

## Comment on:

# “Technical note: Consistent calculation of aquatic gross production from oxygen triple isotope measurements” by Kaiser (2011)

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**Abstract.** Kaiser (2011) has introduced an improved method for calculating gross productivity from the triple isotopic composition of dissolved oxygen in aquatic systems. His equation avoids approximations of previous methodologies, and also accounts for additional physical processes such as kinetic fractionation during invasion and evasion at the air-sea interface. However, when comparing his new approach to previous methods, Kaiser inconsistently defines the biological end-member with the result of overestimating the degree to which the various approaches of previous studies diverge. In particular, for his base case, Kaiser assigns a  $^{17}\text{O}$  excess to the product of photosynthesis ( $^{17}\delta_{\text{P}}$ ) that is too low, resulting in his result being  $\sim 30\%$  too high when compared to previous equations. When this is corrected, I find that Kaiser’s equations are consistent with all previous study methodologies within about  $\pm 20\%$  for realistic conditions of metabolic balance ( $f$ ) and gross productivity ( $g$ ). A methodological bias of  $\pm 20\%$  is of similar magnitude to current uncertainty in the wind-speed dependence of the air-sea gas transfer velocity,  $k$ , which directly impacts calculated gross productivity rates as well. While previous results could and should be revisited and corrected using the proposed improved equations, the magnitude of such corrections may be much less than implied by Kaiser.

## 1 Introduction

In the manuscript “Consistent calculation of aquatic gross production from oxygen triple isotope measurements” Kaiser derives exact equations for calculating gross oxygen pro-

duction (GOP) from the triple oxygen isotopic composition of dissolved oxygen ( $^{17}\Delta$ ). The derived equations improve upon previous methods of calculating GOP in that they avoid approximations and account for additional processes such as kinetic fractionation during air-sea evasion and invasion of oxygen. These new equations and similar results of Prokopenko et al. (2011), provide improved methodology that should be applied to future studies that interpret triple oxygen isotopic composition of dissolved oxygen in seawater.

However, in comparing the results of these new equations to previous methods of calculating GOP, I believe Kaiser has misinterpreted previous results with the consequence of overstating the difference between various previous methods of calculating GOP (e.g. Kaiser’s Fig. 3). Since differing definitions of  $^{17}\text{O}$  excess are used, I repeat here definitions 4 and 7 from Kaiser (2011)

$$^{17}\Delta^{\dagger} = ^{17}\delta - \kappa ^{18}\delta \quad (1)$$

$$^{17}\Delta^{\#} = \ln(1 + ^{17}\delta) - \lambda \ln(1 + ^{18}\delta) \quad (2)$$

where  $\kappa$  and  $\lambda$  are mass dependent fractionation slopes. For Kaiser’s “base case”, both are assigned the observed slope for a  $\ln(1 + ^{18}\delta)$  vs.  $\ln(1 + ^{17}\delta)$  plot for dark respiration of  $\gamma_{\text{R}} = 0.5179$  (Luz and Barkan, 2005).

The crux of the discrepancy is in the assumptions Kaiser uses to calculate the relation between  $^{17}\delta_{\text{P}}$  and  $^{18}\delta_{\text{P}}$ , where the subscript “P” refers to dissolved oxygen produced by photosynthesis. In his “base case” used for comparison of methods, Kaiser uses Eq. (2) by assuming a  $^{17}\Delta_{\text{P}}^{\#} (\lambda = 0.518) = 249$  ppm where 249 ppm is the biological end-member value reported by Luz and Barkan (2000). I will argue that the 249 must be applied instead to oxygen in biological steady state with seawater ( $^{17}\Delta_{\text{S0}}$ ) which is influenced by photosynthesis and respiration, rather than  $^{17}\Delta_{\text{P}}$  in



