

## RESEARCH LETTER

10.1002/2014GL060741

## Key Points:

- A uWUE was tested to better describe nonlinear relationships among GPP, ET, and VPD
- $GPP \cdot VPD^{0.5}$  is optimally correlated with ET at subdaily scales for 42 AmeriFlux sites
- GPP and  $VPD^{0.5}$  combination is supported by reducing time lags among GPP, ET, and VPD

## Supporting Information:

- Readme
- Table S1
- Table S2
- Text S1
- Text S2
- Figure S1

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## Citation:

Zhou, S., B. Yu, Y. Huang, and G. Wang (2014), The effect of vapor pressure deficit on water use efficiency at the subdaily time scale, *Geophys. Res. Lett.*, *41*, 5005–5013, doi:10.1002/2014GL060741.

Received 5 JUN 2014

Accepted 10 JUL 2014

Accepted article online 14 JUL 2014

Published online 28 JUL 2014

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## The effect of vapor pressure deficit on water use efficiency at the subdaily time scale

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**Abstract** Water use efficiency is a critical index for describing carbon-water coupling in terrestrial ecosystems. However, the nonlinear effect of vapor pressure deficit (VPD) on carbon-water coupling has not been fully considered. To improve the relationship between gross primary production (GPP) and evapotranspiration (ET) at the subdaily time scale, we propose a new underlying water use efficiency ( $uWUE = GPP \cdot VPD^{0.5}/ET$ ) and a hysteresis model to minimize time lags among GPP, ET, and VPD. Half-hourly data were used to validate uWUE for seven vegetation types from 42 AmeriFlux sites. Correlation analysis shows that the  $GPP \cdot VPD^{0.5}$  and ET relationship ( $r = 0.844$ ) is better than that between  $GPP \cdot VPD$  and ET ( $r = 0.802$ ). The hysteresis model supports the  $GPP \cdot VPD^{0.5}$  and ET relationship. As uWUE is related to  $CO_2$  concentration, its use can improve estimates of GPP and ET and help understand the effect of  $CO_2$  fertilization on carbon storage and water loss.

### 1. Introduction

Water use efficiency (WUE), the ratio of photosynthetic carbon assimilation over transpiration, has been widely recognized as a critical link between carbon and water cycling in terrestrial ecosystems [Niu *et al.*, 2011]. At the ecosystem scale, WUE was calculated as the ratio of gross primary production (GPP) over evapotranspiration (ET) [Law *et al.*, 2002; Hu *et al.*, 2008] derived from eddy covariance measurements. Furthermore, inherent water use efficiency (IWUE) was proposed to incorporate the effects of vapor pressure deficit (VPD) with reference to photosynthesis-transpiration relationship via stomatal conductance [Bierhuizen and Slatyer, 1965; Beer *et al.*, 2009; Launiainen *et al.*, 2011]. Both WUE and IWUE have been used to estimate GPP or ET based on eddy covariance measurements and satellite-derived estimations [Beer *et al.*, 2007; Yang *et al.*, 2013]. IWUE has also been used to identify the ecosystem responses to environmental changes, such as rising  $CO_2$  concentrations [Silva and Horwath, 2013; Battipaglia *et al.*, 2013; Keenan *et al.*, 2013], since the ratio is related to the difference between ambient and inner leaf partial pressures of  $CO_2$  ( $c_a - c_i$ ) [Beer *et al.*, 2009]. Several biophysical process-based models have been used to evaluate the response of WUE and IWUE to climate change, elevated  $CO_2$ , and other environmental controls [Zhu *et al.*, 2011; Zhang *et al.*, 2014b]. Studies of WUE and IWUE therefore contribute to in-depth understanding of the carbon and water dynamics in terrestrial ecosystems.

