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Correcting CDOM fluorescence measurements for temperature effects under field conditions in freshwaters

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Abstract

A method recently proposed by Ryder et al. (2012) as the preferred way to compensate for temperature quenching of CDOM fluorescence is mathematically equivalent to the prior method that they claim to improve upon.

Comment

In a recent article published in *Limnology and Oceanography: Methods*, Ryder and co-authors (2012) propose a temperature compensation method for field measurements of CDOM fluorescence. They argue that their method improves upon a prior method proposed by Watras et al. (2011). Unfortunately, Ryder et al (2012) misapplied the prior method and obtained erroneous results that invalidate their comparison. In fact, it can be shown that the two methods are mathematically equivalent.

Watras et al (2011) proposed a temperature-specific coefficient of fluorescence, (ρ), that is calculated as the quotient: "slope/intercept at a given reference temperature." Since ρ was shown to be relatively constant for the relationship between temperature and CDOM fluorescence across a wide DOM concentration range, the equation $CDOM_r = CDOM_m/(1 + \rho[T_m - T_r])$ could be used to remove the effects of temperature quench as DOM increases (cf. Baker 2005; Downing et al. 2012). An analogous equation is used widely in limnology and oceanography to correct field measurements of conductivity.

Unfortunately, Ryder et al (2012) miscalculated ρ as the quotient: "slope/CDOM fluorescence at 0°C." This miscalculation leads to errors that increase as the reference temperature departs from 0°C. It explains why their use of our equation gave poor results. To illustrate this, we recalculated ρ using data from their Table 1. For the Glenamong site on 3 January 2011, the intercept at 20°C is 214 – (2.45 × 20) = 165, yielding ρ = –0.2.45/165 = –0.015. Substituting this correct value for ρ, rather than their computed value of –0.011, removes the temperature effect from the data. This can be shown to be true in every case, invalidating the comparisons presented on Tables 1, 2, and 3 and on Figs. 3 and 4 in Ryder et al (2012).

More importantly, it can be demonstrated that the two methods are actually equivalent when properly applied.

Given (from Ryder et al. 2012)

$$CDOM_{ref} = \{CDOM_{meas} \cdot [1 + f_t \cdot (T_{ref} - T_{meas})]\} \quad (1)$$

and

$$f_t = m/(T_{meas} \cdot m + C) \quad (2)$$

by substitution

$$CDOM_{ref} = \{CDOM_{meas} \cdot [1 + m \cdot (T_{ref} - T_{meas})/(T_{meas} \cdot m + C)]\} \quad (3)$$

and

$$CDOM_{ref} = \{CDOM_{meas} \cdot [(T_{meas} \cdot m + C + m \cdot T_{ref} - m \cdot T_{meas})/(T_{meas} \cdot m + C)]\} \quad (4)$$

$$CDOM_{ref} = CDOM_{meas} \cdot [(m \cdot T_{ref} + C)/ (m \cdot T_{meas} + C)] \quad (5)$$

$$CDOM_{ref} = CDOM_{meas} \cdot [1/\{(m \cdot T_{meas} + C)/ (m \cdot T_{ref} + C)\}] \quad (6)$$

$$CDOM_{ref} = CDOM_{meas} \cdot [1/\{(m \cdot T_{meas} + C + m \cdot T_{ref} - m \cdot T_{ref})/(m \cdot T_{ref} + C)\}] \quad (7)$$

$$CDOM_{ref} = CDOM_{meas} \cdot [1/\{1 + (m \cdot T_{meas} - m \cdot T_{ref})/ (m \cdot T_{ref} + C)\}] \quad (8)$$

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$$CDOM_{ref} = CDOM_{meas} \cdot [1/\{1 + m\cdot(T_{meas} - T_{ref})/ (m\cdot T_{ref} + C)\}] \quad (9)$$

but since

$$m/(m\cdot T_{ref} + C) = \rho \quad (10)$$

we arrive back at Watras et al. (2011)

$$CDOM_{ref} = CDOM_{meas} \cdot [1/\{1 + \rho\cdot(T_{meas} - T_{ref})\}] \quad (11)$$

Considering that the method proposed by Ryder et al. (2012) does not demonstrate any improvement over the prior method proposed by Watras et al (2011), and considering that the prior method was shown to apply over a wide range of DOM, we do not agree that the Ryder method is preferable.

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