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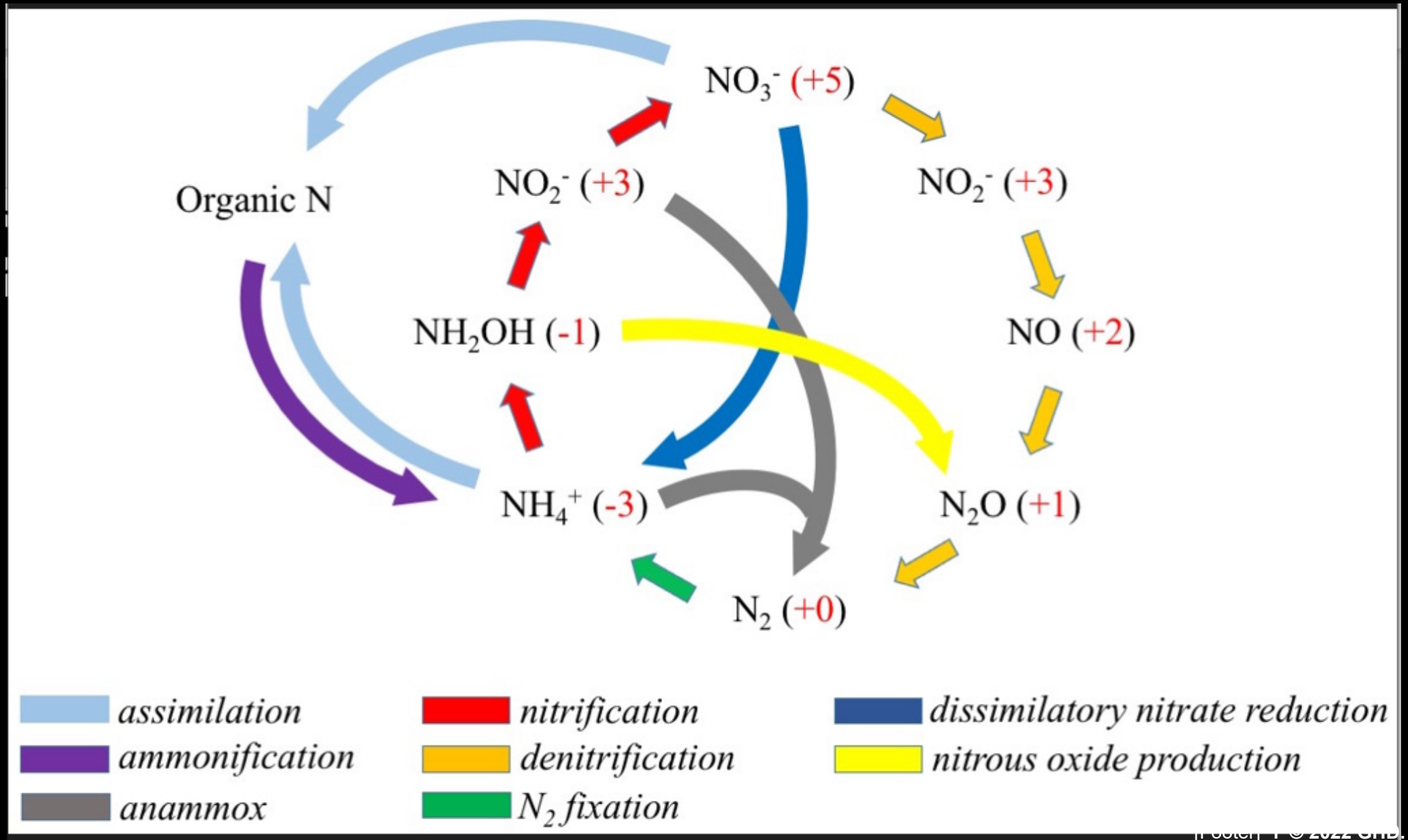
GHD

Compound Specific Isotope Analysis to Identify the Source of Ammonia and Nitrate in Surface Water Adjacent to a Fertilizer Plant

