# STABLE ISOTOPIC SIGNATURES OF NITRATE IN WASTEWATER EFFLUENT AND LOS ANGELES RIVER

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# INTRODUCTION

- Nitrate ($NO_3$), a nutrient originating safely from natural sources and dangerously from human activities.
- Contamination levels mainly arise from runoff, garden fertilizer, septic tanks, and sewage.

# OBJECTIVES

Identify the NO3 Interplay between the LA River and WWTP's

Interpret NO3 Isotopic Signatures

# WWTP INFLUENCE

- Nitrification and Denitrification are applied to the wastewater primarily to manage the concentration of ammonia.

Nitrification is the process of breaking down ammonia contaminants into nitrite though the use of ammonia-oxidizing bacteria.

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$

Next, a similar technique is used by utilizing a nitrite-oxidizing bacteria to oxidize the produced nitrite into nitrate

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

Denitrification extends this process by adding a step that reduces nitrate into nitrogen gas by using facultative anaerobes such as fungi.

$$6\ NO_3^- + 2\ CH_3OH \rightarrow 6\ NO_2^- + 2\ CO_2 + 4\ H_2O$$

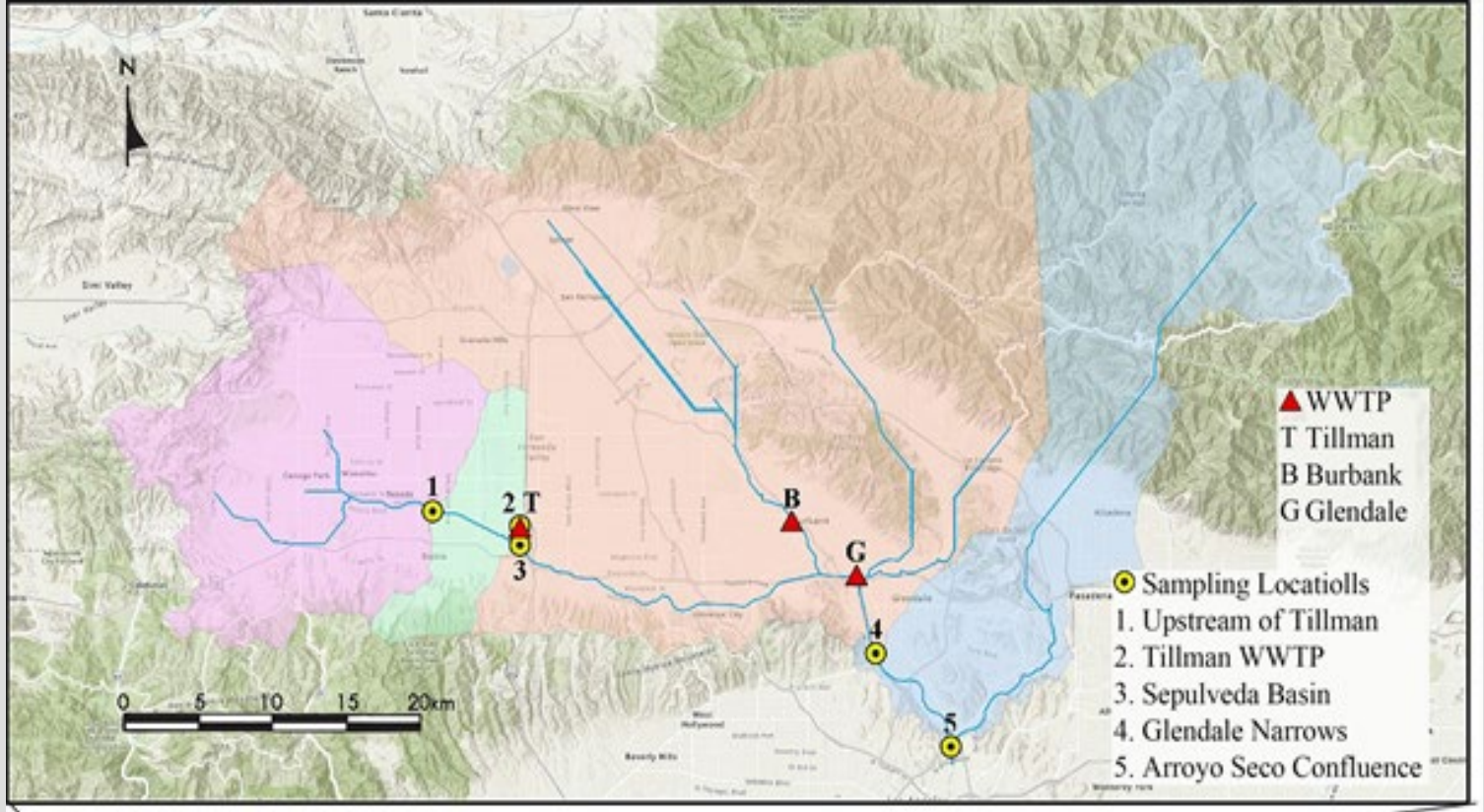
$$6\ NO_2^- + 3\ CH_3OH \rightarrow 3\ N_2 + 3\ CO_2 + 3\ H_2O + 6\ OH^-$$