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order for consistent comparison between calculation methods. I introduce the notation  $^{17}\Delta_{S0}$  to refer specifically to the biological steady-state condition in which  $P = R$  (and thus  $f = 0$ , where  $f$  is the net to gross production ratio).  $^{17}\Delta_{S0}$  is distinctly different than  $^{17}\Delta_P$  as noted by Kaiser, because  $^{17}\Delta_P$  is the pure photosynthetic product, while  $^{17}\Delta_{S0}$  is a balance of  $P$  and  $R$ . The 249 ppm value published by Luz and Barkan (2000) was a measure of  $^{17}\Delta_{S0}$  and not  $^{17}\Delta_P$  because the original experiment measured dissolved oxygen in an aquarium experiment which was in biological steady state ( $P \approx R$ ). For a system in biological steady state, it has been demonstrated that the appropriate slope ( $\lambda_{BSS}$ ) for relating the composition of  $^{17}\Delta_{S0}$  and  $^{17}\Delta_P$  is systematically less than  $\gamma_R$  (Angert et al., 2003). In the following sections I will describe how  $^{17}\delta_P$  and  $^{18}\delta_P$  should have been defined using a slope of  $\lambda_{BSS} = 0.5154$  instead of  $\gamma_R$ . With this correction, Kaiser's "base case"  $^{17}\Delta$  value would have been 58 ppm higher (see Sect. 3) and the discrepancy between the calculation methods of earlier studies and the new method proposed by Kaiser becomes much smaller.

I will focus my comments on this aspect of the manuscript and stress that I am not questioning the validity of the equations derived by Kaiser, but rather how he has interpreted previous results and measurements in order to fairly compare GOP from previous calculation methods to the proposed new equations. To communicate the difference between previous methodology and the proposed method, it is important to clarify the relative roles of (1) measured physical parameters used in calculations, such as  $^{17}\delta$  and  $^{18}\delta$  and fractionation factors  $^{18}\epsilon_R$  and (2) the accuracy of various equations under varying conditions of metabolic balance ( $f$ ) and productivity ( $g$ ) when the same physical parameters are used.

## 2 Biological steady state

Understanding the distinction between composition of photosynthetic oxygen ( $P$ ) and oxygen in biological steady-state ( $S$ ) is essential to the following discussion. Photosynthetic oxygen is produced from seawater with only a small fractionation (Eisenstadt et al., 2010) and thus has a  $^{18}\delta_P$  much closer to that of VSMOW, than to air (Kaiser's base case is  $^{18}\delta_P = -22.835\%$ , where air is the standard). Biological steady-state refers to the composition of dissolved oxygen reached with a constant rate of photosynthesis and respiration (see Kaiser Sect. 3.4). For the special case where  $P = R$ , I use the subscript "S0". Angert et al. (2003) described the relationship between  $^*\delta_P$  and  $^*\delta_{S0}$  using the mass balance equation

$$P(1 + ^*\delta_P) = ^*\alpha_R R(1 + ^*\delta_{S0}) \quad \text{where } P = R \quad (3)$$

where "\*" indicates 17 or 18 and  $\alpha_R$  is the fractionation factor for respiration. Since average ocean  $\alpha_R$  is 0.980 ( $^{18}\alpha_R = 1 + ^{18}\epsilon_R = -20\%$ ) (Kiddon et al., 1993),  $^*\delta_{S0}$  is much closer to 0‰ (with air as the standard) than to  $^*\delta_{VSMOW}$ .

Inferring  $^{17}\Delta_P$  from an observed  $^{17}\Delta_{S0}$  involves extrapolating across a large difference in  $^{18}\delta$  and thus large error can be introduced if an incorrect mass dependent slope is used (Luz and Barkan, 2005) causing  $^{17}\Delta_P$  and  $^{17}\Delta_{S0}$  to differ significantly unless an appropriate "tuned" definition is used. Angert et al. (2003) demonstrated that  $^{17}\Delta_P$  equals  $^{17}\Delta_{S0}$  when the following definition is used (see Appendix for derivation of Eqs. 4 and 5):

$$^{17}\Delta^{BSS} = \ln(1 + ^{17}\delta) - \lambda_{BSS} \ln(1 + ^{18}\delta) \quad (4)$$

