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Sent: Tuesday, June 13, 2006 4:34 PM
Subject: Historic HJA Silica Data Quality

Please mark silica data prior to 17 March 1983 as questionable. A quick inspection of the historic records indicates that many, if not all, of the samples prior to that date were frozen prior to analysis for silica. Freezing samples prior to analysis for silica will reduce the final analyzed concentration of reactive silica (the form we have historically determined).

Another complicating factor is that the methodology changed about this same time. Previously, a stannous chloride method was used to determine silica. The stannous chloride method is more prone to variability due to reagent instability. It appears that the combination of these two factors is the main cause of the variability in the results for silica prior to 17 March 1983. With further investigation it is possible that some of the early data could be validated by cross-checking calibration information (for the stannous chloride factor) and checking the field & lab sample information for freezing, but this will take a significant amount of time and definitely a project to consider for the future.

Some considerations that need to be weighed when evaluating silica data from the early years of collection:

Review of silica analytical history:

1968 - 1978 manual analysis by stannous chloride method
1978 - 1982 automated analysis by stannous chloride method
1982 - Present automated analysis by ascorbic acid method

The changeover date in the automated analysis from stannous chloride to ascorbic acid method is not clear at this time. Further investigation could better define this date.

The stannous chloride method does have an inherent analytical concern. The working solution for the stannous chloride reagent is unstable which can lead to loss of silica sensitivity. This could lead to analytical variability. Quality assurance checks within each analytical batch should have exposed this possible variability but without examining each batch I can't be certain this was or wasn't the case.

Another possible source of silica variability would be if the samples had been frozen prior to analysis. Freezing causes silica to form unreactive complexes. The analysis protocols from that time (pre 1982/1983) call for allowing samples to sit at room temperature for 48 hours after thawing frozen samples. My experience has shown that unreactive silica complexes from frozen samples do not become reactive silica within that timeframe and do not become reactive at the same rate amongst different samples. It seems the rate of reactivation is more related to matrix. Even samples from the same site that are collected at different times seem to have different reactivation rates. None of this is documented, however, and is based entirely on my observations. If the 1967 - 1982 period includes significantly different field collection protocols (i.e. no gauge houses) it would be interesting to know if any of the winter samples became frozen.