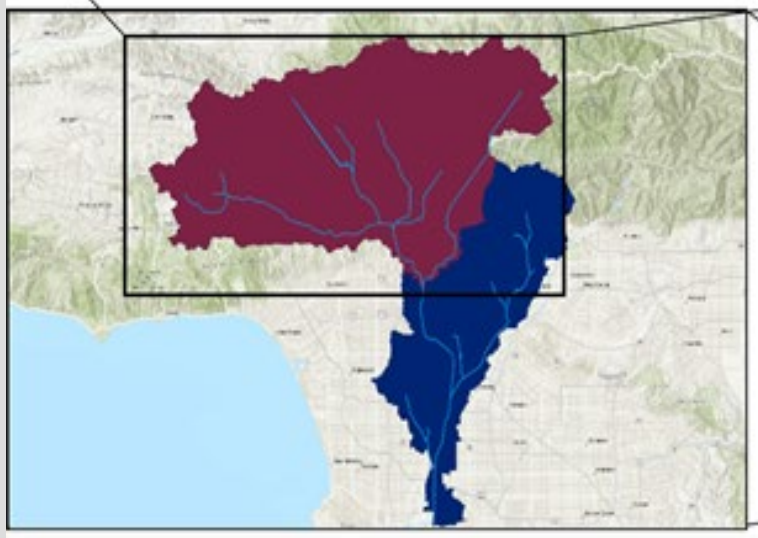
Study Area

5 Sampling Locations

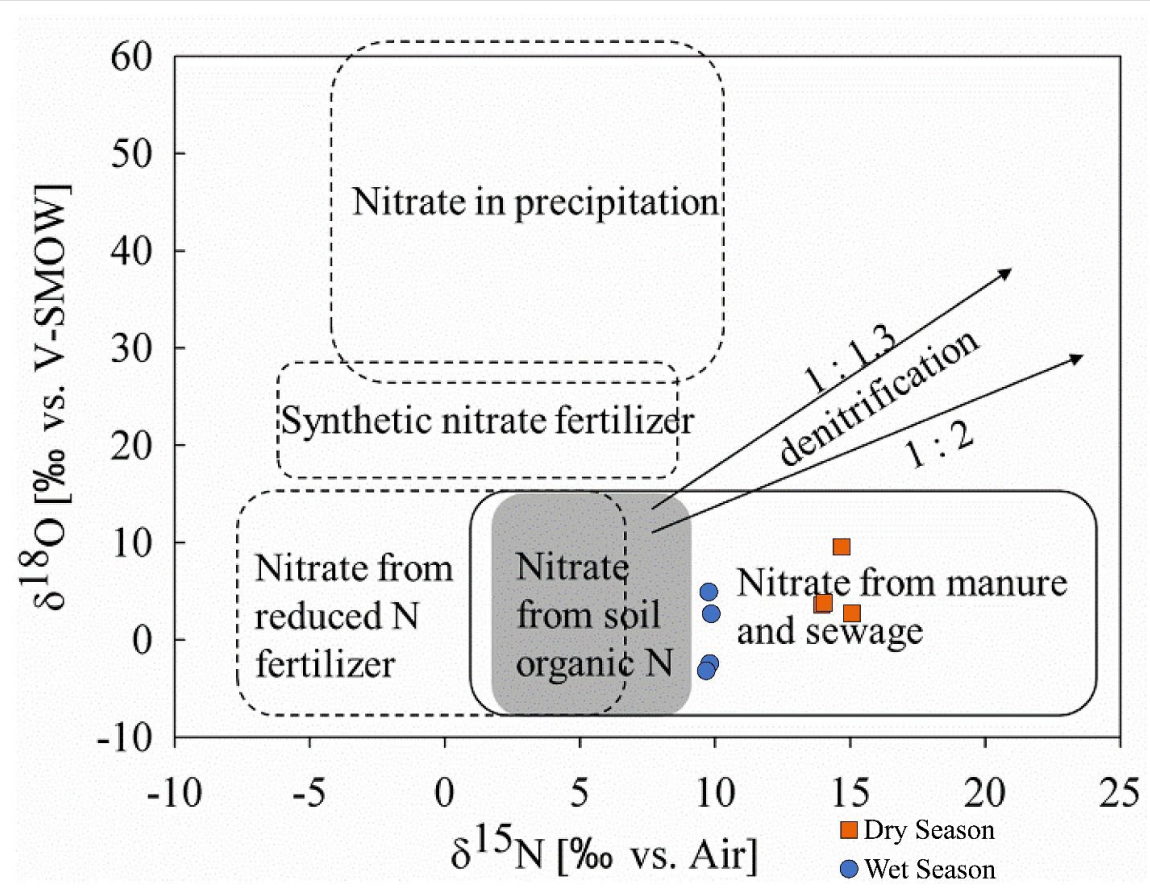
3 Isotope Sample Locations

3 Wastewater Treatment Plants



# ISOTOPE DATA

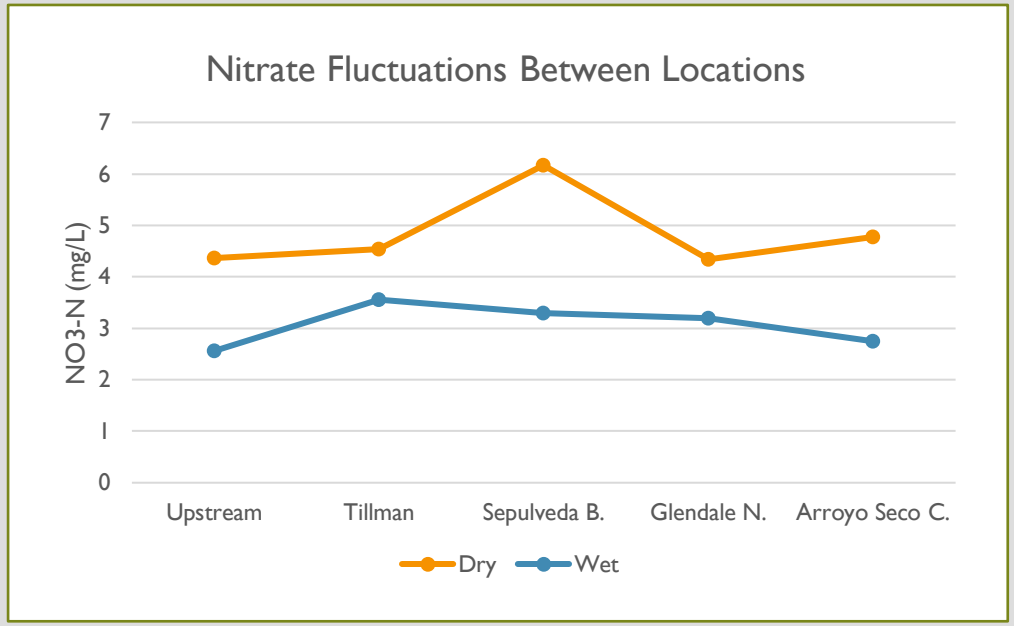



| | | 2022 Dry Season | | 2023 Wet Season | |
|---|---|---|---|---|---|
| | Distance km (miles) | δ15Nair (‰) | δ18OVSMOW (‰) | δ15Nair (‰) | δ18OVSMOW (‰) |
| Upstream | 0 | 14.72 | 9.49 | 9.74 | 5.11 |
| Tillman | 5.07 (3.2) | 13.92 | 3.48 | 9.79 | −2.49 |
| Tillman (lab duplicate) | N/A | 14.03 | 3.69 | 9.7 | −3.01 |
| Sepulveda Basin | 6.25 (3.9) | 15.09 | 2.7 | 9.86 | 2.84 |