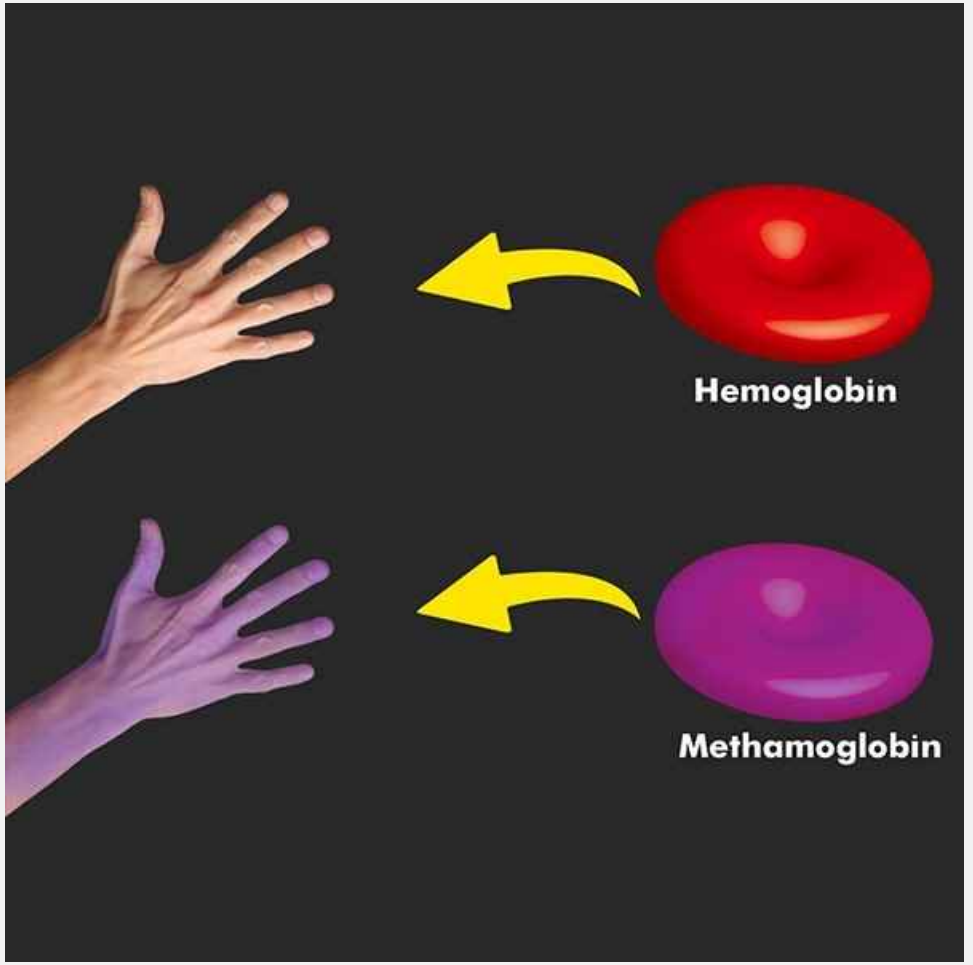
Welcome

Nitrogen Cycle



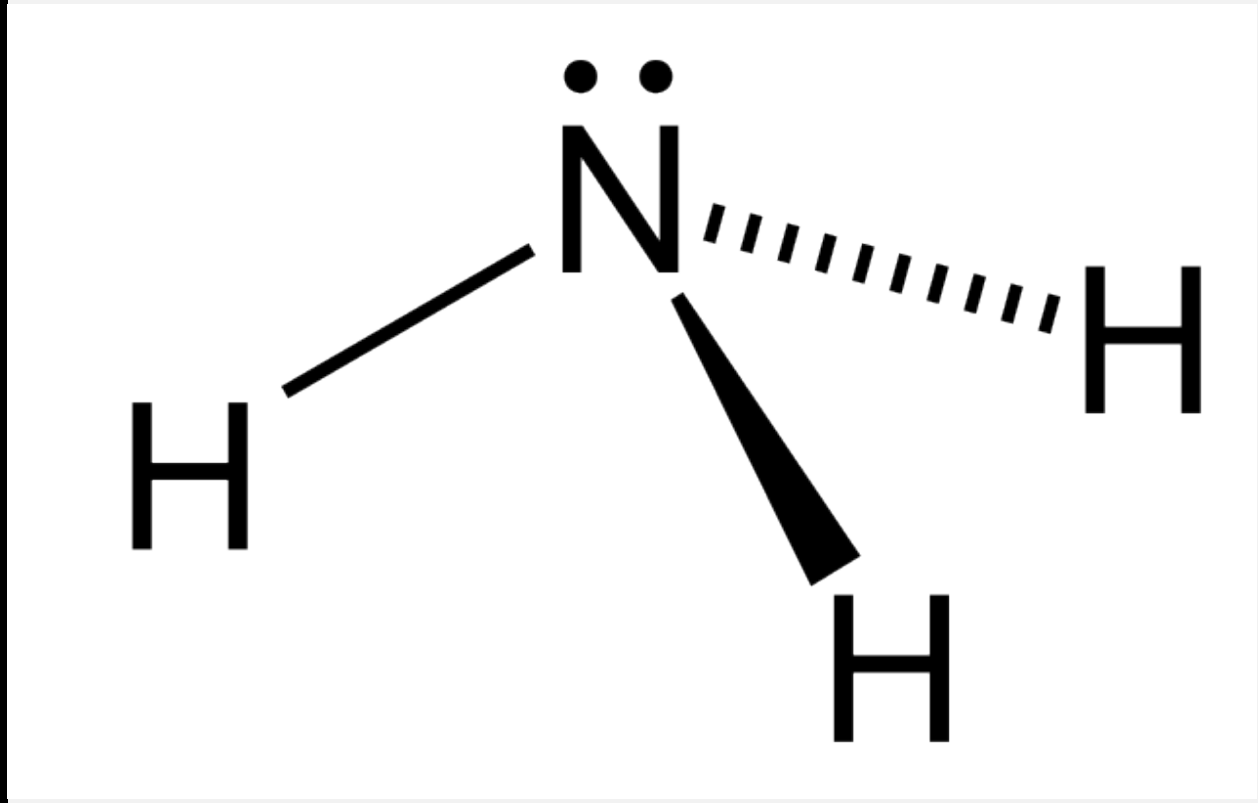
→ **Nitrate**

- Affects how blood carries oxygen
- Turns hemoglobin into methemoglobin
- Contains ferric rather than ferrous iron
- Unable to bind oxygen
- Blue baby syndrome



→ Ammonia

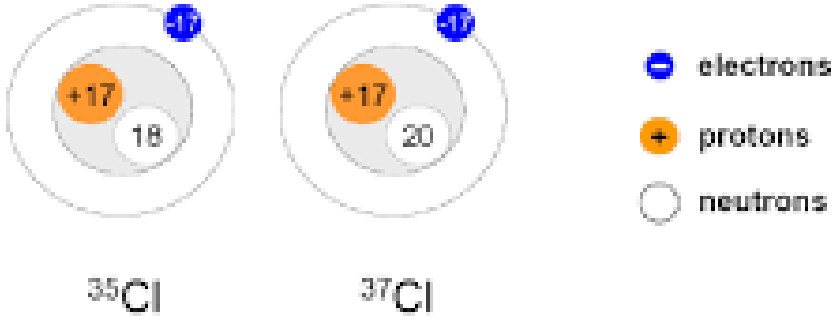
- Can irritate skin, mouth throat, lungs, eyes
- Long term exposure in drinking water can cause damage to organ systems
- Toxic to fish and aquatic animals at low concentrations



Compound Specific Isotope Analysis

Stable isotope = not radio active

Number of electrons	→ same
Number of protons	→ same
Number of neutrons	→ different
Mass	→ different