The slope ( $\lambda_{BSS}$ ) that satisfies the criteria that  $^{17}\Delta_P^{BSS} = ^{17}\Delta_{S0}^{BSS}$  depends on the magnitude of fractionation during respiration such that

$$\lambda_{BSS} = \frac{\ln(^{17}\alpha_R)}{\ln(^{18}\alpha_R)} = \frac{\ln(1 + \gamma_R ^{18}\epsilon_R)}{\ln(1 + ^{18}\epsilon_R)} \quad (5)$$

Thus, for  $^{18}\epsilon_R = -20\%$  and  $\gamma_R = 0.5179$  I calculate  $\lambda_{BSS} = 0.5154$ . Additionally, assuming an error in  $^{18}\epsilon_R$  of  $\pm 2\%$  the difference between  $\gamma_R$  and  $\lambda_{BSS}$  is well constrained ( $\gamma_R - \lambda_{BSS} = 2.5 \times 10^{-3} \pm 2.5 \times 10^{-4}$ ).

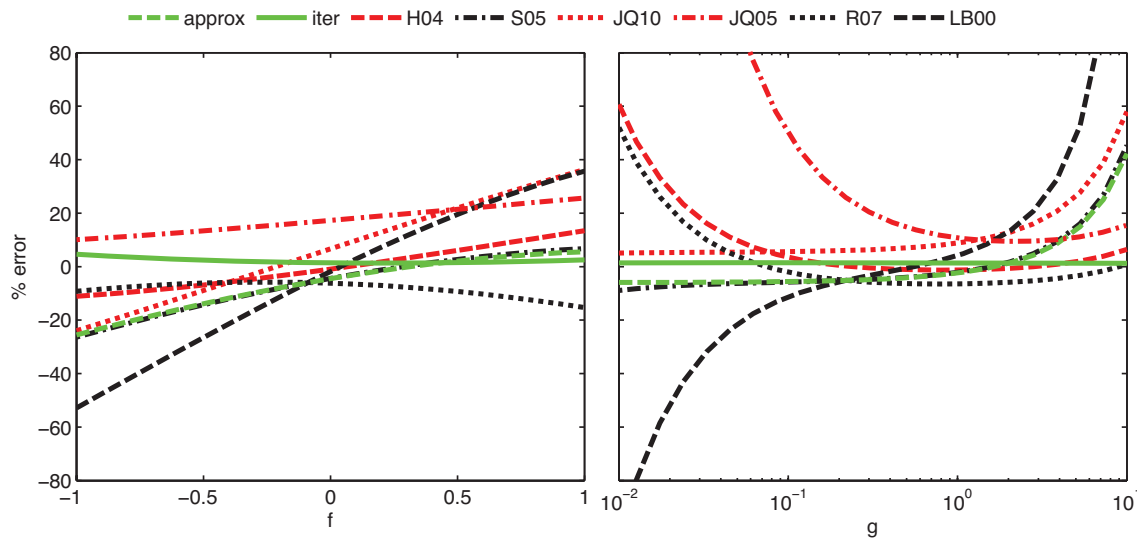
For the above definition, the same  $^{17}\Delta^{BSS}$  should be acquired whether measuring the direct product of photosynthesis or a system in biological steady-state ( $^{17}\Delta_{S0}^{BSS} = ^{17}\Delta_P^{BSS}$ ). The experimental determination of the biological end-member by Luz and Barkan (2000), ( $^{17}\Delta_{bio} = 249 \pm 15$  ppm) was a measurement of dissolved oxygen in biological steady-state with seawater ( $P \approx R$ ) and thus its composition relative to seawater should be governed by Eq. (4) (Angert et al., 2003; Luz and Barkan, 2000). A more descriptive definition of the original approximate equation for calculating  $g$  (Luz and Barkan, 2000) can then be written

$$g = \frac{P}{k c_{sat}} = \frac{^{17}\Delta^{\#} - ^{17}\Delta_{sat}^{\#}}{^{17}\Delta^{BSS} - ^{17}\Delta^{\#}} \quad (6)$$

It is important to note that  $^{17}\Delta^{BSS}$  is the appropriate photosynthetic end-member term, not  $^{17}\Delta_P^{\#}$ .

