

SOURCES OF UNCERTAINTY IN NUTRIENT SAMPLING BELOW A POINT SOURCE

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Goal:

Estimate uncertainty associated with taking nutrient samples below a wastewater treatment plant

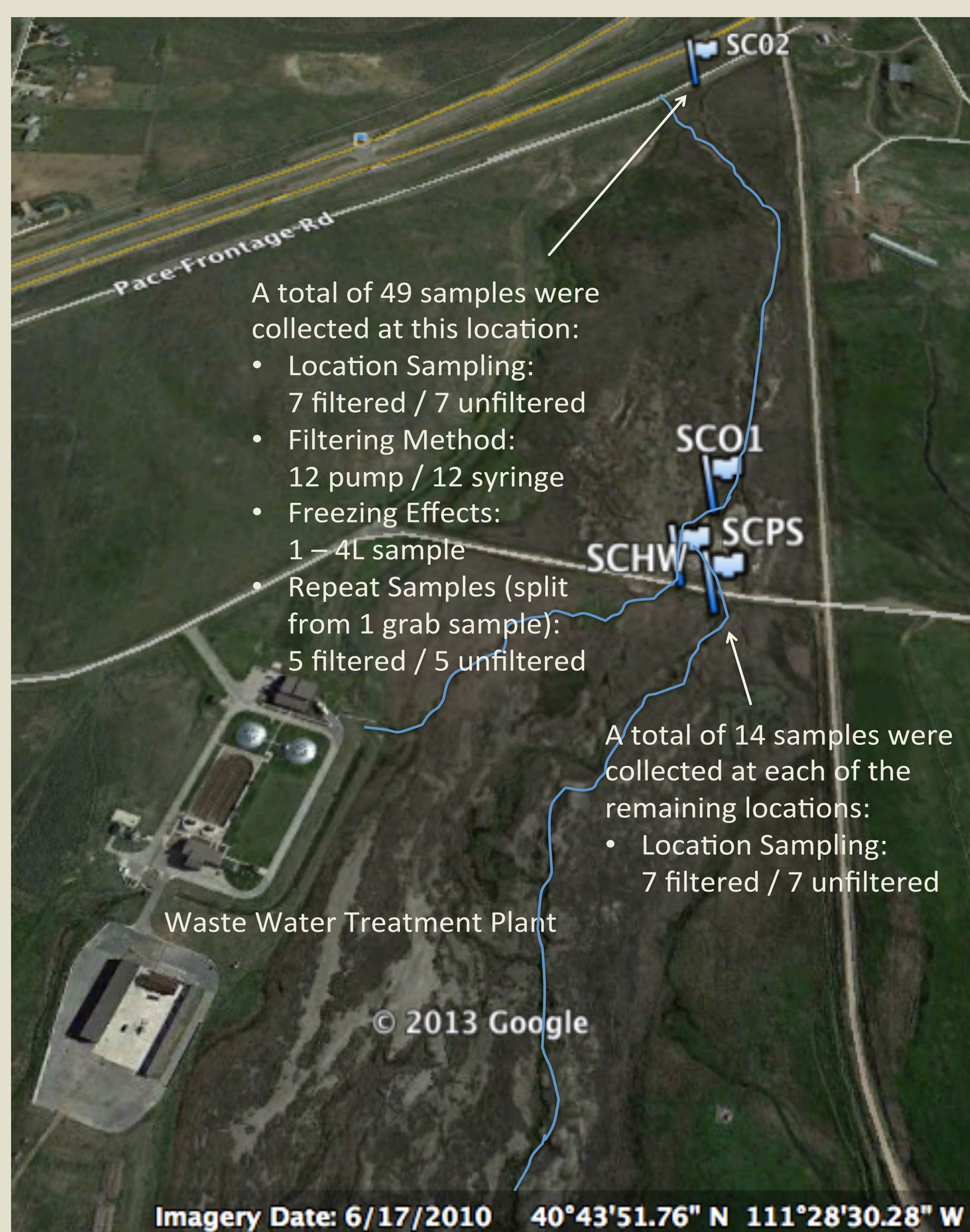
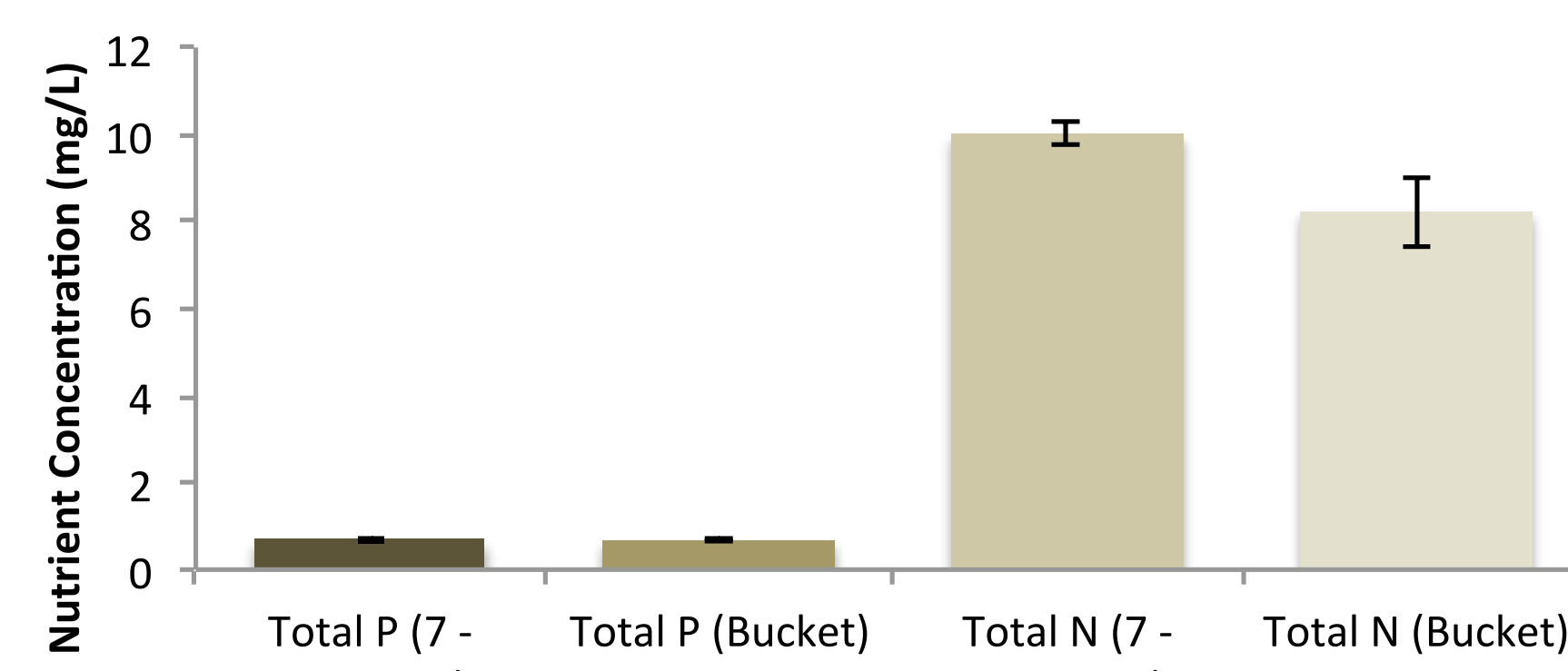


