Notes on comparison of alkaline persulfate nitrogen (method TN:L01) to the sum of total particulate nitrogen (method PN:L01) and total dissolved nitrogen (method TDN:L01).

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This work is a follow-up to a Feb 9, 2009 memo published by Greg Mohrman, Acting Chief, USGS Office of Water Quality, which reports on potential bias in alkaline persulfate analysis of total nitrogen in whole water samples and recommendations for quantifying bias in whole water samples. In short, their studies show that TN analyzed by the alkaline persulfate nitrogen are biased low. Their studies also show that the bias is due to incomplete digestion of sediment or soil materials in the Standard Reference Materials by alkaline persulfate reagents. Thus the bias will increase as sediment components of the sample increase.

The data reviewed here were provided by Mike Mallonee as the file

vadeq_rimsites_2004_present_5params_with_bmdls.xlsx

which includes data for the following parameters:

PN	- particulate nitrogen, high temperature combustion (HTCO)
TDN	- total dissolved nitrogen, alkaline persulfate wet oxidation
TN	- total nitrogen, alkaline persulfate digestion
TSS	- total suspended solids dried at 103-105 degrees
SSC_TOTAL	- suspended sediment concentration

in addition to the usual reference data such as station, date, method, and etc. These data are not censored by detection limits. If any record was missing one of the five key variables, that record was deleted. As a result, the sample size was reduced from 530 to 500. Using these data, the following variables are computed:

TDN.PN	=	TDN + PN
tn.diff	=	TN -TDN.PN
tn.mean	=	(TDN.PN+TN)/2

The initial assessments of these data are graphical. A plot of TN against (PN+TDN) observations shows (Figure 1A) that if anything, the TN observations are bias high relative to the PN + TDN observations. This bias appears to be greatest in the 0.5 to 1.0 mg/l range and less at lower and higher concentrations. A second plot (Figure 1B) shows the difference of TN minus (PN + TDN), henceforth called the **TN difference**, against the mean of TN and (PN + TDN), hence forth called the **TN mean**. This confirms that the TN is biased high in the 0.5 to 1.0 mg/l range and is possibly bias low at higher TN. Note that the tendency of the LOESS regression line to trend positive for concentrations > 2.25 mg/l is based on too little data to be considered significant.