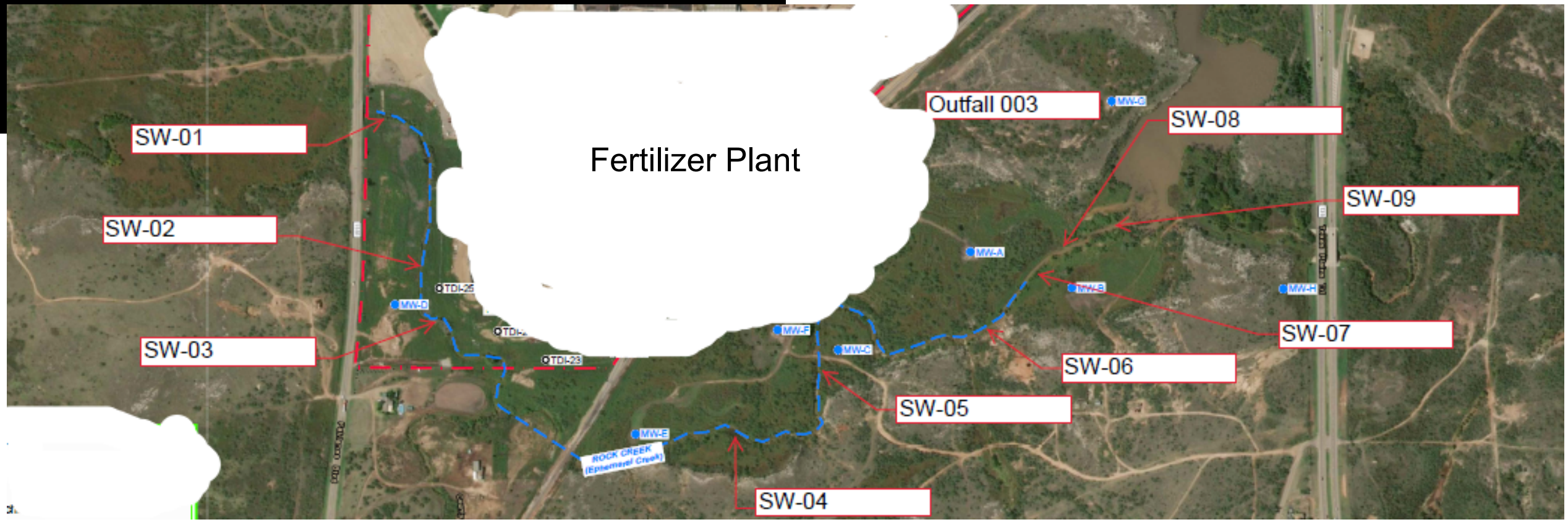
- Many elements have naturally occurring stable isotopes
- Examples of these include ^{13}C, ^{18}O, ^{37}Cl, ^{2}H, and ^{15}N.
- The ratio between the different isotopes can differ depending on the source of the material.
- In biological systems the lighter isotope is used preferentially to the heavier isotope therefore where biodegradation is occurring, undegraded materials have a higher concentration of the heavier isotope since the lighter isotopes have been degraded.
- The ratio between the heavier and lighter isotope is expressed as a delta value (δ).
- The δ value is calculated according to the following equation:

$$\delta(‰) = (R(sample)/R(standard)-1)X1000$$

R= ratio of heavy to light isotope

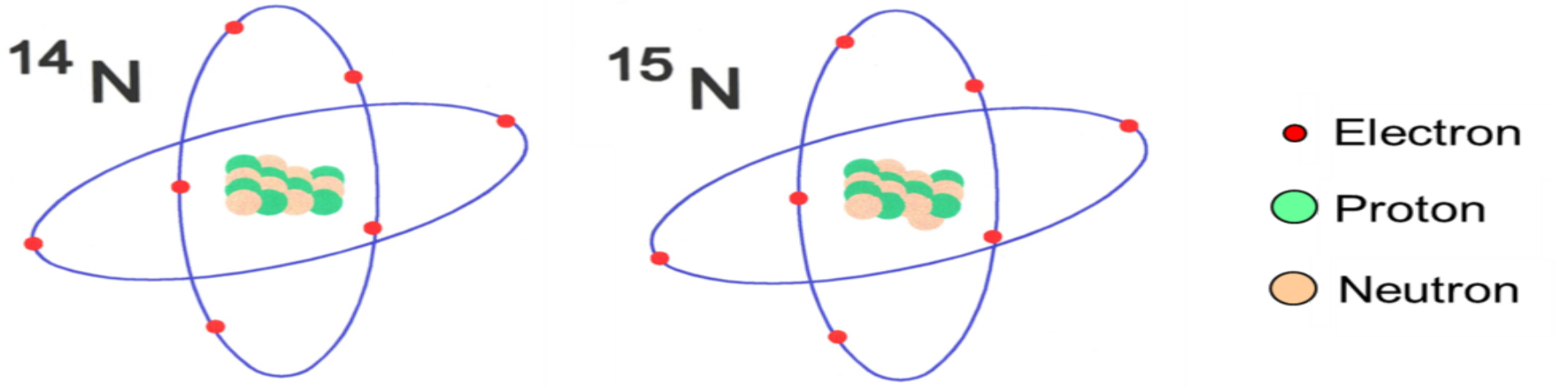
Fertilizer Site

- Is the ammonia present in the creek from the Plant?
- Is the nitrate present in the creek from ammonia from the Plant?
- Does groundwater from the Plant site exfiltrate into the creek?