Figure 1. Locations of sampling, the number of samples collected at each location and the test for which they will be used

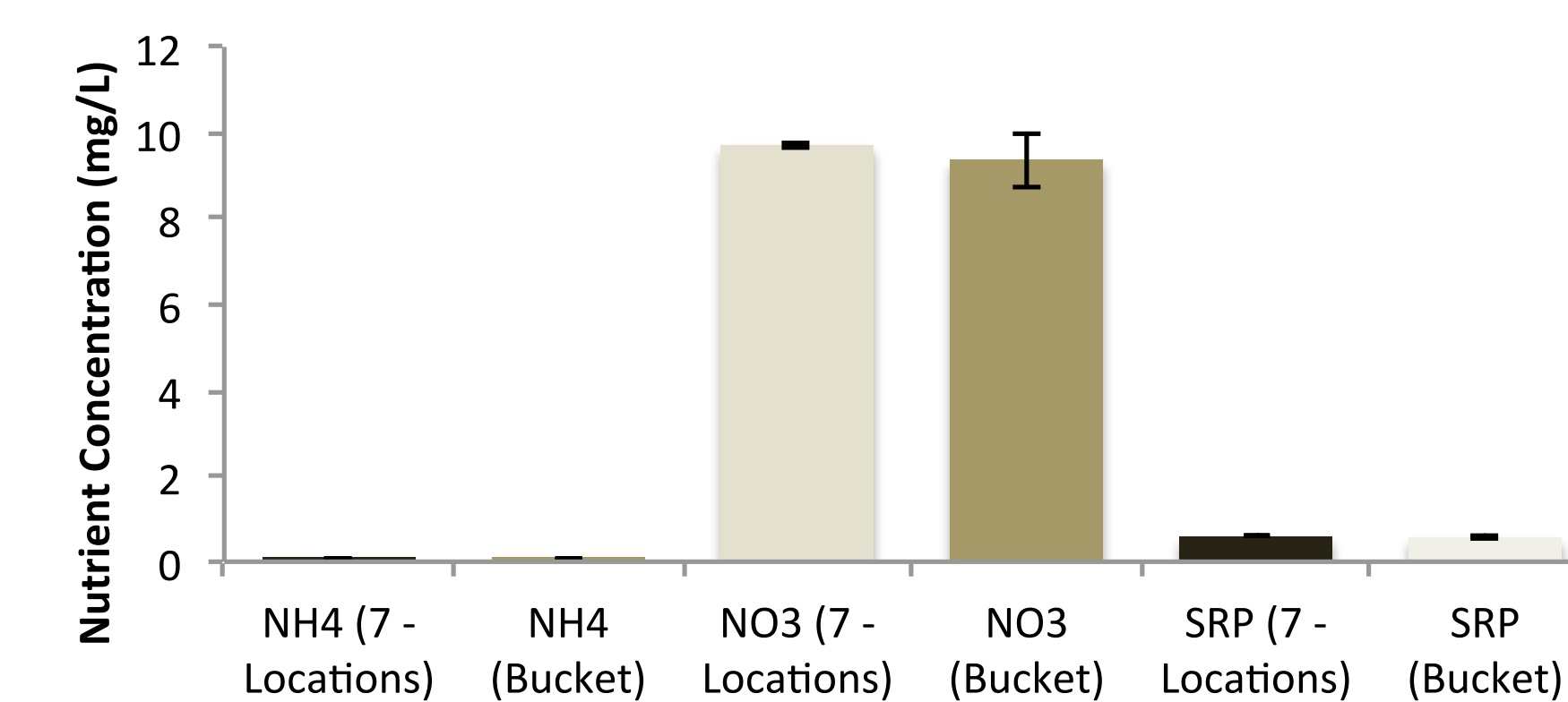
Field Uncertainty:

Figure 2: Comparing Mixed vs. Unmixed Samples (unfiltered)



Uncertainty in the field can come from sampling water that is not well mixed. If this is the case, concentrations should be more variable when collected from 7-locations in a cross section compared to 7 samples from a single, mixed bucket. I did not observe this (Figs 2, 3). Instead, samples from the bucket were more variable for TN (Fig 2) and NO_3 (Fig 3).

Figure 3: Comparing Mixed vs. Unmixed Samples (filtered)