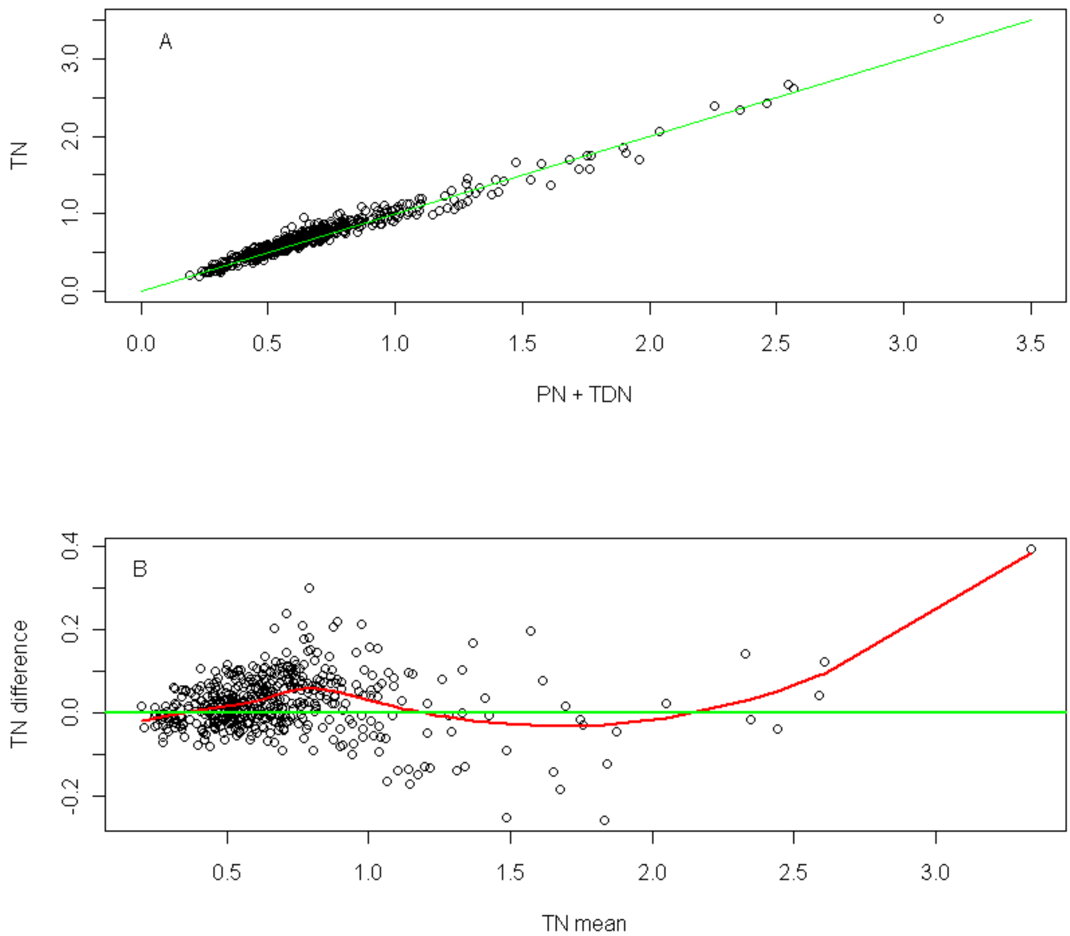


Figure 1. Panel A shows Alkaline Persulfate TN on the ordinate with PN + TDN on the abscissa and the one-to-one line shown in green. Panel B show the difference of (TN - (PN+TDN)) on the ordinate and the mean of TN and (PN + TDN) on the abscissa with a LOESS regression line in red and the zero line in green.

Spatial assessment: The median difference of the TN difference appears elevated at stations TF4.0M, TF4.0P, and TF5.0A (Figure 2 A). This bias appears to be caused by these stations having the majority of TN observations in the 0.5 to 1.0 range (Figure 2 B). Looking at this issue by station does not seem to add any new information.

