Blank corrections in SNICSer

Brett Longworth

January 7, 2019

Snicser performs blank corrections for all samples routinely processed at NOSAMS. Two different corrections are performed, a large blank correction for all samples and a mass balance correction for samples under 100 ug and all DOC samples.

Large Blank

The large blank correction subtracts a single blank value from all samples proportional to their fraction modern. It assumes that samples with Fm of the large blank should be corrected to 0 and that samples with Fm the same as the OX-I standard need no correction since they are normalized to a standard that (presumably contains the same blank.

For large samples the value of FmB is determined by averaging the blanks on the wheel. For small samples, the value is taken from a historical average. Currently, we use three types of large blanks: acetanalide, C-1 or TIRI-F, and a watson blank. The acetanalide blank is used to correct organic samples, the C-1 or TIRI-F to correct HY, WS, GS, and DOC process types, and watson blank to correct watson samples.

The large blank correction is performed for all samples. When applying a mass balance correction, the large-blank-corrected value is used for the measured fraction modern in the mass-balance equation.

The correction uses this equation:

$$R_s = R_m - \frac{R_b(R_{ox} - R_m)}{R_{ox}}$$

Where R_s is the ratio of the unknown sample, R_m is the measured ratio, R_b is the ratio of the blank, and R_{ox} is the ratio of the normalizing standard.

and this snicser function:

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LargeBlankCorrected = Fm - FmB * (FmS - Fm) / FmS
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Where Fm is the measured Fm, FmB is the Fm of the blank, and FmS is the Fm of the normalizing standard.

Error propagation for the large blank uses this equation:

$$\sigma_{R_s}^2 = \left[\sigma_{R_m}\left(1 + \frac{R_b}{R_{ox}}\right)\right]^2 + \left[\sigma_{R_b}\frac{R_m - R_{ox}}{R_{ox}}\right]^2$$

And this function:

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SigLargeBlankCorrected = SigFm ^ 2 * (1 + FmB / FmS) ^ 2 +
    SigFmB ^ 2 * ((Fm - FmS) / FmS) ^ 2

If SigLargeBlankCorrected > 0
    Then SigLargeBlankCorrected = SigLargeBlankCorrected ^ 0.5
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Mass Balance Correction

The blank correction for small samples and DOC assumes that there is a contaminant with constant mass and fraction modern added to the samples during processing. It is assumed that this contaminant is a component of the measured sample and that the fm of the sample can be determined using a mass balance mixing model.

The mass and fraction modern of the contaminant are determined by running modern and dead samples of varying sizes and fitting a mass balance curve. These values are assumed to be stable over time and are checked and adjusted as necessary. The contaminant and sample parameters are retrieved from the dc13 table in the NOSAMS DB and are stored per-sample. The graphite mass (graphite_umols_co2) is used for small samples, and the total mass (total_umols_co2) is used for DOC samples.

The correction is done using this equation:

$$R_s = R_m + \frac{m_c(R_m - R_c)}{m_m}$$

Where R_s is the ratio of the unknown sample, m_c is the mass of the contaminant, R_m is the measured ratio, R_c is the ratio of the contaminant, and m_m is the mass of the measured sample.

and this snicser function:

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FmMassBal = FmC + (FmC - FmB) * MassB / Mass
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Where FmC is LBC corrected Fm, FmB is the Fm of the blank/contaminant, MassB is the mass of the blank/contaminant. and Mass is the mass of the measured sample.

Error propagation is done with the following equation:

$$\sigma_{R_s}^2 = \left[\sigma_{R_m}\frac{1+m_c}{m_m}\right]^2 + \left[\sigma_{m_m}\frac{m_c(R_m-R_c)}{m_m^2}\right]^2 + \left[\sigma_{R_c}\frac{m_c}{m_m}\right]^2 + \left[\sigma_{m_b}\frac{R_m-R_c}{m_m}\right]^2$$

And this snicser function:

```
If M <= Mb Then Return 42 ' flag anomalous situation

SigFmMassBal = SigFmC ^ 2 * (1 + Mb / M) ^ 2 +
SigMass ^ 2 * ((FmC - FmB) * Mb / M ^ 2) ^ 2 +
SigFmB ^ 2 * (Mb / M) ^ 2 +
SigMassB ^ 2 * ((FmC - FmB) / M) ^ 2

If SigFmMassBal > 0 Then SigFmMassBal = SigFmMassBal ^ 0.5
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