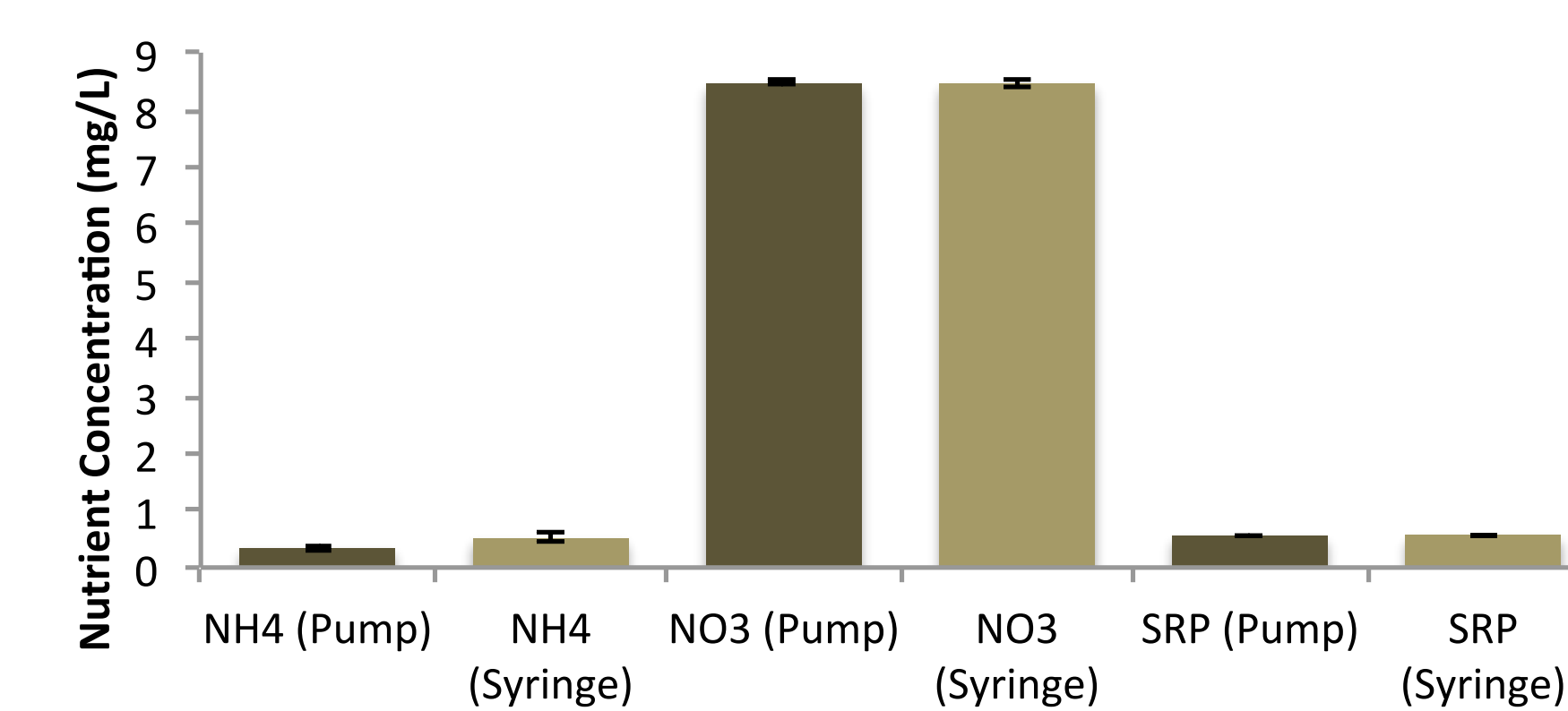


Sampling across a cross section of Silver Creek.



Filtering using a syringe.

Figure 4: Comparison of Filtration Techniques



We compared filtering using a pump and syringe (Fig. 4) and found that variation was similar, but the mean NH_4 concentration was higher using the syringe filter.

Lab Uncertainty:

Figure 5: Dilutions I Made vs. Lab Dilutions

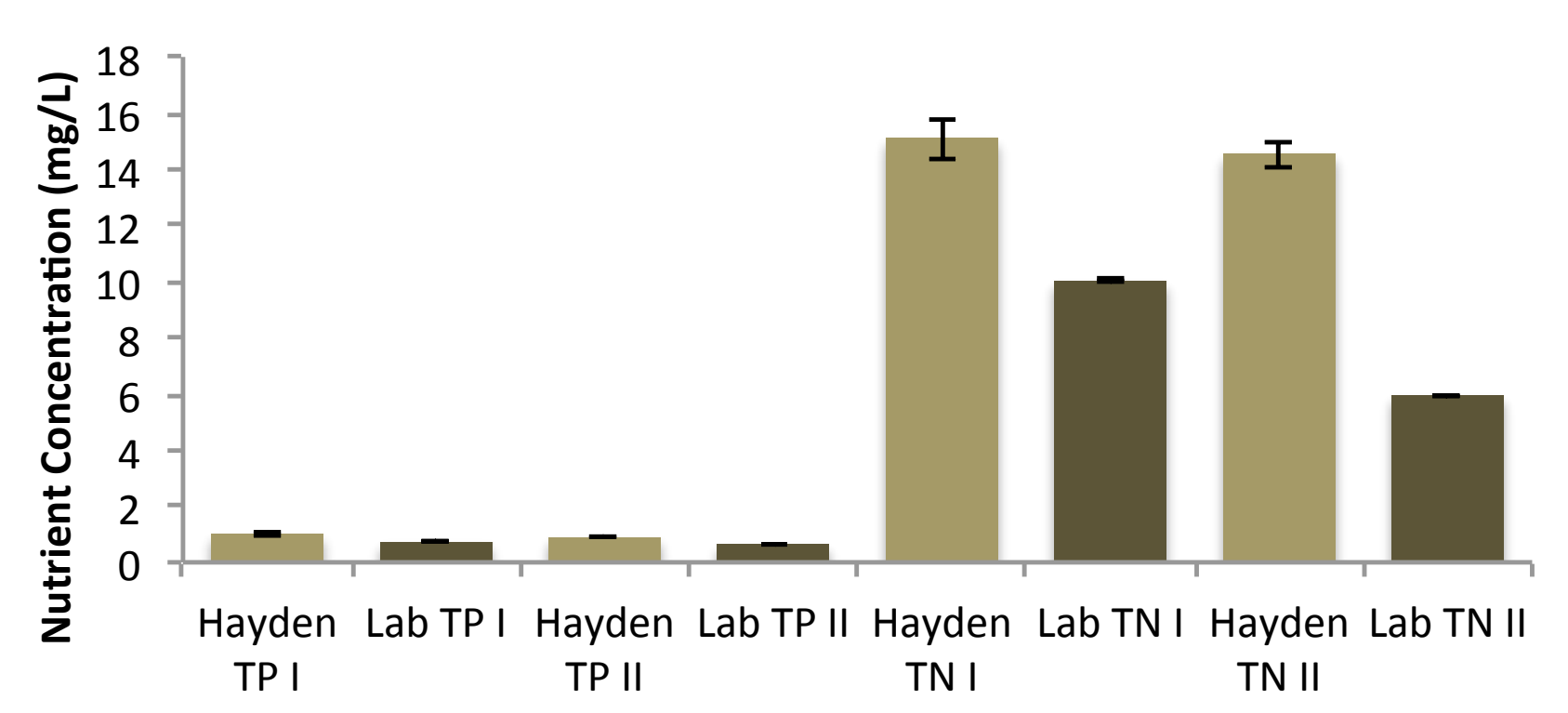


Table 1. Effect of Freezing and Thawing on Nutrient Concentrations

TP Method Detection Limit:	0.04294809
TP difference between opened once and opened twice:	-0.007
TP difference between opened twice and opened three times:	0.02914286
TN Method Detection Limit:	0.01048113
TN difference between opened once and opened twice:	1.593
TN difference between opened twice and opened three times:	0.90957143

Uncertainty in the lab can arise from different protocols, analysts, and sample handling. Dilutions I made vs. those made before analysis were consistently higher in concentration (Fig 5). Freezing and thawing samples increased TN concentrations, but did not influence TP concentrations (Table 1).

Table 2. Lab QA/CC results for spiked samples.