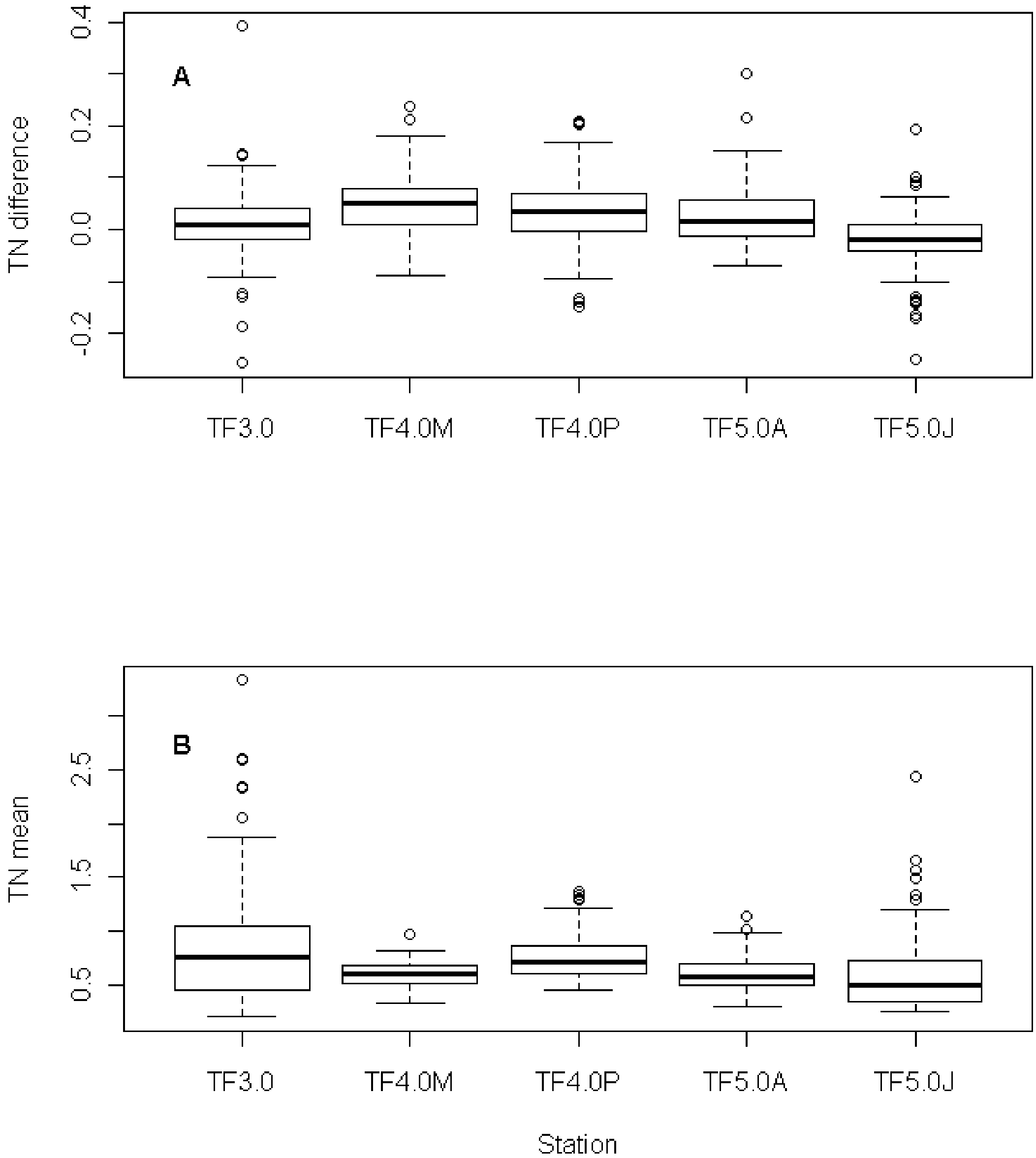


Figure 2. Box and Whisker plots comparing the distribution across stations of the difference TN minus (PN+TDN) (panel A) and the mean of TN and (PN + TDN) (panel B.)

Seasonal Assessment: The is some tendency for the TN difference to be high during the period May to August (Figure 3A). It is not clear that this pattern is associated with a pattern in mean TN (Figure 3B).