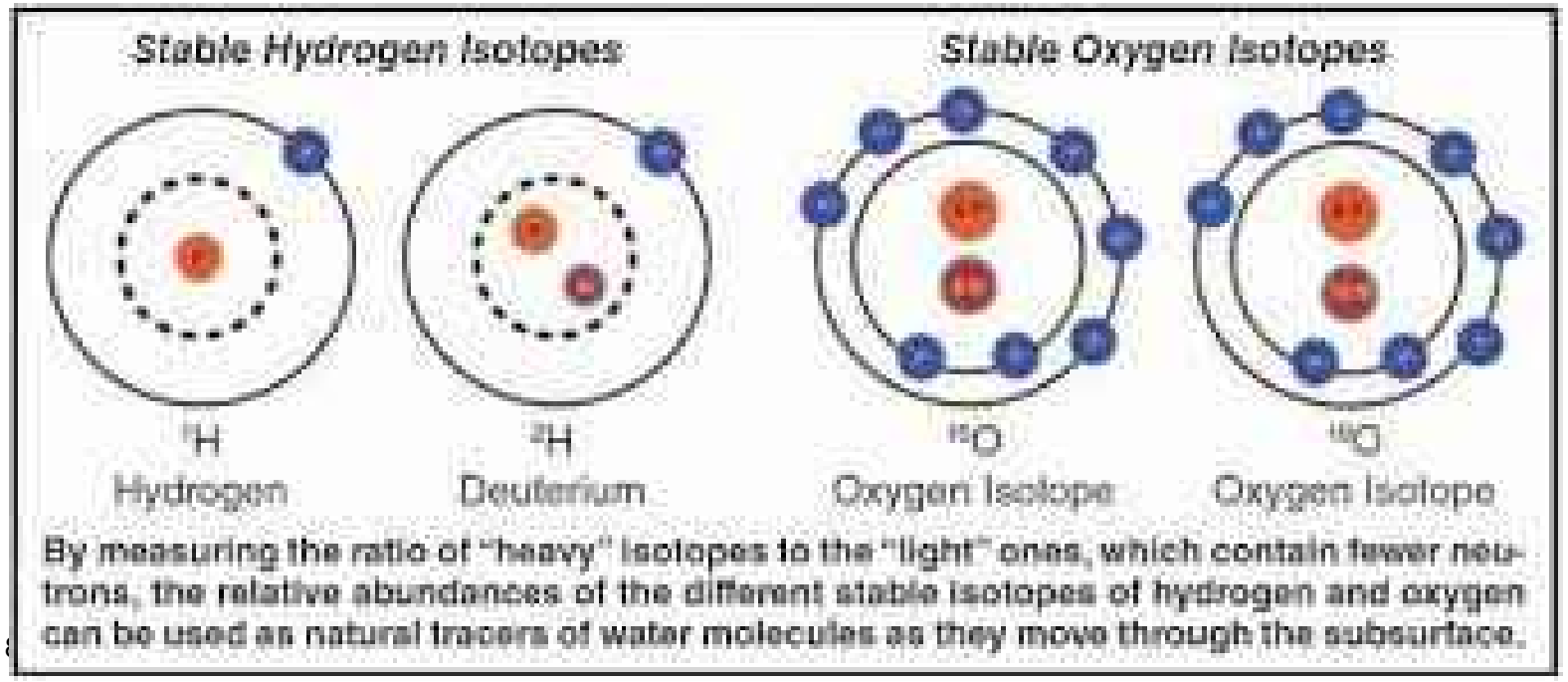
Compound Specific Isotope Analysis – Ammonia and Nitrate

- Industrially produced fertilizer - δ ^{15}N for ammonia of +/- 3‰
- Biologically produced ammonia - δ ^{15}N of between +10 and +25‰.
- Nitrate is not produced at the Site therefore all nitrate in the groundwater is derived from the bio-oxidation of ammonia



Compound Specific Isotope Analysis – Water

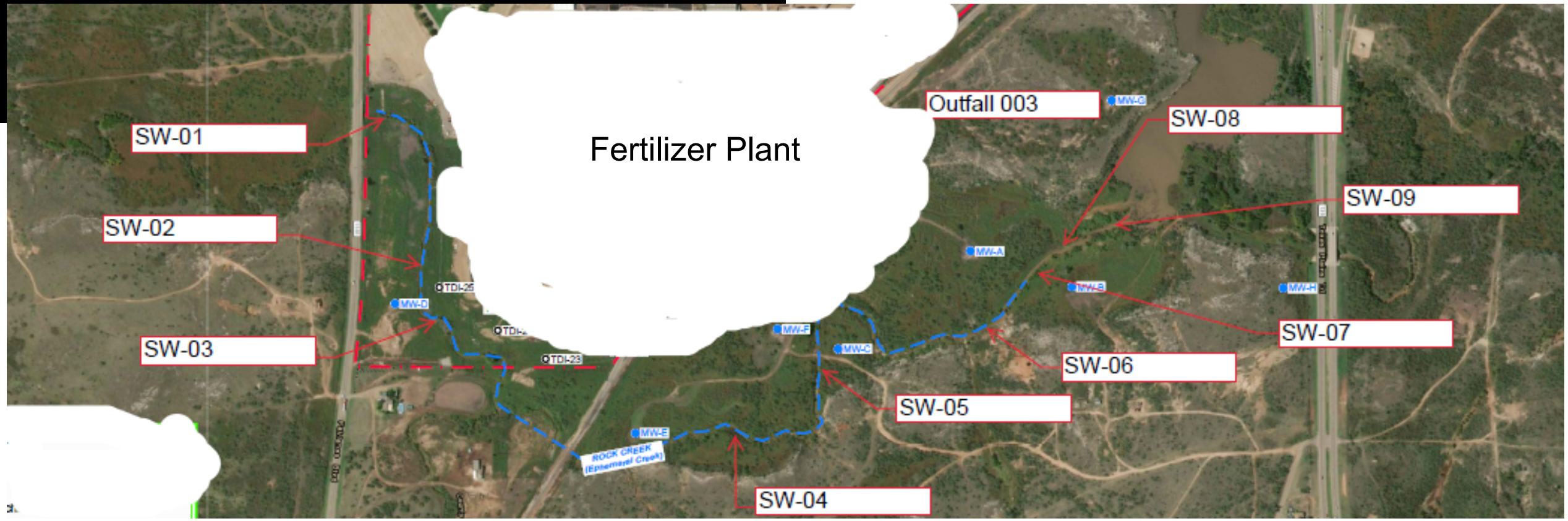
- Hydrogen and oxygen isotope ratios can be measured for water
- Ratios are compared to the Global Meteoric Line which indicates the typical values for rainwater.
- Difference from Global Meteoric Line indicate whether the water has been subject to evaporation or other processes that would change the isotopic signature,