Beer *et al.* [2009] used daily GPP, VPD, and ET data from 43 sites around the world to show that the relationship between  $GPP \cdot VPD$  and ET is stronger than that between GPP and ET by taking into account the nonlinear effect of VPD on ET. IWUE involving the VPD term has therefore been widely used in numerous studies to explore the mechanism and processes of carbon and water coupling [Loader *et al.*, 2011; Leonardi *et al.*, 2012; Battipaglia *et al.*, 2013; Grossiord *et al.*, 2014]. However, there are at least two limitations in Beer *et al.* [2009]. First, the linear relationship between  $GPP \cdot VPD$  and ET was considered and tested at daily to annual time scales, and diurnal variations in GPP, ET, and VPD were neglected when exploring their linear relationship using daily data. Second, the  $GPP \cdot VPD$  versus ET relationship depends on the assumed constancy of the ratio of interleaf over ambient partial pressure of  $CO_2$  ( $c_i/c_a$ ) within the canopy under certain environmental conditions, and diurnal and seasonal variations in the ratio  $c_i/c_a$  may lead to nonlinear relationships between  $GPP \cdot VPD$  and ET [Wong *et al.*, 1979; Katul *et al.*, 2000]. Several studies have showed that variations in  $c_i/c_a$  depend on VPD itself at diurnal and seasonal scales [Lloyd, 1991; Farquhar *et al.*, 1993; Lloyd and Farquhar, 1994; Zhang and Nobel, 1996; Herbst *et al.*, 2002; Tang *et al.*, 2006; Batista *et al.*, 2012]. The variation of  $c_i/c_a$  at the leaf scale may directly result in a nonlinear relationship between  $GPP \cdot VPD$  and ET at the ecosystem scale, which has not yet been considered in previous studies [Beer *et al.*, 2009; Keenan *et al.*, 2013]. In addition, without considering the effect of VPD on  $c_i/c_a$ , attribution of the increase in forest IWUE to an elevated

atmospheric CO<sub>2</sub> ( $c_a$ ) exclusively may lead to an overestimation of the effect of  $c_a$  on IWUE [Keenan *et al.*, 2013], as argued in Medlyn and De Kauwe [2013]. Neglecting the diurnal variations in  $c_i/c_a$  offers a reasonable explanation for the differing trends of IWUE and biomass growth in the long term [Nock *et al.*, 2011; Andreu-Hayles *et al.*, 2011].

While the IWUE shows an improved linear relationship among GPP, ET, and VPD at the daily to annual time scales, there are three questions to be clarified: (1) whether a linear relationship among GPP, ET, and VPD exists at the subdaily time scale; (2) whether alternative combinations of GPP and VPD would lead to a better, or an optimal, measure of WUE when considering the effect of VPD on  $c_i/c_a$ ; and (3) whether linear relationship among GPP, ET, and VPD can be interpreted and explained by the subdaily fluctuations of these variables. To address these research questions, the role of VPD in affecting water use efficiency was investigated with diurnal half-hourly data of GPP, ET, and VPD during the growth season from 42 AmeriFlux sites. The objective of this paper is to develop an underlying WUE model (uWUE) at the subdaily time scale to improve the linear relationship among GPP, ET, and VPD, by taking into account the effect of VPD on  $c_i/c_a$  and their subdaily variations.

## 2. Methods and Data

In order to develop a better or an optimal linear relationship among GPP, ET, and VPD at the ecosystem level, we propose to test two alternative models: the first is based on an improvement of IWUE, with an aim to establish an underlying water use efficiency (uWUE) by considering the relationship between VPD and  $c_i/c_a$  at the subdaily time scale; and the second is the hysteresis model, which is based on sinusoidal functions to describe diurnal variations in GPP, ET, and VPD and to test whether an optimal combination of GPP, ET, and VPD can in fact be achieved by eliminating or minimizing the time lags between these variables. The hysteresis model and data descriptions are provided as supporting information of the paper.

### 2.1. Underlying Water Use Efficiency

Stomatal conductance critically determines both photosynthetic uptake of CO<sub>2</sub> and the loss of water transpired from the leaf. Thus, the rate of CO<sub>2</sub> assimilation,  $A$ , in  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and water transpiration,  $T$ , in  $\mu\text{mol m}^{-2} \text{s}^{-1}$  can be computed as follows [Beer *et al.*, 2009]:

$$A = g_s \cdot \frac{(c_a - c_i)}{p_a} \tag{1}$$

$$T = 1.6 \cdot g_s \cdot \frac{(e_i - e_a)}{p_a} \tag{2}$$

where  $g_s$  is the stomatal conductance of CO<sub>2</sub> ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ),  $p_a$  is the atmospheric pressure (hPa),  $(c_a - c_i)$  is the difference between ambient and inner leaf partial pressures of CO<sub>2</sub> (hPa), and  $(e_i - e_a)$  is the water vapor pressure difference between inner leaf and ambient air (hPa). The constant 1.6 in equation (2) is the ratio of molecular diffusion coefficient for water vapor relative to that for CO<sub>2</sub>.