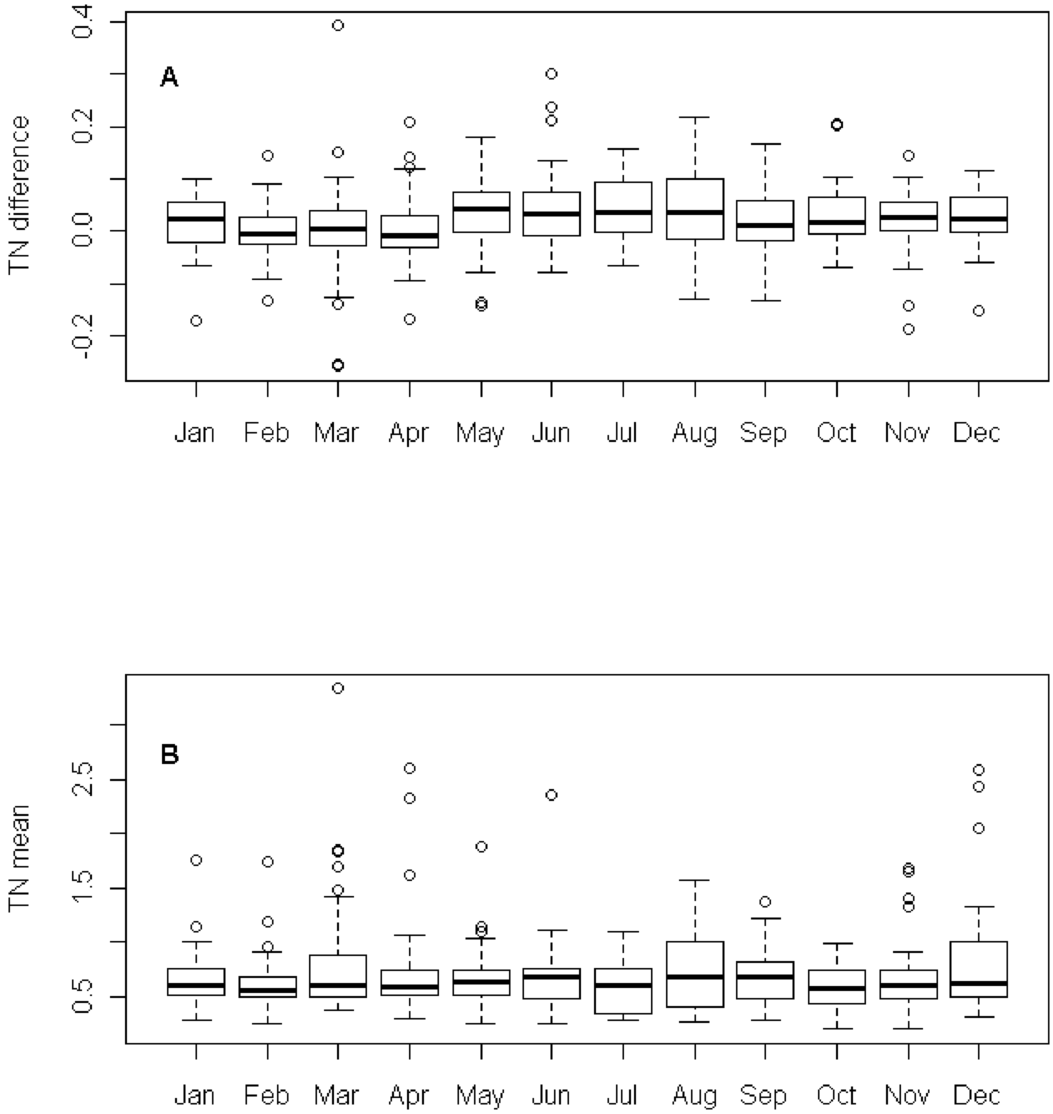


Figure 3. Box and Whisker plots comparing the distribution across months of the difference TN minus (PN+TDN) (panel A) and the mean of TN and (PN + TDN) (panel B.)

Association with Solids: It is clear that TN has a strong association with SSC and it is generally