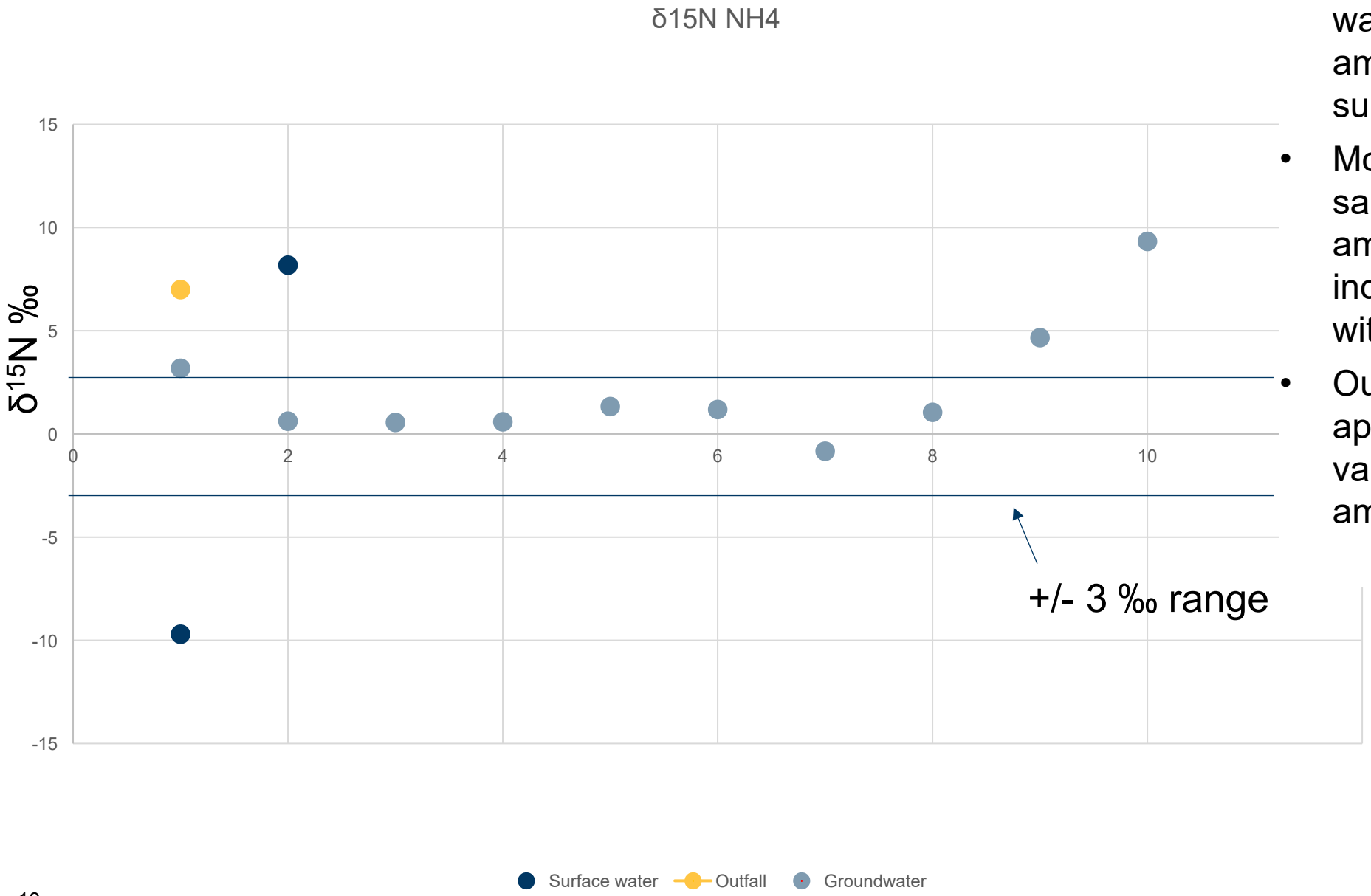
By measuring the ratio of "heavy" isotopes to the "light" ones, which contain fewer neutrons, the relative abundances of the different stable isotopes of hydrogen and oxygen can be used as natural tracers of water molecules as they move through the subsurface.

Approach

- Sample groundwater from wells high in ammonia and nitrate
- Sample the Outfall
- Sample surface water upgradient, adjacent to and downgradient of the Plant
- Upgradient surface water samples could not be collected because stream was dry in this area