## 3 Consistent comparison of equations used to calculate $g$

Equation (6) for calculating  $g$  uses  $^{17}\Delta^{BSS}$  as the biological end member, while both the iterative equation (Hendricks et al., 2004) and Kaiser's equation use  $^{17}\delta_P$  and  $^{18}\delta_P$ . To consistently compare the skill of such equations relative to each other, Eq. (4) and  $\lambda_{BSS}$  must be used to relate  $^{17}\delta_P$  to  $^{17}\Delta^{BSS}$ . However for the default case, Kaiser calculates values for  $^{17}\delta_P = -11.646\%$  and  $^{18}\delta_P = -22.835\%$  (Kaiser Table 2) by applying the equation for  $^{17}\Delta^{\#}$  (Eq. 2) rather than  $^{17}\Delta^{BSS}$  (Eq. 4), effectively underestimating the  $^{17}\text{O}$  excess of photosynthetically produced oxygen. The implied  $^{17}\Delta^{BSS}$  from Kaiser's "base case" scenario using Eq. (4) is 191 ppm rather than 249 ppm.



**Fig. 1.** Relative deviation of  $g$  from the “corrected base case” as calculated using the equation proposed by Kaiser. All values are the same as Kaiser’s base case except  $^{17}\delta_{\text{P}} = -11.588\%$  instead of  $^{17}\delta_{\text{P}} = -11.646\%$  as described in Sect. 3. The dashed green line “approx” shows error when “modified base case” values are used with the approximate equation from Luz and Barkan (2000) (Eq. 5) and  $^{17}\Delta^{\#}$  ( $\lambda = 0.5179$ ). The solid green line “iter” shows error due to using the corrected “base case” values ( $^{17}\delta_{\text{P}} = -11.588\%$ ,  $^{18}\varepsilon_{\text{R}} = -20\%$  and  $\lambda = 0.5179$ ) with the iterative method from Hendricks et al. (2004). Red and black lines show deviation from base case using the parameters and approaches employed in previous studies (see Table 3 in Kaiser, 2011 for details). They are calculated from the same values as used by Kaiser, except now compared against the “corrected base case”. Within typical oceanic conditions ( $-0.1 < f < 0.4$  and  $0.01 < g < 1$ ), the methods generally agree within  $\pm 20\%$ . The following abbreviations are used to refer to previous studies: (H04: Hendricks et al., 2004; S05: Sarma et al., 2005; JQ10: Juranek and Quay, 2010; JQ05: Juranek and Quay, 2005; R07: Reuer et al., 2007; LB00: Luz and Barkan, 2000; S05).

Using Eqs. (4) and (5) instead with values of  $^{17}\Delta^{\text{BSS}} = 249$  ppm,  $^{18}\delta_{\text{P}} = -22.835\%$ ,  $\gamma_{\text{R}} = 0.5179$  and  $^{18}\varepsilon_{\text{R}} = -20\%$ , I calculate  $^{17}\delta_{\text{P}} = -11.588\%$ . Using  $^{17}\delta_{\text{P}} = -11.588\%$  in Eq. (1) yields  $^{17}\Delta^{\dagger}$  ( $\kappa = 0.5179$ ) = 238 ppm rather than 180 ppm as reported by Kaiser. Thus if the value of 249 ppm is used for  $^{17}\Delta^{\text{BSS}}$  in Eq. (5), then the comparable  $^{17}\delta_{\text{P}}$  for an equivalent calculation using Kaiser’s Eq. (48) should be  $-11.588\%$  not  $-11.646\%$ . This correction has a significant impact when comparing various equations (Hendricks et al., 2004; Luz and Barkan, 2000, 2005; Miller, 2002) that have previously been used to calculate  $g$  and  $^{17}\Delta$  to the equation derived by Kaiser.

