Supplementary Information 1: Effect of NaN$_3$ blank on CDOM parameters

1. Contribution of NaN$_3$ to the total absorption coefficient

NaN$_3$ absorbs in the UV region at wavelengths lower than 300 nm (McDonald et al., 1970). Figure 1 shows the percentage contribution of our NaN$_3$ blanks to the total Napierian absorption coefficient (*i.e.* CDOM + NaN$_3$) from 250 – 320 nm for our dataset. The NaN$_3$ accounts for 0 – 95% of the total absorption coefficient at 250 nm, but the blank contribution rapidly drops to mostly <15% at wavelengths above 270 nm, and essentially no contribution from NaN$_3$ is observed at wavelengths above 310 nm. NaN$_3$ did not contribute blank fluorescence.
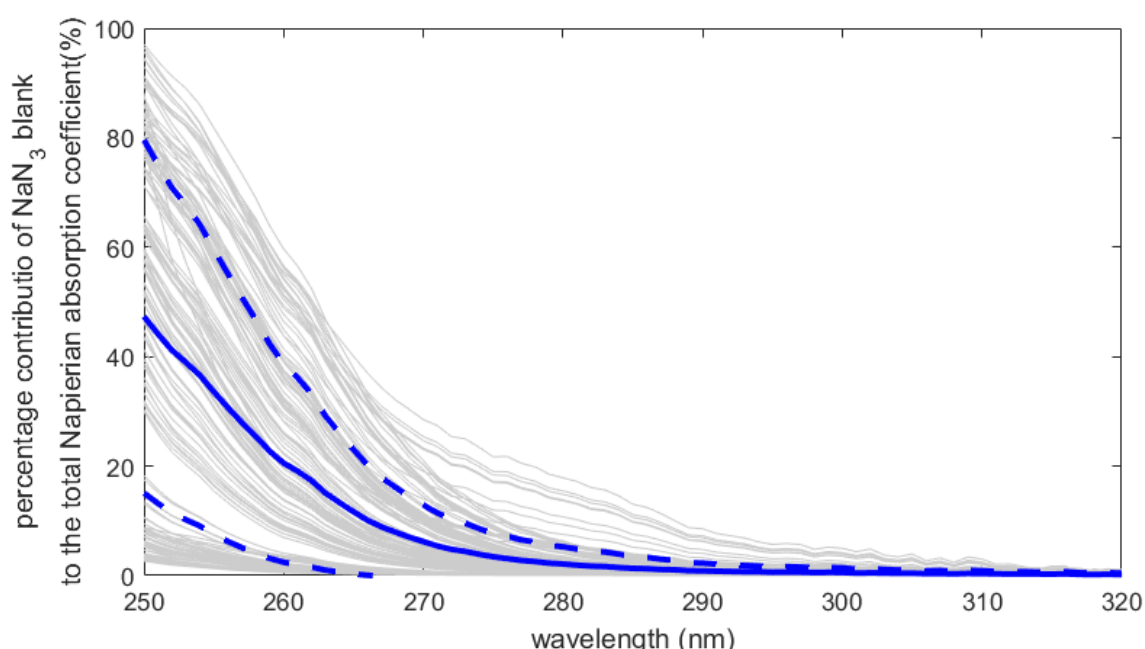

Figure 1. Compilation of the percentage contribution of NaN$_3$ to the total absorption at each wavelength from 250 nm to 320 nm for all individual samples (grey solid lines), and the overall mean value for the whole dataset (blue solid line). The blue dashed lines show 1 standard deviation around the mean.

2. Uncertainty analysis of NaN$_3$ blank and effects on CDOM parameters

2.1 Uncertainty of NaN$_3$ concentration in the water sample

Subtracting the NaN$_3$ blank absorption adds uncertainty to the sample CDOM spectrum, because of variability in the exact NaN$_3$ concentration between samples. Here, we first estimate the uncertainty in NaN$_3$ concentration in each sample, and thus the uncertainty in the CDOM spectrum of each sample. We then analyze the degree to which this uncertainty affects the estimates of specific UV absorbance (SUVA$_{254}$) and UV spectral slope (S$_{275-295}$) used in the

present paper and in Martin et al. (2018).