a monotone increasing trend (Figure 4A). The TN difference also has a trend with SSC, but the trend is initially increasing and then decreasing (Figure 4B) which is similar to the trend of the TN difference to TN mean.

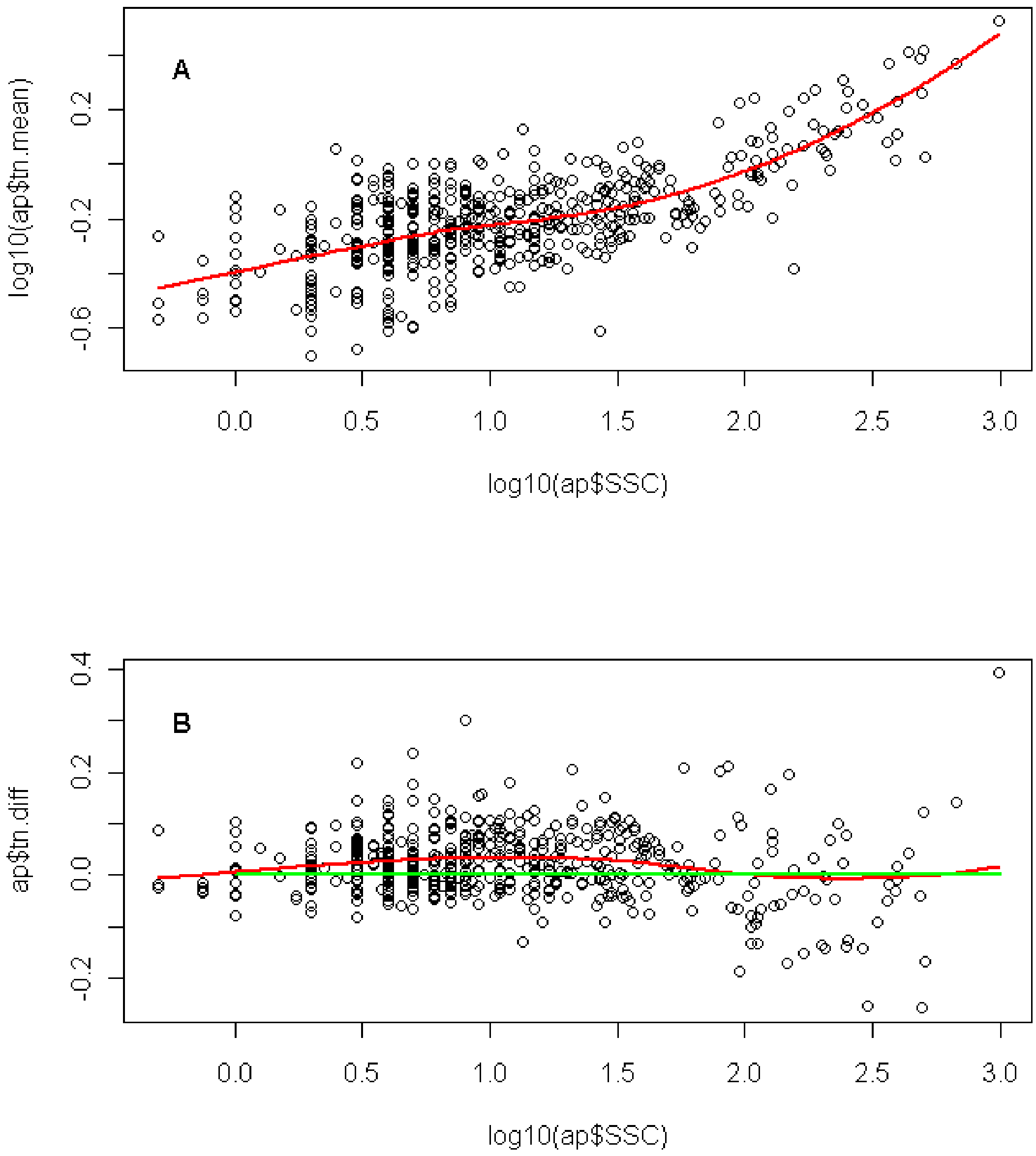
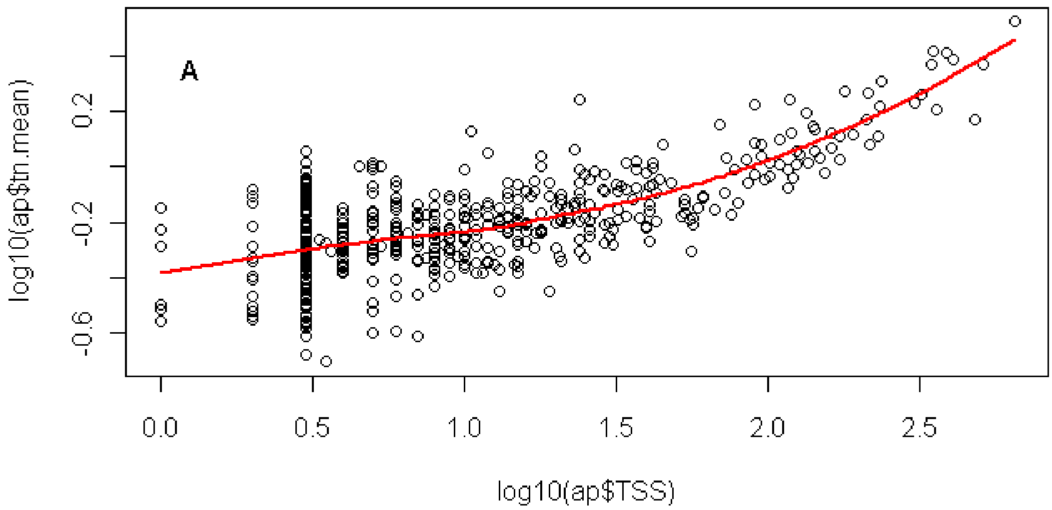