Research indicates that in naturally occurring nitrate, only one oxygen atom is sourced from atmospheric O2, while the other two originate from water, which tends to be significantly depleted in $\delta^{18}O$.

This stands in contrast to nitrate found in synthetic fertilizers, where the oxygen is primarily derived from atmospheric $O_2$ and will resultingly be less depleted, and possibly enriched.

# NITRATE DATA




| | | 2012 Dry Season | 2013 Wet Season | 2017 Dry Season | 2018 Wet Season | 2022 Dry Season | 2023 Wet Season |
|---|---|---|---|---|---|---|---|
| **Sample Location** | Distance km (miles) | $NO_3$-N (mg/l) | $NO_3$-N (mg/l) | $NO_3$-N (mg/l) | $NO_3$-N (mg/l) | $NO_3$-N (mg/l) | $NO_3$-N (mg/l) |
| **Upstream** | 0 | ND | ND | ND | ND | 4.36 | 2.56 |
| **Tillman WWTP** | 5.07 (3.2) | ND | ND | ND | ND | 4.54 | 3.55 |
| **Sepulveda Basin** | 6.25 (3.9) | 3.8 | 3.86 | 4.04 | 4.2 | 6.17 | 3.3 |
| **Glendale Narrows** | 35.77 (22.2) | 4.86 | 1.63 | 4.2 | 2.78 | 4.34 | 3.2 |
| **Arroyo Seco** | 44.52 (27.7) | 4.16 | 2.53 | 3.68 | 1.3 | 4.77 | 2.75 |
| | Average | 4.27 | 2.67 | 3.98 | 2.76 | 4.84 | 3.07 |
| | STDEV | 0.54 | 1.12 | 0.27 | 1.45 | 0.77 | 0.41 |
| | MIN | 3.8 | 1.63 | 3.68 | 1.3 | 4.34 | 2.56 |
| | MEDIAN | 4.16 | 2.53 | 4.04 | 2.78 | 4.54 | 3.2 |
| | MAX | 4.86 | 3.86 | 4.2 | 4.2 | 6.17 | 3.55 |

# DATA ANALYSIS

| | | Dry | Season | 2022 | | Wet | Season | 2023 | |
|---|---|---|---|---|---|---|---|---|---|
| Sample Location | Distance km (miles) | pH | Temp (˚C) | Salinity (ppt) | DO (ppm) | pH | Temp (˚C) | Salinity (ppt) | DO (ppm) |
| Upstream | 0 | 7.07 | 21.7 | 1.1 | ND | 6.95 | 8.9 | 0.87 | 2.58 |
| Tillman WWTP | 5.07 (3.2) | 6.54 | 24.5 | 0.5 | ND | 6.65 | 16.4 | 0.46 | 4.68 |
| Sepulveda Basin | 6.25 (3.9) | 5.72 | 22.6 | 0.5 | ND | 6.58 | 11 | 0.7 | 4.66 |
| Glendale Narrows | 35.77 (22.2) | 6.7 | 24.8 | 0.5 | ND | 7.05 | 15.2 | 0.6 | 3.25 |
| Arroyo Seco | 44.52 (27.7) | 8.1 | 23.7 | 0.4 | ND | 8.74 | 15.2 | 0.41 | 1.4 |
| | Average | 6.83 | 23.46 | 0.6 | | 7.19 | 13.34 | 0.608 | 3.314 |
| | STDEV | 0.87 | 1.3 | 0.28 | | 0.89 | 3.22 | 0.19 | 1.4 |
| | MIN | 5.72 | 21.7 | 0.4 | | 6.58 | 8.9 | 0.41 | 1.4 |
| | MEDIAN | 6.7 | 23.7 | 0.5 | | 6.95 | 15.2 | 0.6 | 3.25 |
| | MAX | 8.1 | 24.8 | 1.1 | | 8.74 | 16.4 | 0.87 | 4.68 |