Based on the changes I describe, I illustrate the importance of the suggested correction by recalculating Fig. 3a and b from Kaiser (2011). In addition to the results presented by Kaiser, I have added two green lines to the plot that show the error induced by the choice of equation form alone (Fig. 1). For these two cases,  $^{17}\text{O}$  excess is calculated using the “base case” values from Kaiser except with  $^{17}\delta_{\text{P}} = -11.588\%$  as described above. Using the approximate Eq. (6) results in an error no greater than about  $-25\%$  at the extremely heterotrophic conditions (Fig. 1a) and  $40\%$  at very high production rates (Fig. 1b). Under more typical conditions ( $-0.1 < f < 0.4$  and  $0.01 < g < 1$ ) the error is less than  $\sim 10\%$ . Using the iterative method of Hendricks et al. (2004), the bias is much less still, overestimating  $g$  by

less than  $5\%$  under all conditions. The  $\sim 5\%$  overestimate is caused primarily by the kinetic fractionating effects during gas exchange (i.e.  $\varepsilon_{\text{I}}$  and  $\varepsilon_{\text{E}}$ ) which are accounted for by Kaiser but not by earlier equations.

The red and black lines are calculated from Kaiser Table 3 data except for one correction: in column 6 showing results of Juranek and Quay (2010) the  $\gamma_{\text{R}}$  value should be 0.5205 (not 0.518) because, although not detailed in the publication, the relationship  $^{17}\alpha_{\text{R}} = (^{18}\alpha_{\text{R}})^{\lambda}$  was used (L. W. Juranek, personal communication, 2011), similarly to Hendricks et al. (2004) and Reuer et al. (2007). In Kaiser’s Fig. 3, relative error for many of the methods clusters around  $-30\%$  for  $f \sim 0$  (Kaiser Fig. 3a) and  $g \sim 0.5$ . Although notation varied, each study using an iterative approach defined the composition of  $^{17}\delta_{\text{P}}$  using a  $\lambda_{\text{BSS}}$  slope  $\approx 2.5 \times 10^{-3}$  less than the implied respiratory fractionation slope ( $\gamma_{\text{R}}$ ) as described by Eq. (4). Thus, despite taking various approaches, each previous study has calculated  $g$  in a manner that is accurate to within about  $20\%$  for the relevant environmental conditions. The more precise equation introduced by Kaiser and Prokopenko is superior to previous methods and should be applied to future studies, however much care should be taken in any attempt to “reinterpret” previous results.

Effectively, Kaiser has compared previous equations with a  $^{17}\Delta^{\text{BSS}} = 249$  ppm to his equation using  $^{17}\Delta^{\text{BSS}} = 191$  ppm (the  $^{17}\Delta^{\text{BSS}}$  value for Kaiser’s “base case” values).

This difference is responsible for the majority of the apparent discrepancy between methods. The significantly lower  $^{17}\Delta^{\text{BSS}}$  of 191 ppm is why Kaiser's calculations yield  $g \sim 30\%$  higher than most other calculation methods (Kaiser Fig. 3). After correcting Kaiser's "base case" with  $^{17}\delta_{\text{P}} = -11.588\%$  (and thus  $^{17}\Delta^{\text{BSS}} = 249$  ppm), the remaining differences have clear explanations. Variations in the slope  $\lambda$  from the base case cause an error dependent on  $f$  where slopes greater than the base case causing an overestimate under strongly autotrophic conditions ( $f > 0$ ) and underestimate for heterotrophic conditions ( $f < 0$ ) (Fig. 1a). If a lower gas exchange end-member ( $^{17}\Delta_{\text{sat}}$ ) is used,  $g$  is overestimated, particularly for low values of  $g$  (Fig. 1b). Neglecting kinetic fractionation during gas exchange causes iterative methods to be slightly too high. When regressing the results of Reuer et al. (2007), Kaiser arrives at a result  $\sim 40\%$  higher than Reuer (Kaiser Fig. 4). I find that about 30% of the discrepancy is due to the difference in implied  $^{17}\Delta^{\text{BSS}}$  while the remaining difference is due to how the gas exchange end member was parameterized.