Figure 4. Logarithm of Mean TN (A) and TN difference (B) plotted against the base 10 logarithm of Suspended Sediment Concentration with a loess regression line (red). In panel B, a zero reference line is added in green.

The trends of the TN mean and TN difference with TSS are essentially the same as with SSC (Figure 5A and 5B). This is not surprising given the strong association between SSC and TSS (Figure 6A.). Note that SSC tends to have to have low concentrations is summer (Figure 6B) which may in part explain the monthly trend in TN difference (Figure 3A).



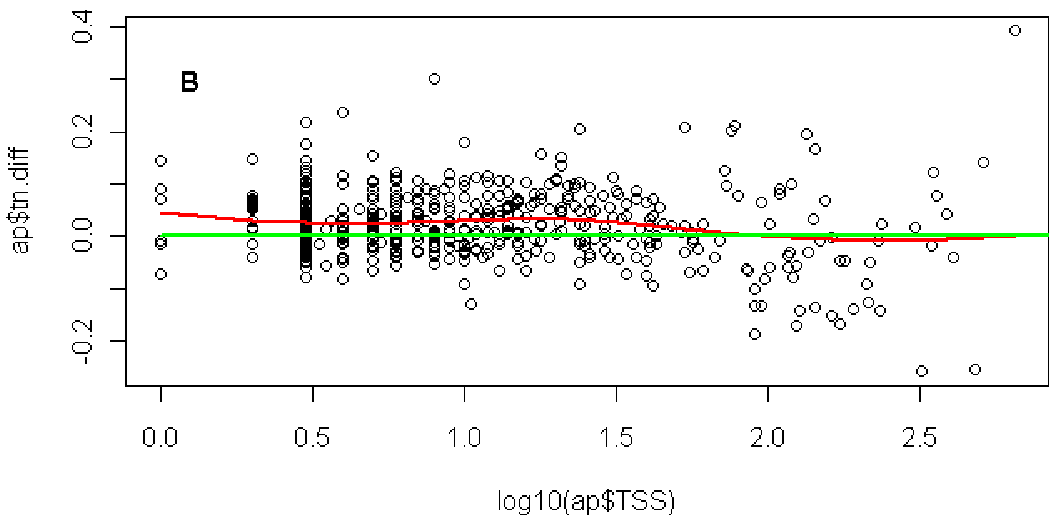


Figure 5. Logarithm of Mean TN (A) and TN difference (B) plotted against the base 10 logarithm of Total Suspended Solids with a loess regression line (red). In panel B, a zero reference line is added in green.

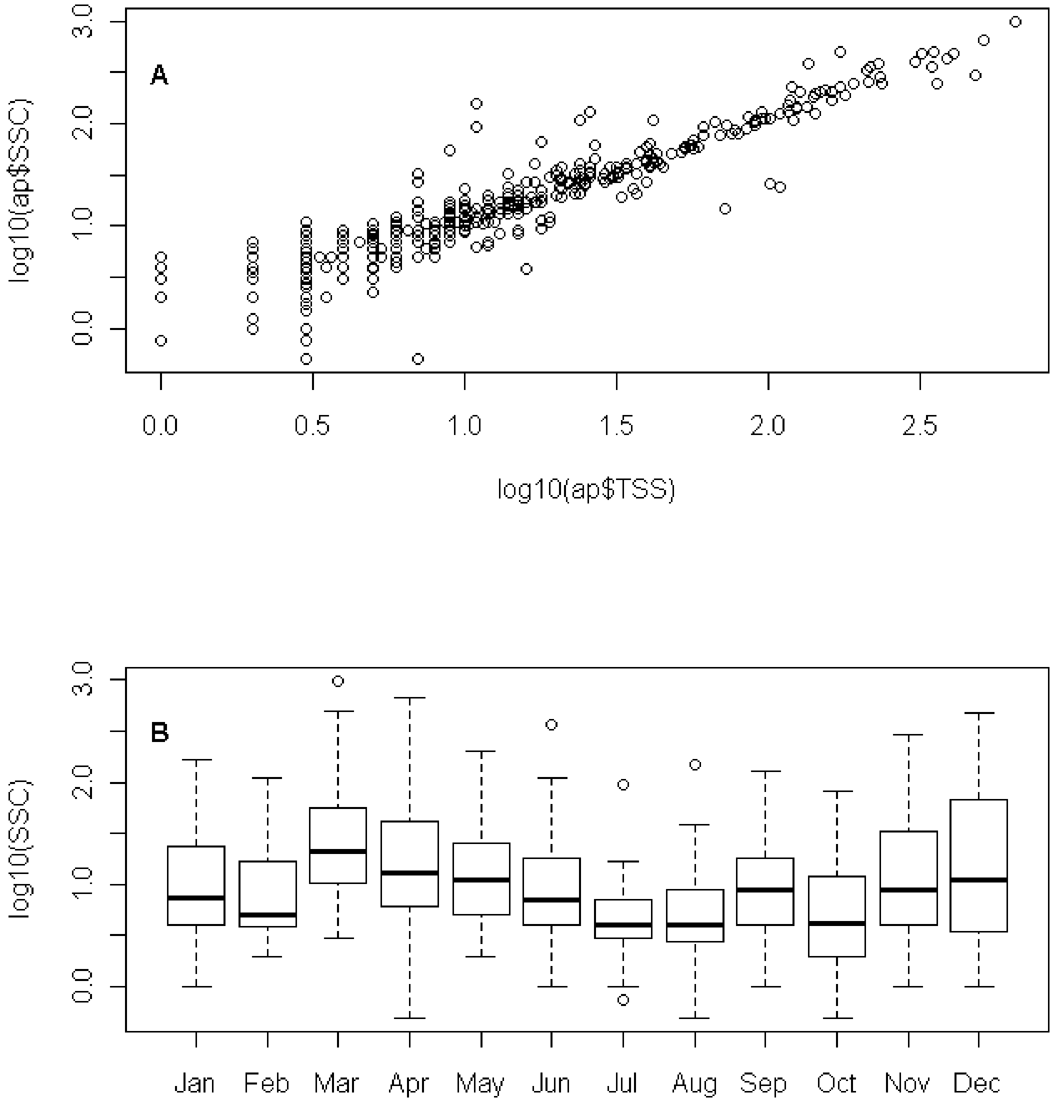


Figure 6. Panel A: Logarithm of SSC plotted vs. logarithm of TSS (A) and Panel B: monthly Box and Whisker plots of base 10 logarithm of SSC.