At the leaf level, WUE is calculated as the ratio of carbon uptake and water lost through transpiration ( $\text{WUE} = A/T$ ). Assuming that leaves and the atmosphere are of the same temperature, water vapor pressure difference ( $e_i - e_a$ ) can be approximated by atmospheric VPD. Then the leaf WUE can be expressed as a function of  $c_a$ ,  $c_i/c_a$ , and VPD deriving from equations (1) and (2):

$$\text{WUE}_{\text{leaf}} = \frac{c_a \left(1 - \frac{c_i}{c_a}\right)}{1.6 \text{ VPD}} \tag{3a}$$

or

$$\frac{A \cdot \text{VPD}}{T} = \frac{c_a}{1.6} \left(1 - \frac{c_i}{c_a}\right) \tag{3b}$$

according to Beer *et al.* [2009]. For given VPD, the  $(1 - c_i/c_a)$  term on the right-hand side of equation (3b) tends to remain constant in leaves, but this term increases as VPD increases [Wong *et al.*, 1979].  $\text{WUE}_{\text{leaf}} \cdot \text{VPD}$  is therefore affected by variations in VPD, which could lead to nonlinear relationship between GPP · VPD and ET from leaf to ecosystem scales. Comparing eight models that estimate  $c_i/c_a$  in mole fraction, namely  $C_i/C_a$ , Katul *et al.* [2000] demonstrate that the Farquhar model in Lloyd and Farquhar [1994] could best describe the underlying physiological mechanisms affecting  $C_i/C_a$ .

Estimation of  $C_i/C_a$  has a long history [Cowan, 1977; Cowan and Farquhar, 1977; Farquhar et al., 1980; Lloyd, 1991; Farquhar et al., 1993; Lloyd and Farquhar, 1994], and numerous studies of the optimal stomatal behavior of carbon dioxide uptake with respect to water loss have demonstrated that there is a linear relationship between  $(1 - C_i/C_a)$  and the square root of leaf to air vapor mole fraction difference ( $D^{0.5}$ ) for the  $C_3$  plants of different biomes [Lloyd, 1991; Farquhar et al., 1993; Lloyd and Farquhar, 1994], as is shown in equation (4).

$$1 - \frac{C_i}{C_a} = \sqrt{\frac{1.6 D(C_a - \Gamma)}{\lambda_{cf} C_a^2}} \quad (4)$$

where  $\Gamma$  is the leaf  $CO_2$  compensation point and  $\lambda_{cf}$  is the ratio of  $\partial T/\partial g_s$  to  $\partial A/\partial g_s$ ;  $\lambda_{cf}$  is almost constant within a certain vegetation type provided  $\partial^2 T/\partial^2 A > 0$  based on a model of optimal stomatal behavior [Cowan and Farquhar, 1977]. According to the Raoult's law, the partial gas pressure is proportional to its mole fraction for ideal liquid [Butler et al., 1933]. Thus,  $C_i/C_a$  and  $D$  can be approximated by  $c_i/c_a$  and VPD, respectively, and the  $(1 - c_i/c_a)$  term in equation (3b) can be replaced with  $(1 - C_i/C_a)$  involving the square root of VPD. After dividing equation (3b) by  $\sqrt{VPD}$ , the relationship between  $A$ ,  $T$ , and VPD can be expressed as

$$\frac{A\sqrt{VPD}}{T} = \sqrt{\frac{C_a - \Gamma}{1.6 \lambda_{cf}}} \quad (5)$$

where the right-hand side involves  $C_a$ ,  $\Gamma$ , and  $\lambda_{cf}$  and remains essentially constant for certain vegetation types in the short term. At the very least, the right-hand side of equation (5) has much less variation in comparison to that of equation (3b). Thus, we can define an underlying WUE (uWUE) at the leaf level as follows:

$$uWUE_{leaf} = \frac{A\sqrt{VPD}}{T} \quad (6)$$

Under steady state conditions,  $(C_a - \Gamma)$  is constant, and  $\lambda_{cf}$  is essentially constant for a certain vegetation type, so that equation (6) describes a linear relationship between  $A\sqrt{VPD}$  and  $T$  at the leaf scale. When  $(C_a - \Gamma)$  changes with atmospheric conditions, or  $\lambda_{cf}$  varies among different vegetation types, the underlying water use efficiency, uWUE, could change accordingly.

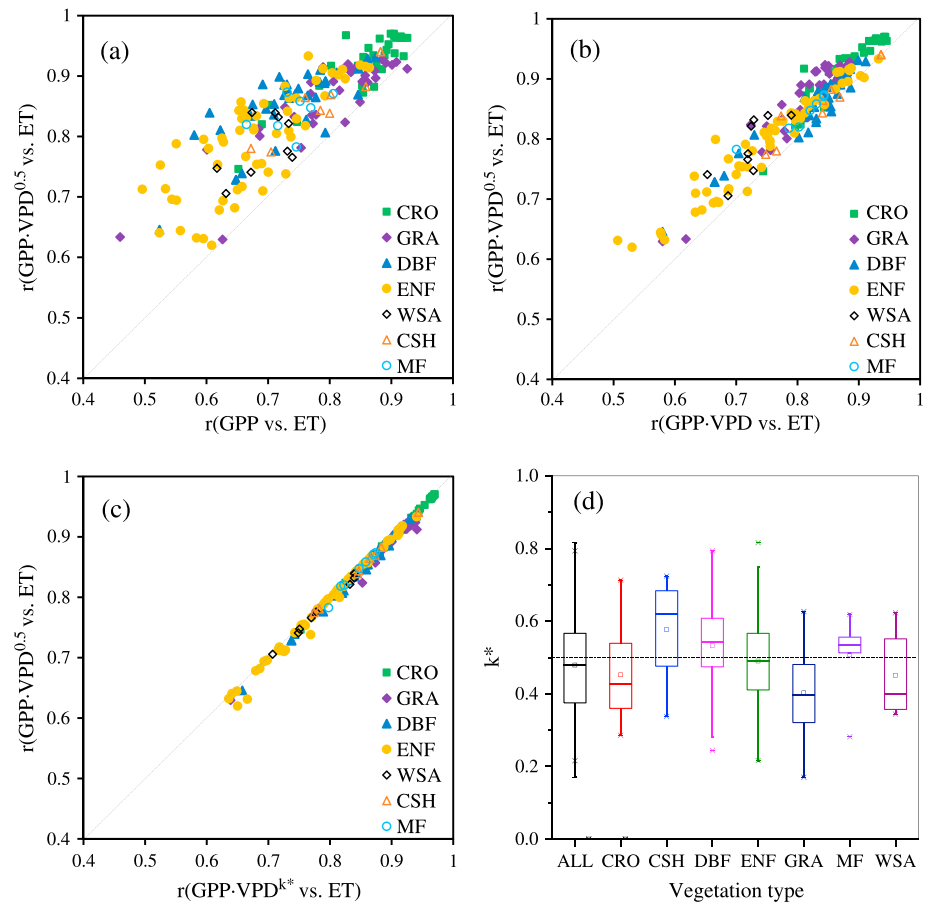
The coupled carbon-water relationship at the leaf scale provides support for the carbon assimilation and water transpiration relationship at the ecosystem scale, which is important for large-scale estimations of gross primary production (GPP) and evapotranspiration (ET). Equation (6) can be used to inform an appropriate relationship between GPP and ET at the ecosystem level:

$$uWUE = \frac{GPP\sqrt{VPD}}{ET} \quad (7)$$

Equation (7) is established by assuming the following: (1) the canopy and the atmosphere are of the same temperature so that leaf to air vapor pressure difference ( $e_i - e_a$ ) can be approximated by atmosphere VPD; (2) soil evapotranspiration is small, and canopy transpiration ( $T$ ) takes up a large proportion of ET, so that  $T$  is treated as a surrogate of ET; and (3) the ideal gas model is approximately satisfied, and partial vapor pressure is proportional to gas mole fraction. Thus, uWUE according to equation (7) may be a better linear relationship between GPP and ET, adjusted by  $VPD^{0.5}$ , as  $\lambda_{cf}$  and  $C_a$  are essentially constant for a certain vegetation type during a growth season. For this paper, uWUE was evaluated by comparing the correlation coefficients for the relationships between (1) GPP and ET, (2)  $GPP \cdot VPD$  and ET, and (3)  $GPP \cdot VPD^{0.5}$  and ET using subdaily data during the growth season from 42 AmeriFlux sites. In addition, we also considered a generic model for ET in the form

$$GPP \cdot VPD^k = \gamma ET \quad (8)$$

It can be seen that  $\gamma$  represents WUE, uWUE, and IWUE, when  $k=0, 0.5$ , and  $1$ , respectively. The linear correlation coefficient was computed at each value of  $k$  at 0.001 increment from 0 to 1 using the half-hourly data of each site year to estimate an optimal  $k$ , i.e.,  $k^*$ , when the correlation coefficient was the largest. Furthermore, correlation coefficients of the relationship between  $GPP \cdot VPD^{0.5}$  and ET are compared with those of the relationship between  $GPP \cdot VPD^{k^*}$  and ET to validate the uWUE model.



**Figure 1.** Comparisons of the correlation coefficient ( $r$ ) for the relationships between  $GPP \cdot VPD^{0.5}$  versus ET and (a) GPP versus ET, (b)  $GPP \cdot VPD$  versus ET, (c)  $GPP \cdot VPD^{k^*}$  versus ET for the 184 site years in North America. The exponent associated with the maximum correlation coefficient for the relationship between  $GPP \cdot VPD^{k^*}$  and ET for each site year for the seven vegetation types (CRO = Cropland, DBF = Deciduous Broadleaf Forest, ENF = Evergreen Needle leaf Forest, GRA = Grassland, WSA = Woody Savannas, CSH = Closed Shrublands, and MF = Mixed Forest) is  $k^*$ . (d) Box plots of the distribution of the optimal exponent  $k^*$  for the seven vegetation types and the overall distribution for all site years.

### 3. Results

#### 3.1. Validation of the Underlying Water Use Efficiency Model at Each Site Year

Figure 1 shows comparisons of the correlation coefficients for relationships between ET and various combinations of GPP and VPD during the growth season for the 42 sites in North America. It is clear from Figure 1a that including the  $VPD^{0.5}$  term would improve the correlation with ET considerably. It can also be seen that the relationship between  $GPP \cdot VPD^{0.5}$  and ET is systematically stronger than that between  $GPP \cdot VPD$  and ET (Figure 1b). Figure 1c indicates that the relationship between  $GPP \cdot VPD^{0.5}$  is nearly optimal since there is little further improvement when the optimal exponent  $k^*$  for each site year was used. The average correlation coefficients between  $GPP \cdot VPD^{0.5}$  and ET for the seven vegetation types vary from 0.785 to 0.920, and the overall average is 0.844 for all the 184 site years (Table 1). The average increase in the correlation coefficient for the seven vegetation types from the GPP versus ET relationship to the  $GPP \cdot VPD^{0.5}$  versus ET relationship is about 0.065–0.119 and about 0.019–0.063 from the  $GPP \cdot VPD$  versus ET relationship to the  $GPP \cdot VPD^{0.5}$  versus ET relationship. The average difference in the correlation coefficient between  $GPP \cdot VPD^{0.5}$  versus ET and  $GPP \cdot VPD^{k^*}$  versus ET relationships is less than 0.005 (Table 1), again indicating that a  $k$  value of 0.5 is nearly optimal for practical purposes. These results show that the uWUE model tested in the paper for the 184 site years during the growth season is superior to other measures of water use efficiency in terms of a strong linear relationship among GPP, ET, and VPD by taking into account of the effect of VPD on  $c_i/c_a$  and is nearly as good as the optimal relationship, namely  $GPP \cdot VPD^{k^*}$  versus ET. In practice, the  $GPP \cdot VPD^{0.5}$