As the CDOM absorption coefficients were derived by subtracting the NaN_3 blank from the total absorption coefficients of the sample, the uncertainty in CDOM absorption coefficients arises from both the uncertainty in the volume of NaN_3 added, and the uncertainty in the volume of the water sample collected in the field. We collected 30 ml of water per sample by filling a 40-mL borosilicate EPA vial to an identical pre-determined height (owing to the size of the filtration flask, pipetting the sample water was not possible). We determined the uncertainty in sample volume empirically by filling eleven replicate vials with this method and measuring the weight of water. We found that the uncertainty in the water sample weight is ±1.4%. For each water sample, 150 µL NaN_3 was added using a 100-1000 µL pipette, which introduces a random error of up to ±0.6% (Operating manual, Eppendorf Research plus, www.eppendorf.com). Propagating these two errors gives an uncertainty in the NaN_3 concentration in each 30-mL water sample of about ±1.5%.

2.2 Uncertainty in SUVA$_{254}$

The SUVA$_{254}$ was calculated using equation (1):

$$SUVA_{254} = \frac{(\text{total decadic absorption coefficient} - \text{NaN3 decadic absorption coefficient}) \, \lambda = 254nm}{\text{DOC concentration}} \quad (1)$$

The DOC concentration has an uncertainty of around ±4.3%, given the long-term mean ± 1SD of 47 ± 2.0 µmol L^{-1} of DOC in the certified deep-sea water measured in our lab (Martin et al., 2018). The uncertainty in NaN_3 concentration of ±1.5% equates to an uncertainty in the NaN_3 decadic absorption coefficient at 254 nm of 0.06 m^{-1} for each sample. By propagating these errors for each individual sample, we estimate that the uncertainty in SUVA$_{254}$ of our samples is always within the range of ±10%, and mostly less than ±5% (Figure 2).
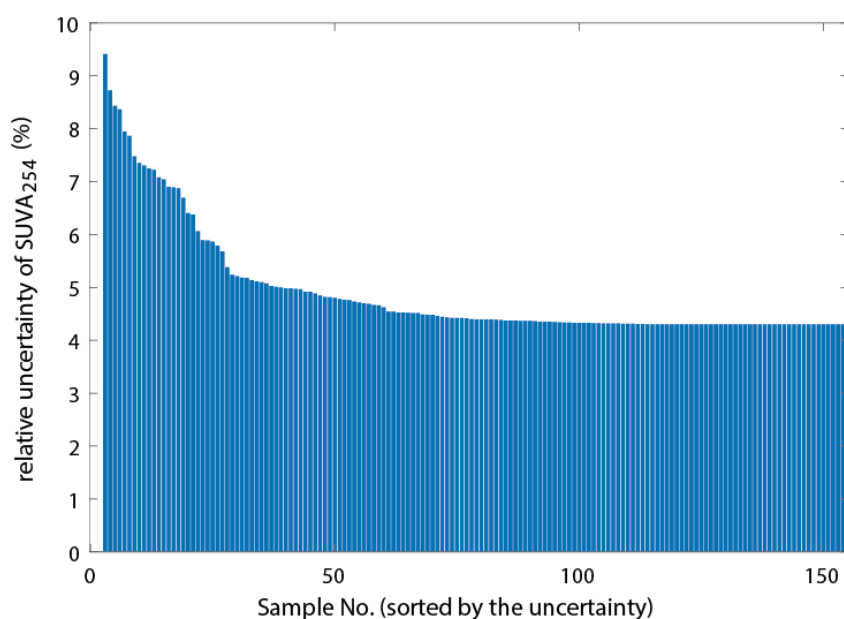

Figure 2. Relative uncertainty in SUVA$_{254}$ for each sample, based on propagating the estimated uncertainty in DOC concentration and in the decadic absorption coefficient of the NaN_3 blank.