To assess the statistical significance of the bias observed in Figure 1, two types of smoothing models have been applied to assess the TN difference as a function of the TN mean. One model is the loess smooth (Figure 7) which is the same as shown in Figure 1 except that here confidence intervals are added to assess statistical significance. A second model type is the Generalized Additive Model (GAM) (Figure 8.) which is also presented with confidence intervals. Both models show that there is a region of positive bias for low TN and a region of negative bias at higher TN. These regions are labeled interval A and interval B respectively for each model. Each region was identified by as the interval where the confidence bounds for the estimated bias curve do not include zero. The Loess regression places the positive bias region in the interval (0.46 to 1.08) while the Gam estimates this interval as (0.46,1.01). The Loess regression places the negative bias region in the interval (1.40,1.88) while the Gam yields a wider estimate for this interval of (1.30,2.02).

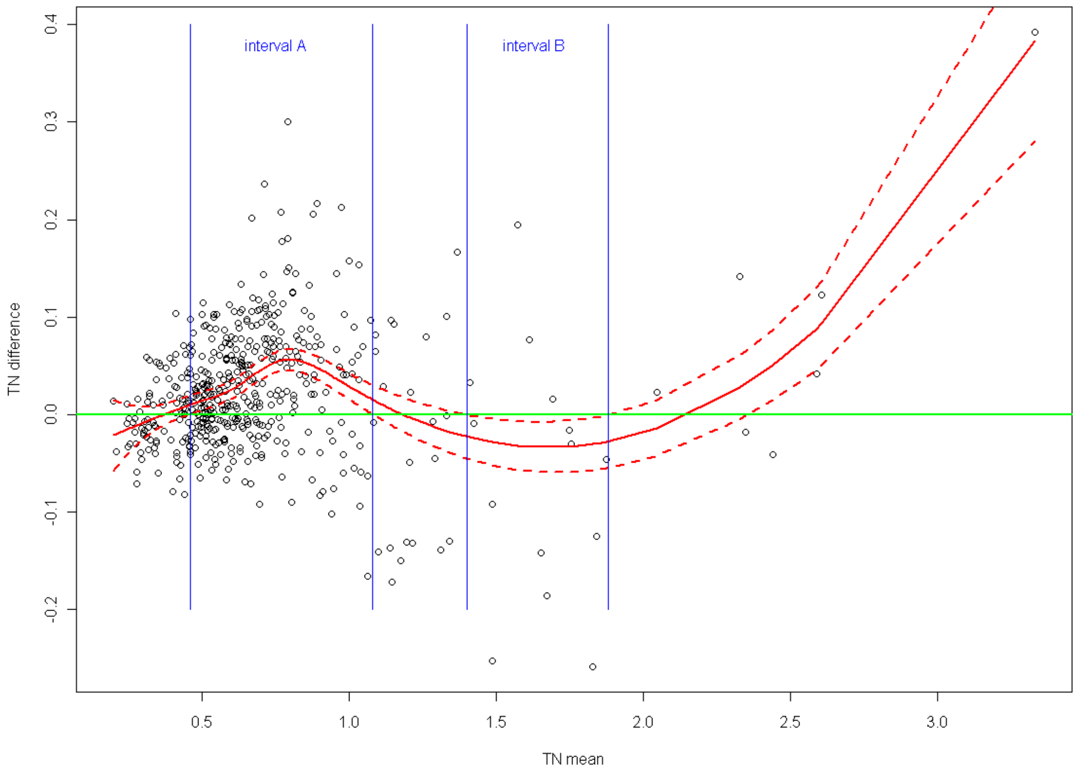


Figure 7. Loess regression of the TN difference against TN mean with confidence intervals. A zero reference line is shown in green. Intervals of statistically significant departure from zero difference are shown by blue reference lines.

