistically significant phosphate measurement events for each site, defined as events greater than or equal to three standard deviations.

Lastly, “Figure 15” is a graph of the frequency of statistically significant events per season depict three important trends:

1. Statistically significant nitrate events are most likely to occur during the winter months.
2. Statistically significant phosphate events are most likely to occur during the summer and fall months.
3. The seasonal occurrence of nitrate and phosphate events appear to be negatively correlated.

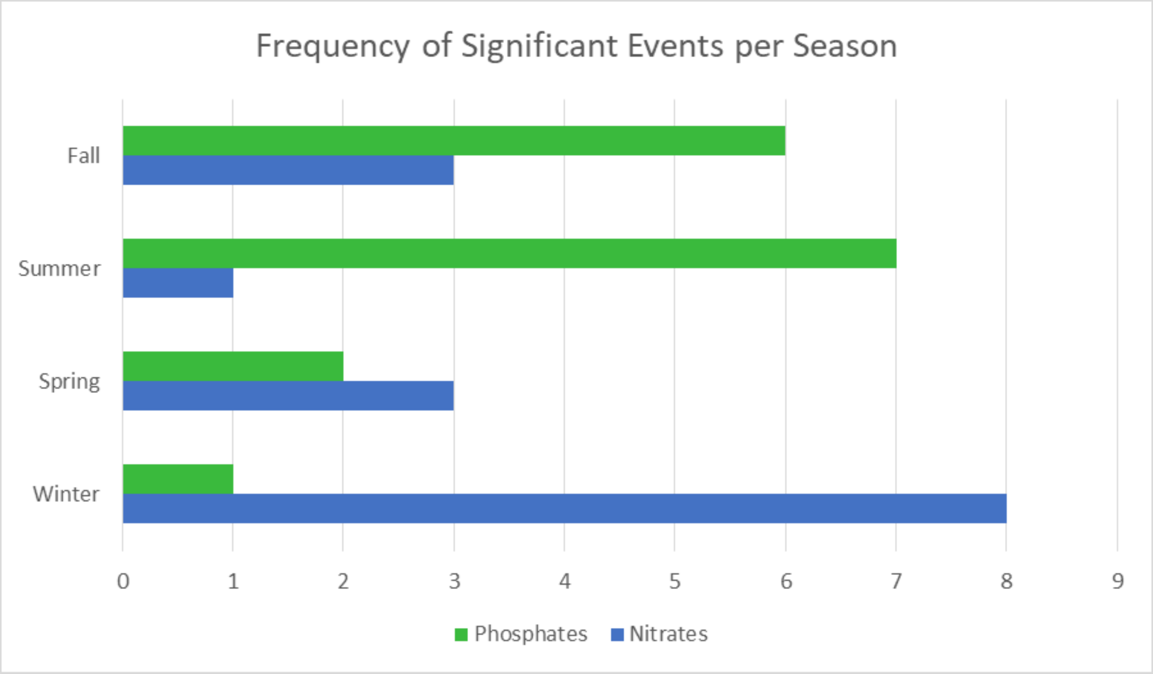

Figure 15: Frequency of statistically significant events (greater than three standard deviations) per season.

Discussion

The results show that nitrates vary, as referenced by very different standard deviations for each site. Nitrates are highest, on average, at site RW-016. This is to be expected, as RW-016 also known as Forester Creek, is a tributary fed by a large concrete lined channel extending for miles. This channel picks up runoff from at least two cities in its journey, which may act to collect nutrients until it enters Forester Creek. Nutrients are quickly transformed or immobilized once entering the creek, as shown by an average decrease in nitrates before reaching the next sampling location.

There is a tendency for peak nitrate events to occur during the winter. This correlates with the rainy season for San Diego. It is possible that nitrates in the San Diego River peak as a result of runoff from surrounding urban areas. Alternatively, during the summer months, nitrate levels may be lower due to uptake by biota during the growing season. During the winter, nitrates may become more soluble and abundant in the water as a result of mineralization by microbes in response to plant decay. Whatever the case, the more perplexing of the two nutrients is phosphate.

Phosphates, when compared to nitrates, have far less variability in the San Diego River, again reference the lower standard deviations. Phosphates are consistently higher at site RW-013. Intuitively, this might be expected when considering the sampling location. The site is downstream of a large golf course. While this is speculation, it generally takes a bit of fertilizer and a large input of water to keep grass green here in San Diego. Runoff of phosphates in fertilizer from the golf course is a possible explanation for the higher than average levels of phosphates at site RW-013.

Phosphates tend to peak seasonally, during summer and fall. This might be contrary to what one might expect; if phosphates are supplied by runoff, shouldn’t they peak during a time when runoff is the greatest? One might expect runoff to be greatest during the rainy season, or winter months. However, for phosphates, runoff from irrigation during warmer months may be more important. Irrigation during the warmer months may be providing a concentrated source of phosphates from fertilizers in runoff, not to mention, fertilizer use may be greater during the growing season. Additionally, there may be an alternative explanation which ties back in with the nitrate data.

Phosphates may bind to iron, essentially immobilizing the compound. In anaerobic conditions, the iron in the compound may be reduced, releasing phosphate to the system. The process is inhibited by denitrification. This could potentially explain the negative correlation between significant nitrate and phosphate events. Without further study, it is difficult to determine the ultimate cause. The cause of phosphate enrichment in the San Diego River is a topic that deserves further study, as there may be an indication that legacy phosphorus could become a problem in the future.

There are some key flaws in this process that could prevent its usefulness as a guide to understanding nutrients in the San Diego River. First, I compiled samples from sites within close proximity to increase sample size, which might have skewed the data. Second, as a result of the lack of trend development, I decided to narrow down the search by focusing on statistically significant nutrient events. While this did yield important insights, it is based on a much smaller sample size that represents a very small proportion of the data. Focus on the significant events, however, does effectively eliminate normal or baseline data, subjecting the most unique events to analysis. A holistic picture of nutrients would require more information about hydrology, weather, and a host of other variables. If nothing else, the process of this study has determined the need for more data.

This student recommends a revision to the RiverWatch sampling process, if resources were not an issue. There would be benefit to sampling nutrients at each site, not just sites of interest, and/or multiple samples per site. This could allow one to develop a model of nutrient mobility along the river, to determine a baseline for nutrients, and identify fluxes that may impact nutrient levels. This is also necessary if, ultimately, nutrient thresholds were to be developed to monitor the effectiveness of management efforts.

Conclusion

Nitrate and phosphate data in the San Diego River has been collected for over a decade. A simple graph of nutrient data does not help to determine trends, nor to understand sources of nutrients. There is great variability between sites and variability in nutrient highs between sites. Highs for nitrates and phosphates occur at different times of year and at different sites. A lack of trends has likely led to the conclusion that nutrients in the San Diego River are of non-point origin and unpredictable. The analysis of peak nutrient data, however, may indicate trends in nutrients after all. The analysis in this paper estimates peaks in nitrates tend to occur during the winter months, while peaks in phosphates tend to occur during the summer and into fall. The peaks and negative correlation between nitrates and phosphates may be explained simply by biogeochemistry; however, there is ultimately a need for more data.

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