2.3 Effects of uncertainty of NaN₃ concentration on S₂₇₅₋₂₉₅

2.3 Effects of uncertainty of NaN_3 concentration on $S_{275-295}$

Because NaN_3 still absorbs in the wavelength range of 275–295 nm, the uncertainty in NaN_3 concentration also contributes uncertainty to the calculated spectral slope $S_{275-295}$. To estimate this uncertainty, we changed the CDOM absorption spectrum of every sample by adding or subtracting 1.5% of the NaN_3 blank for the appropriate wavelength, and recalculated $S_{275-295}$. Note that any variation in NaN_3 blank is necessarily correlated across wavelengths, *i.e.*, if a sample contains 1.5% more NaN_3 than average, then the absorption at every wavelength is greater by 1.5% of the blank absorption spectrum; the variation cannot be randomly ±1.5% within a sample. The relative uncertainty in spectral slope is therefore potentially less than the relative uncertainty in NaN_3 concentration.
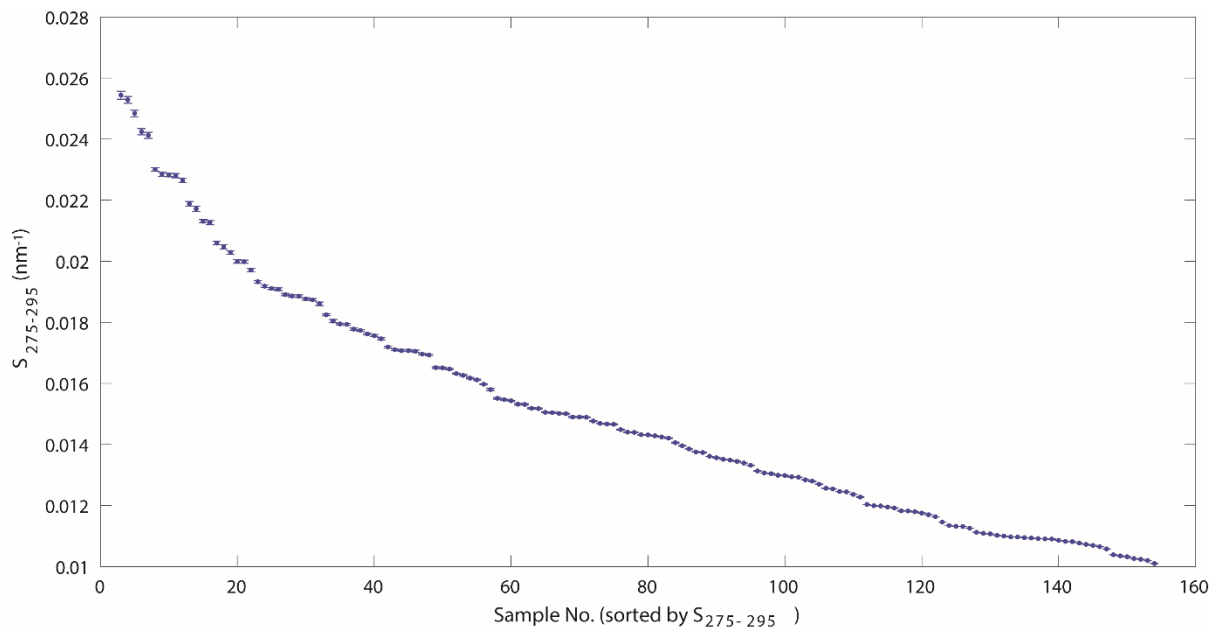

Figure 3. Effects of changing NaN_3 blank absorption by ±1.5% on $S_{275-295}$ of CDOM for all individual samples. Dots indicate the original estimate of $S_{275-295}$, error bars show the effect of having an NaN_3 blank that is higher or lower by 1.5% than the mean blank.

This analysis indicates that the uncertainty in the NaN_3 concentration only has a very small effect on $S_{275-295}$: the relative change compared to the originally calculated $S_{275-295}$ is always below 0.5% (Figure 3). The impact is greatest for those samples with the highest $S_{275-295}$ (because these samples had the lowest CDOM absorption values), but decreases even further for samples with lower $S_{275-295}$ values.

3. Conclusion

Our analysis of uncertainty demonstrates that the CDOM data used in this study and in Martin et al. (2018) were not significantly impacted by the use of NaN_3 as a preservative. This is because the variation in NaN_3 concentration in the samples was small, and the high blank at wavelengths below 300 nm could therefore be subtracted with high accuracy.

References

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McDonald, J. R., Rabalais, J. W. and McGlynn, S. P.: Electronic Spectra of the Azide Ion, Hydrazoic Acid, and Azido Molecules, J. Chem. Phys., 52(3), 1332–1340, doi:10.1063/1.1673134, 1970.