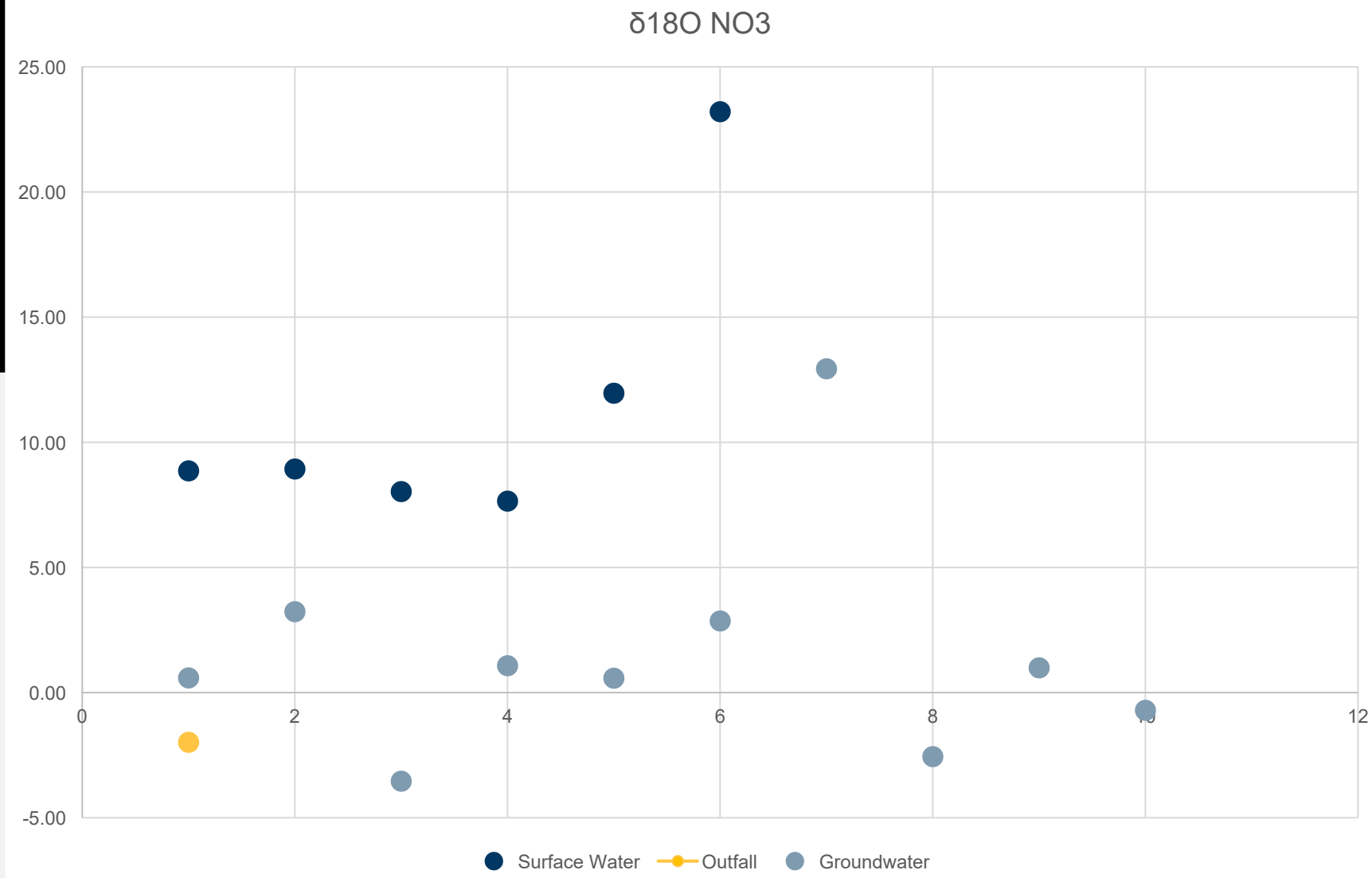


δ15N NH4 Data



- $\delta^{15}N$ data for ammonia is only available for two of the surface water samples due to low ammonia concentrations in the surface water.
- Most of the groundwater samples have a $\delta^{15}N$ for ammonia of +/- 3‰ which indicates that it is associated with the plant.
- Outfall value of 6.99 approaches the expected $\delta^{15}N$ value for biologically produced ammonia.