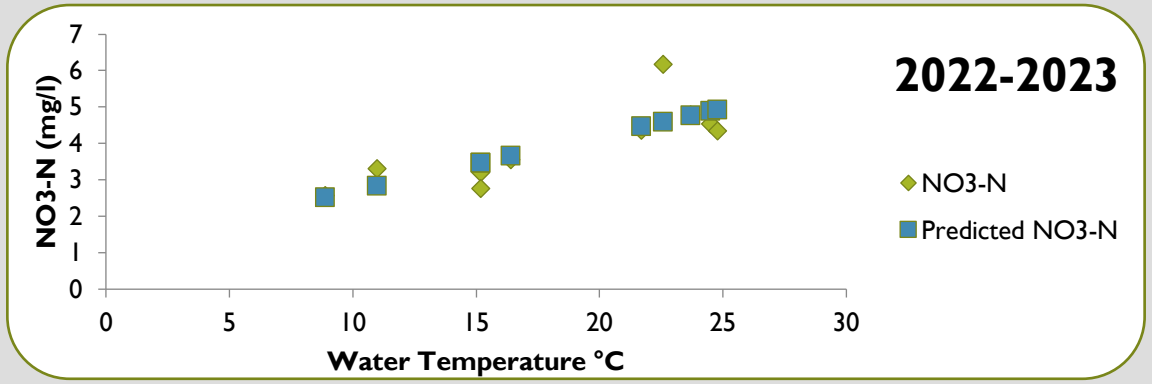
Hypothesis

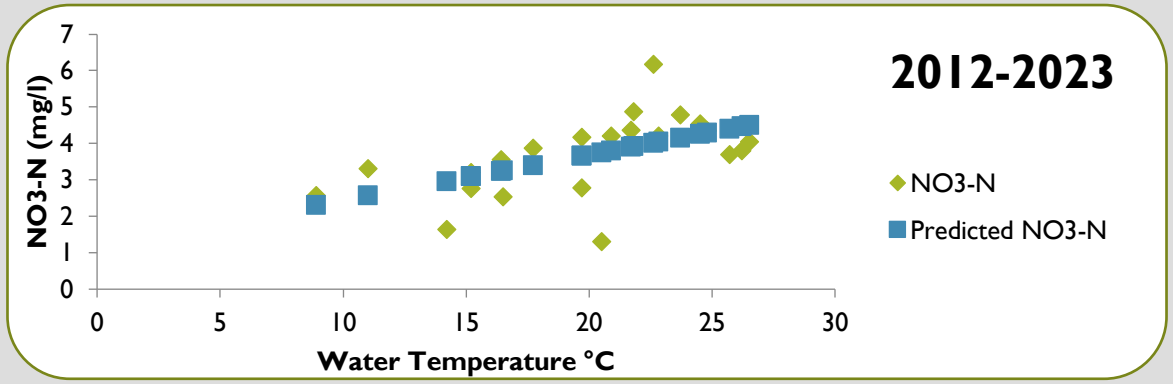
- $H_1$: There is a significant impact of pH on Nitrate concentration
- $H_2$: There is a significant impact of Salinity on Nitrate concentration
- $H_3$: There is a significant impact of water Temperature on Nitrate concentration