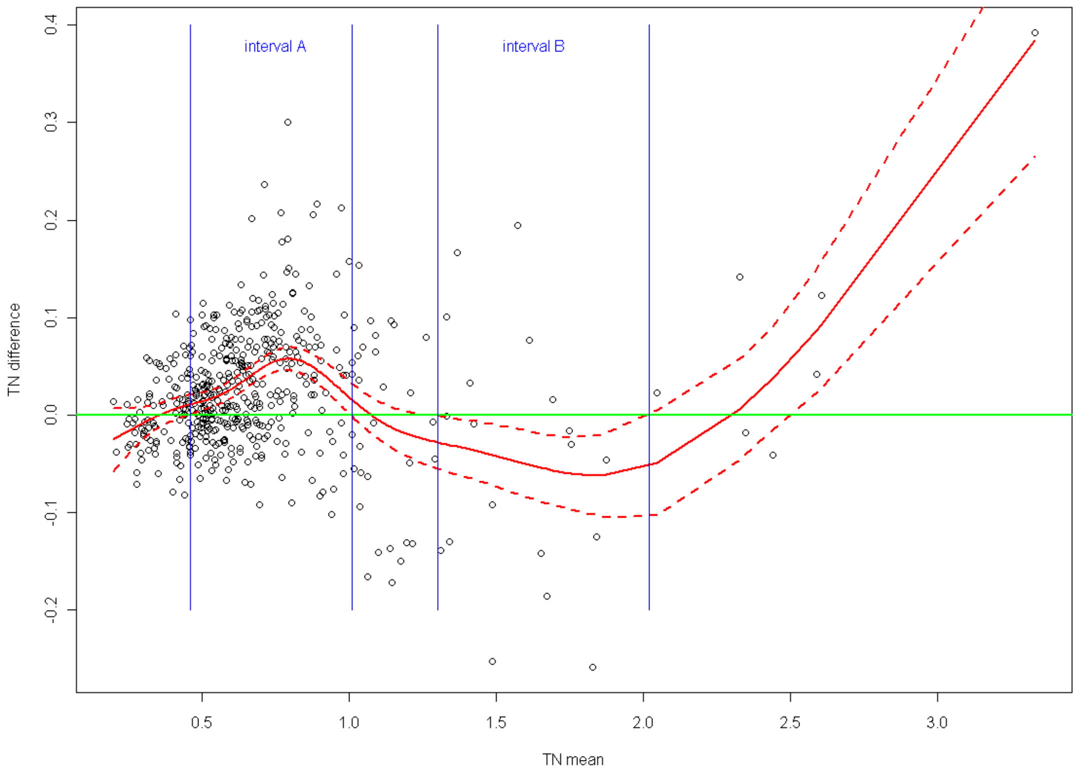


Figure 8. Generalized Additive Model (GAM) regression of the TN difference against TN mean with confidence intervals. A zero reference line is shown in green. Intervals of statistically significant departure from zero difference are shown by blue reference lines.

Discussion:

The results of this study are not completely consistent with the results reported in the Mohrman memo. The trend of the bias is similar. Mohrman reported that bias of the Alkaline Persulfate method was negligible at low TN and bias increased in a negative direction as TN increased. The results reported here show negligible at very low TN, positive bias at moderately low TN with the bias becoming negative as TN increases. Thus in both studies, the TN bias is moving in a negative direction over a wide range of TN.

Through the use of Standard Reference Materials, the USGS team makes a strong case for explaining that the bias in Alkaline Persulfate method is the result of incomplete digestion. While this might explain the negative bias observed in these data (interval B), it does not seem like a logical explanation for the positive bias (interval A). It seems that there is some other issue with these data.

One possible explanation for the results observed here is that the sum of (PN + TDN) is consistently biased low while the Alkaline Persulfate method has a negative bias that increases as a function of TN. At very low TN the bias difference is obscured by noise as observed in the region to the left of interval A. At moderately low TN, the Alkaline Persulfate method has little bias and thus the difference between the two methods is positive as shown in interval A. As TN increases, the bias of the two methods becomes approximately equal so that the TN difference is near zero as shown in the region between intervals A and B. And finally the bias of the Alkaline Persulfate method exceeds the bias of the (PN+TDN) method as shown in interval B.

Before going on to develop methods to adjust for these biases, it would be good to pause and have others consider plausible explanations for the inconsistency of what was observed here and what was reported in the Mohrman memo. Perhaps additional testing of both of these methods using standard reference materials would help with this assessment.