δ15N Nitrate Data

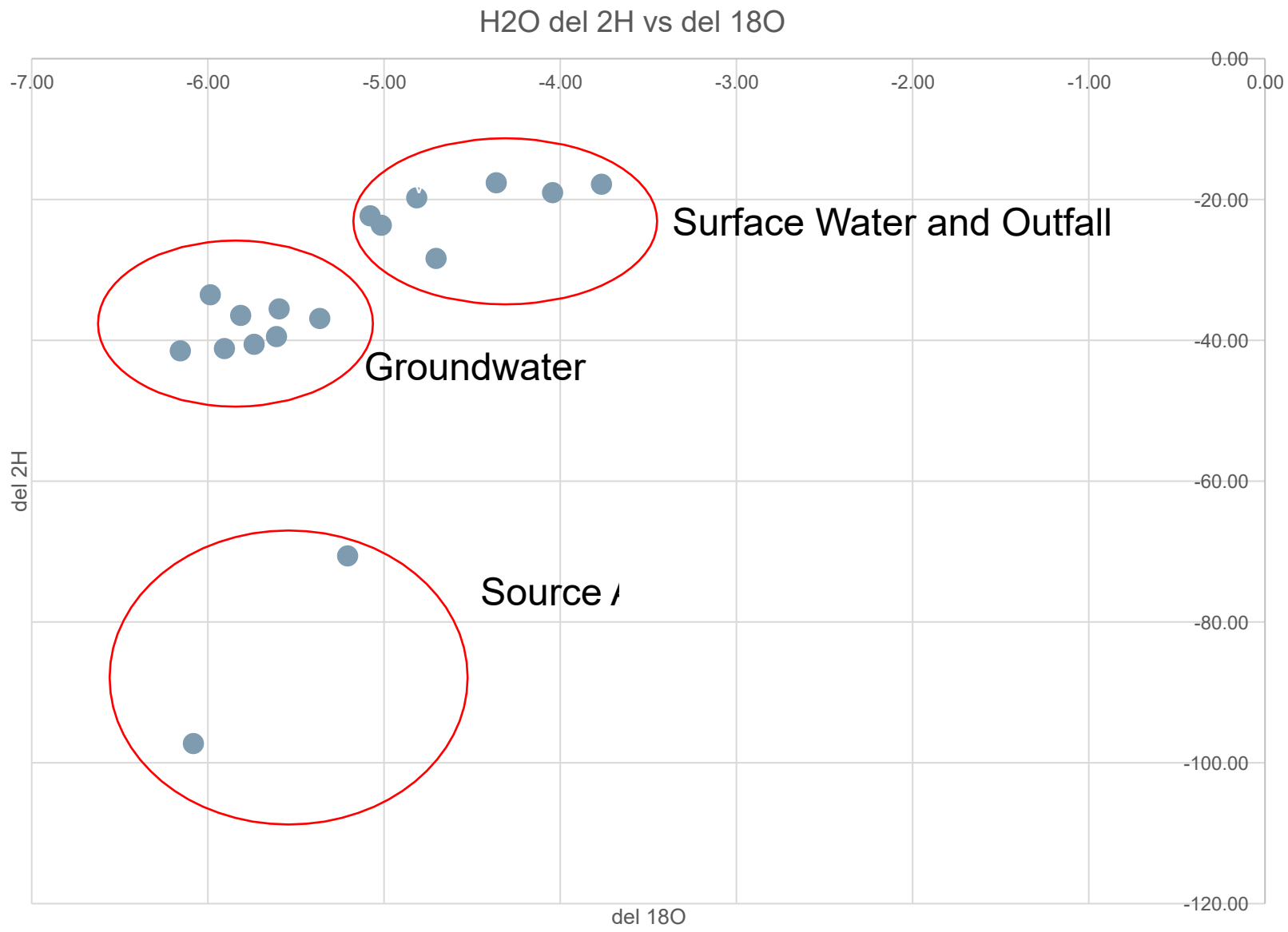


- The 6 surface water samples have similar $\delta^{15}N$ values
- Groundwater samples TDI-3R, P-23, P-1 and TDI-17 (downgradient wells) have values that resemble the surface water values
- The $\delta^{15}N$ data from nitrate indicate that the nitrate in the surface water is most likely from biologically produced ammonia and that the nitrate in certain groundwater samples may also be from biologically produced ammonia.
- The Outfall sample appears to have a $\delta^{15}N$ value for nitrate that is similar to that of the groundwater samples.

Conclusions from $\delta^{15}N$ Analyses

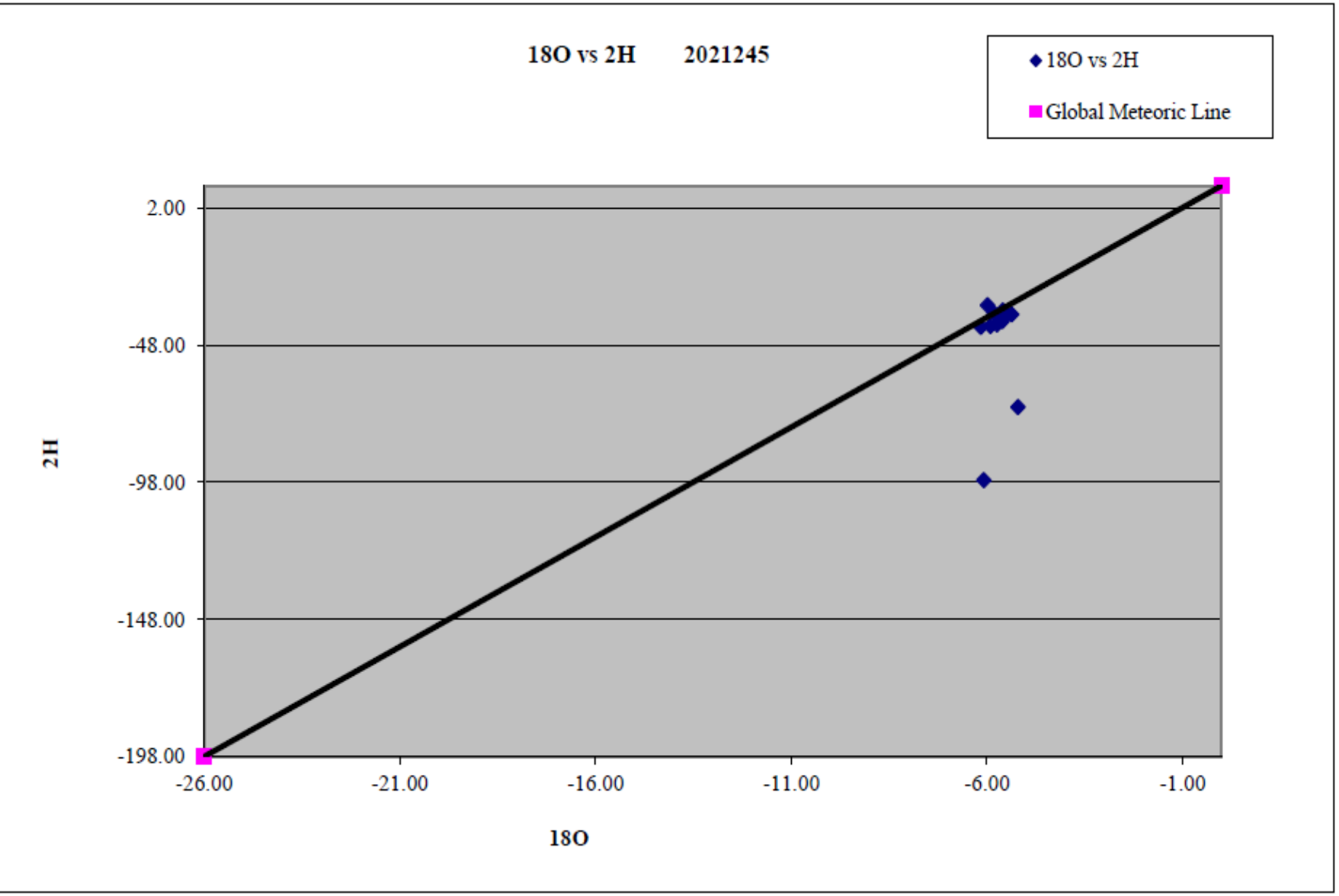
- The $\delta^{15}N$ value for ammonia suggests that most of the groundwater samples contain industrially produced ammonia likely associated with the plant except TDI-17 – the downgradient well
- The two surface water samples and the Outfall sample do not fall in the range for industrially produced ammonia. This suggests that the ammonia in the Outfall, surface water and downgradient groundwater samples has some biologically derived component
- The $\delta^{15}N$ value for nitrate suggests that all of the groundwater samples contain nitrate derived from industrially produced ammonia except groundwater samples TDI-3R, P-23, P-1 and TDI-17 – downgradient wells
- The Outfall sample has a $\delta^{15}N$ value for nitrate that suggests it is derived from industrially produced ammonia. Therefore, although the outfall appeared to contain some biologically derived ammonia, the nitrate present in the Outfall is primarily nitrate derived from industrially produced ammonia.