#### 4 Reconciling measurements of seawater and biological steady-state

Originally, the excess  $^{17}\text{O}$  contained in photosynthetically produced  $\text{O}_2$ , relative to the atmosphere was determined by measuring the biological steady-state condition ( $^{17}\Delta^{\text{BSS}} = 249$  ppm) (Luz and Barkan, 2000). The isotopic composition of seawater could be inferred through assuming little fractionation during photosynthesis. Methodological improvements have led to the recent publication of a more robust direct measure of the isotopic composition of seawater (Barkan and Luz, 2011). As I will outline in this section, these new data (not available at the time Kaiser wrote his initial paper) are consistent with the original measurement ( $^{17}\Delta^{\text{BSS}} = 249$  ppm) by Luz and Barkan (2000).

The oxygen isotopic composition of VSMOW was determined to be  $^{18}\delta_{\text{sw}} = -11.883\%$  and  $^{18}\delta_{\text{sw}} = -23.324\%$  (Barkan and Luz, 2011). Additionally, a fractionation during photosynthesis of a few ppm has been observed (Luz and Barkan, 2011), such that  $^{18}\delta_{\text{P}} = 20\%$ . Given this information,  $^{17}\delta_{\text{P}}$  and thus  $^{17}\Delta_{\text{P}}$  can be calculated in two ways; starting from the  $^{17}\Delta^{\text{BSS}}$  measurement or from the seawater measurement. Using Eqs. (4) and (5),  $^{17}\Delta^{\text{BSS}} = 249$  ppm and  $^{18}\delta_{\text{P}} = -20\%$ , I calculate  $^{17}\delta_{\text{P}} = -10.112\%$ . The  $^{18}\delta_{\text{P}}$  and  $^{17}\delta_{\text{P}}$  values calculate to  $^{17}\Delta_{\text{P}}^{\#}(\lambda = 0.5179) = 300$  ppm (note: Barkan and Luz report 223 ppm using  $\lambda = 0.516$ ). Calculating from the seawater side,  $^{18}\delta_{\text{sw}} = -11.883\%$  and  $^{18}\delta_{\text{sw}} = -23.324\%$  result in  $^{17}\Delta_{\text{sw}}^{\#}(\lambda = 0.5179) = 268$  ppm. Recent observations show on average that  $^{17}\Delta_{\text{P}}^{\#}$  is 26 ppm higher than  $^{17}\Delta_{\text{sw}}^{\#}$ . Thus, a calculation starting with the measurement of seawater yields  $^{17}\Delta_{\text{P}}^{\#}(\lambda = 0.5179) = 304$  ppm which is within analytical error of the  $^{17}\Delta_{\text{P}}^{\#}(\lambda = 0.5179) = 300$  ppm inferred from the original measure of  $^{17}\Delta^{\text{BSS}} = 249$  ppm. In

summary, the best existing analytical evidence consistently supports that  $^{17}\Delta_{\text{P}}^{\#}(\lambda = 0.5179) \approx 300$  ppm and  $^{17}\Delta^{\text{BSS}}(\lambda = 0.5154) = 249$  ppm. Kaiser's base case, which has values of  $^{17}\Delta_{\text{P}}^{\#}(\lambda = 0.5179) \approx 249$  ppm and  $^{17}\Delta^{\text{BSS}}(\lambda = 0.5154) = 191$  ppm is not supported by any analytical evidence.