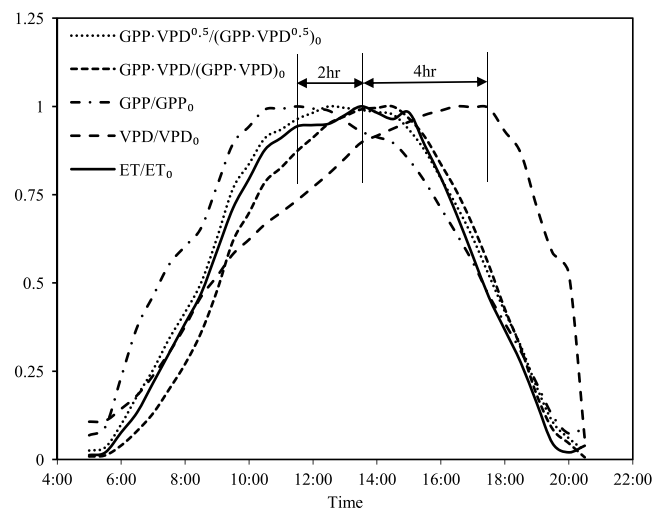
**Table 1.** Average Correlation Coefficients for the Relationships Between Evapotranspiration (ET) and Various Combinations of the Gross Primary Production (GPP) and Vapor Pressure Deficit (VPD) for 184 Site Years and for Seven Vegetation Types During the Growth Season (CRO=Cropland, DBF=Deciduous Broadleaf Forest, ENF=Evergreen Needle Leaf Forest, GRA=Grassland, WSA=Woody Savannas, CSH=Closed Shrublands, MF=Mixed Forest)<sup>a</sup>

	Site Years	GPP Versus ET	GPP · VPD Versus ET	GPP · VPD <sup>0.5</sup> Versus ET	GPP · VPD <sup>k*</sup> Versus ET	k*
CRO	31	0.855	0.878	0.920	0.923	0.452
DBF	37	0.733	0.822	0.852	0.856	0.533
ENF	57	0.677	0.751	0.795	0.800	0.490
GRA	34	0.796	0.809	0.862	0.868	0.403
WSA	9	0.692	0.722	0.785	0.790	0.451
CSH	9	0.794	0.840	0.859	0.862	0.577
MF	7	0.741	0.804	0.839	0.842	0.508
Average		0.750	0.802	0.844	0.848	0.479

<sup>a</sup>The optimal exponent when the highest correlation coefficient for the relationship between GPP · VPD<sup>k\*</sup> and ET was reached is k\*.

versus ET relationship is much easier to use because k\* varies slightly among different vegetation types and among different site years for each vegetation type (Figure 1d).