δ2H vs δ18O Water Data



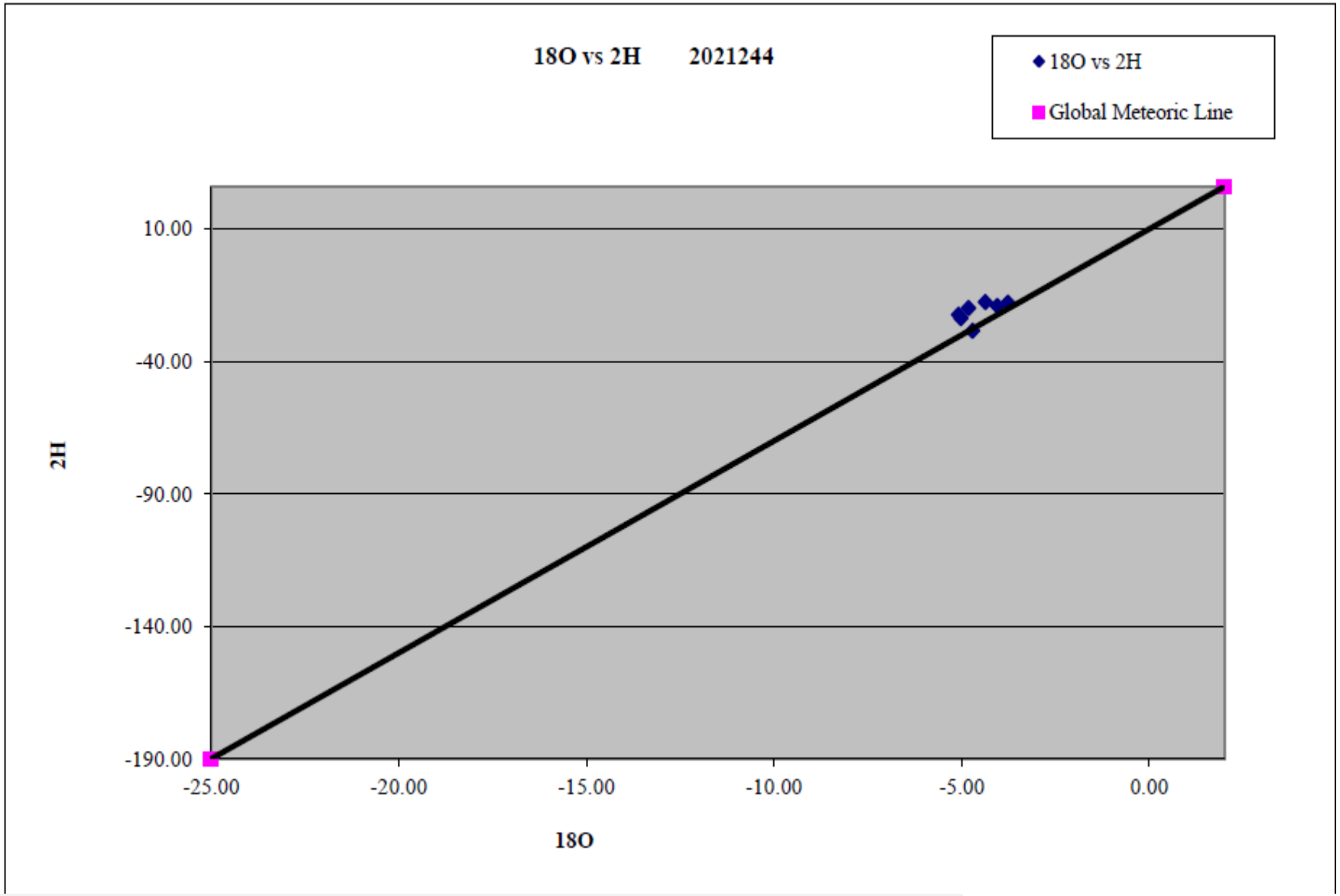
- When the δ ^{18}O is plotted vs the δ ^{2}H data for the samples all of the surface water samples cluster together and the Outfall sample clusters with them
- The Outfall sample consists of surface water.
- The source area wells TW-1 and TW-6 cluster together
- The remainder of the groundwater samples cluster together.

δ2H vs δ18O Goundwater Data



- Most of the groundwater samples fall along the Global Meteoric Line indicating that they have not be subject to evaporation or other processes that would change the isotopic signature
- Samples TW-1 and TW-6 the source area wells, do not fall along this line indicating that they are not similar to rain water. They likely contain a high concentration of process water from the plant

δ2H vs δ18O Surface Water Data



- The Outfall sample appears to fall along the Global Meteoric Line
- The rest of the surface water samples, while close to the line are slightly less negative with respect to δ ^{2}H and samples SW-8 and SW-9 are also slightly less negative with respect to δ ^{18}O
- Water that has undergone evaporation is typically enriched in the heavier isotopes
- The values indicate that the surface water samples, have undergone more evaporation than the Outfall sample or the groundwater samples.

Conclusions from Water Analyses

- When the $\delta\ ^{18}O$ is plotted vs the $\delta\ ^{2}H$ data for the samples all of the surface water samples cluster together and the Outfall sample clusters with them. This makes sense as the Outfall sample consists of surface water. The source area wells TW-1 and TW-6 also cluster together and then the remainder of the groundwater samples cluster together.
- The $\delta\ ^{18}O$ and $\delta\ ^{2}H$ values for most of the groundwater samples resemble rainwater, as does the Outfall water. This indicates that little evaporation from these samples has occurred.
- Source area wells TW-1 and TW-6 are not similar to rain water. They likely contain a high concentration of process water from the plant.
- The surface water samples are slightly different from rain water indicating that some evaporation has occurred from these samples. This is particularly true for downgradient surface water samples.

Overall Conclusions

- Data suggest that the Plant does not have a large impact on the creek