In practice, the choice of  $^{18}\delta_{\text{P}}$  to be  $-20\%$  versus the "base case" value of  $-22.835\%$  does not cause a significant difference in calculated  $g$  values. What is critical, however, is that  $^{17}\delta_{\text{P}}$  is defined a manner that is consistent with Eqs. (4) and (5). Using the wrong slope to calculate  $^{17}\delta_{\text{P}}$  results in Kaiser's base case underestimating the  $^{17}\text{O}$  anomaly of photosynthetic oxygen and overestimating  $g$  by  $\sim 30\%$ .

#### 5 Conclusions

Since the introduction of the triple isotopic composition of dissolved oxygen was introduced as a tracer of gross oxygen production by Luz and Barkan (2000), the methodology for calculating  $g$  from measured isotopic ratios has evolved and improved. While improved equations will better estimates of  $g$ , perhaps the greater cause of error is in analytically determining what the accurate and appropriate photosynthetic and gas exchange end members should be ( $^{17}\delta_{\text{P}}$ ,  $^{18}\delta_{\text{P}}$ ,  $^{17}\delta_{\text{sat}}$  and  $^{18}\delta_{\text{sat}}$ ).

When applying an equation to calculate  $g$  that requires  $^{17}\delta_{\text{P}}$  in the calculation, it is essential to set  $^{17}\delta_{\text{P}}$  using the slope  $\lambda_{\text{BSS}}$  and Eqs. (4) and (5). By erroneously assigning a value of 249 ppm to  $^{17}\Delta_{\text{P}}^{\#}$ , Kaiser's "base case" scenario implies a  $^{17}\Delta^{\text{BSS}} = 191$  ppm, resulting in values of  $g$  that are  $\sim 30\%$  too high when compared to other calculation methods.

#### Appendix A

##### Derivation for biological steady-state

The following derivation is adapted from Angert et al. (2003) and shows the relationship between  $\lambda_{\text{BSS}}$  and  $\gamma_{\text{R}}$  for a  $P = R$  steady-state system.

The slope  $\lambda_{\text{BSS}}$  is defined as the slope for which  $^{17}\Delta_{\text{P}}^{\text{BSS}} = ^{17}\Delta_{\text{S0}}^{\text{BSS}}$  so that from Eq. (4),

$$\begin{aligned} ^{17}\Delta^{\text{BSS}} &= \ln\left(1 + ^{17}\delta_{\text{S0}}\right) - \lambda_{\text{BSS}} \ln\left(1 + ^{18}\delta_{\text{S0}}\right) \\ &= \ln\left(1 + ^{17}\delta_{\text{P}}\right) - \lambda_{\text{BSS}} \ln\left(1 + ^{18}\delta_{\text{P}}\right) \end{aligned} \quad (\text{A1})$$

Which can be rearranged to

$$\lambda_{\text{BSS}} = \frac{\ln\left(\frac{1 + ^{17}\delta_{\text{P}}}{1 + ^{17}\delta_{\text{S0}}}\right)}{\ln\left(\frac{1 + ^{18}\delta_{\text{P}}}{1 + ^{18}\delta_{\text{S0}}}\right)} \quad (\text{A2})$$

Noting that when  $P = R$ , Eq. (3) simplifies to

$$(1 + ^*\delta_{\text{P}}) = ^*\alpha_{\text{R}} (1 + ^*\delta_{\text{S0}}) \quad (\text{A3})$$

Substituting Eq. (A3) into Eq. (A2) and noting  $^{17}\epsilon_R = \gamma_R^{18}\epsilon_R$  and  $1 + ^*\epsilon_R = ^*\alpha_R$  yields  $\lambda_{\text{BSS}}$  as described in Eq. (5)

$$\lambda_{\text{BSS}} = \frac{\ln(^{17}\alpha_R)}{\ln(^{18}\alpha_R)} = \frac{\ln(1 + \gamma_R^{18}\epsilon_R)}{\ln(1 + ^{18}\epsilon_R)} \quad (\text{A4})$$

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