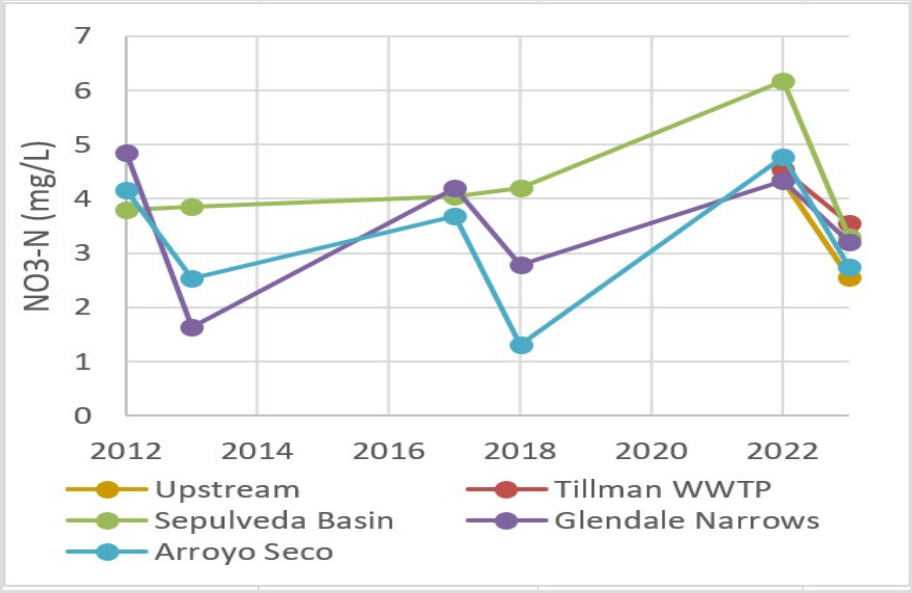
$H_4$: There is a significant historical impact of water temperature on Nitrate concentration from data measured in 2012-2013, 2017-2018, and 2022-2023.

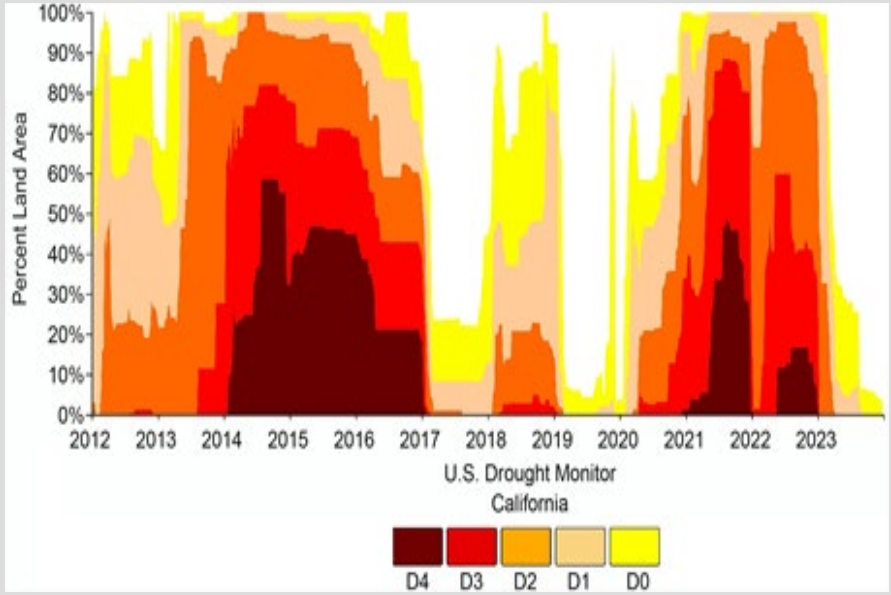
| Hypothesis | Regression Weights | Beta Coefficient | $R^2$ | F | p-value | Hypothesis Supported |
|---|---|---|---|---|---|---|
| $H_1$ | PH → NO3 | -.608 | .222 | 2.286 | .169 | No |
| $H_2$ | SAL → NO3 | -.950 | .038 | .319 | .588 | No |
| $H_3$ | TEMP→ NO3 | .152 | .650 | 14.831 | .005 | Yes |
| $H_4$ | H-TEMP → H-NO3 | 0.125 | .306 | 8.822 | .008 | Yes |

# TEMPERATURE AND NITRATE



# CONCLUSIONS AND LIMITATIONS

- Nitrate signatures show more natural influence in treated water.

- Nitrate concentrations are correlated to Water temperature.

- Dry Seasons have higher NO3 concentrations than Wet Seasons.

- Only two sets of samples from a single WWTP has been investigated.

- Most studies support a link between NO3 and temperature.

- California has distinct dry and wet seasons as well as frequent and severe droughts.