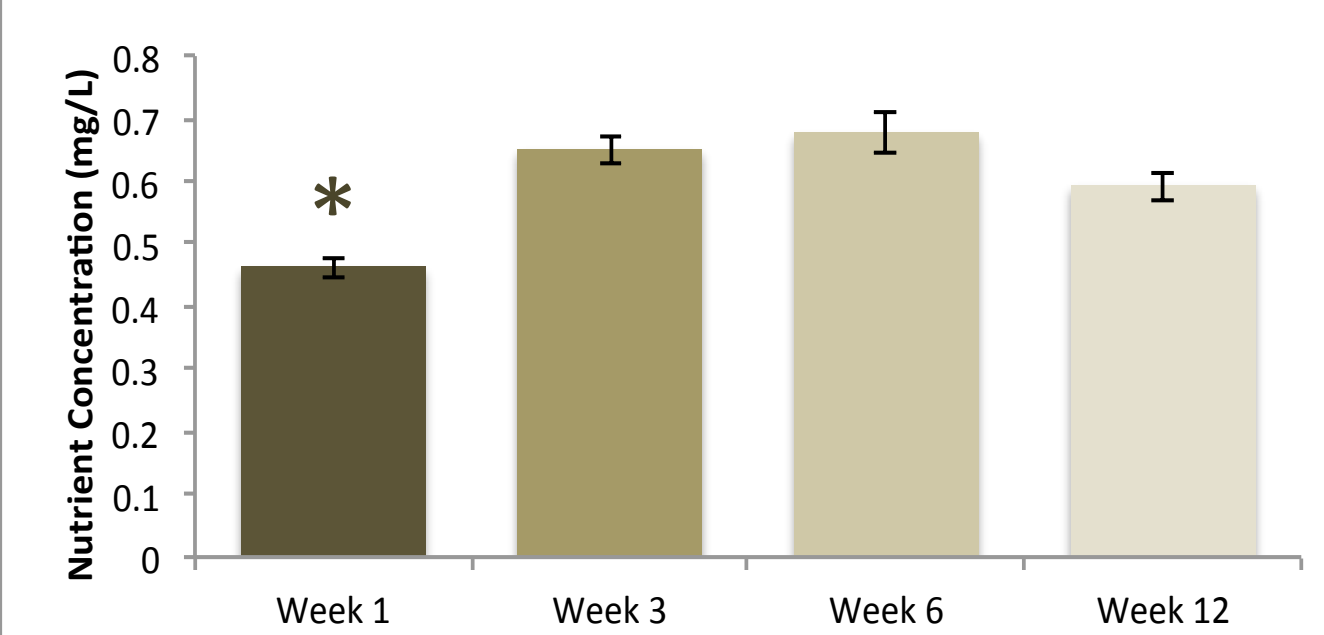
Spiked Samples:		
	Average % Recovery:	Number of Fails:
TN	97.91%	3
TP	101.34%	-
NH_4	93.46%	1
NO_3	93.35%	-
SRP	98.78%	-

Table 3. Lab QA/CC results for duplicate runs.

Duplicates		
	Average COV:	Number of Fails:
TN	4.19%	1
TP	4.52%	1
NH_4	-	4
NO_3	1.17%	-
SRP	6.46%	-

Lab quality assurance and control (QA/QC) uses results from spikes, duplicates, and certified reference materials to assess lab analyses. For this study, QA/QC data beyond 20% were considered fails, and the samples required reanalysis. In most cases the % recovery (Table 2) and COV (Table 3) were much less than 20%.

Figure 6: Uncertainty from Lab Protocol (Total P)



A major source of uncertainty in lab data is protocol failure. The first set of our samples from the freezing experiment were locked overnight in the autoclave, and many samples evaporated. TP concentrations were significantly lower than samples measured using the correct protocol (Figure 6). Interestingly TN was not affected (data not shown).

Conclusions:

Results of these analyses indicate that sources of uncertainty can be found both in the field and in the lab. Specifically,:

- ammonium concentrations generally had the highest uncertainty between samples within a cross section
- filtration with a syringe and a pump differs only in ammonium concentrations, but not variation
- dilutions had highest uncertainty relative to other treatments
- freezing is an adequate storage technique, but for differing amounts of time for different nutrients
- analytical uncertainty was less than uncertainty associated with sample collection and storage (except for unanticipated protocol failure).

Impact:

By testing these potential sources of uncertainty, we can determine more accurate ways to take and analyze nutrient samples at and around point sources. This is important, especially below point sources, in order to ascertain if nutrient quantities exceed water quality management standards.