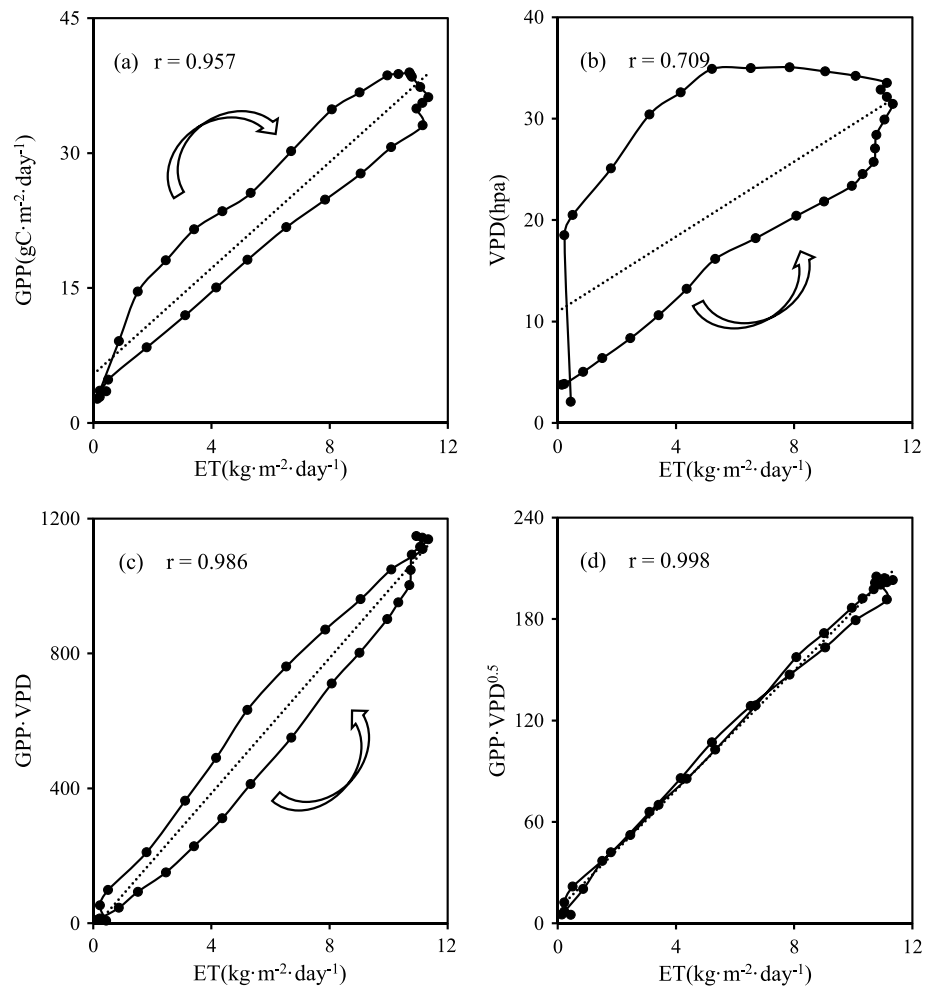
For the seven vegetation types, distributions of k\* are shown in Figure 1d. For most site years, k\* varies from 0.4 to 0.6, and the average k\* of the 184 site years is 0.479, approximating 0.5 (Table 1). For some vegetation types, the average k\* is smaller or larger than 0.5. For example, more than 75% of k\*s are smaller than 0.5 for 34 site years for grassland, and the average k\* is 0.403. The GPP · VPD<sup>0.5</sup> versus ET relationship shows much higher correlation coefficient than the GPP · VPD versus ET relationship in more than half of the 34 site years for grassland, and the average increase is large (0.053) (Table 1). However, k\* distributions of closed shrublands are concentrated above 0.5, and the improvements in terms of the correlation coefficient from GPP · VPD versus ET to GPP · VPD<sup>0.5</sup> versus ET are only 0.019 (Figure 1d and Table 1). All in all, k\* fluctuates in a large range for the seven vegetation types, and the improvements vary considerably both from GPP versus ET and from GPP · VPD versus ET to GPP · VPD<sup>0.5</sup> versus ET (Figures 1a and 1b). In one sense, the distributions and variations of k\* make it certain that as a compromise, a constant value of k at 0.5 is appropriate for most site years. The linear correlation coefficient has increased for 182 out of total 184 site years from GPP versus ET to GPP · VPD<sup>0.5</sup> versus ET relationships and for 178 site years from GPP · VPD versus ET to GPP · VPD<sup>0.5</sup> versus ET relationships.



**Figure 2.** Typical diurnal variations in half-hourly ET, GPP, VPD, GPP · VPD, and GPP · VPD<sup>0.5</sup> on 24 June 2002 at Station US-Ne1 (CRO). The diurnal cycle begins at 5:00 h and ends at 21:00 h. All the variables were scaled with their respective peak values for the day, as indicated by the subscript, 0.

### 3.2. Evaluation of the Hysteresis Model at the Subdaily Time Scale

During a day, GPP, ET, and VPD would follow a regular pattern from sunrise to sunset. As an example, Figure 2 shows the time series at half-hourly intervals for these three variables on 24 June 2002 at Station US-Ne1 (CRO). It can be seen that GPP reaches its peak first, followed by ET, and finally VPD. The time lag between peaks in ET and GPP is about 2 h and that between VPD and ET 4 h. Figure 3 presents paired relationships between GPP, VPD, GPP · VPD, and GPP · VPD<sup>0.5</sup>, with ET for the same day at Station US-Ne1 (CRO). The time lags between these variables would result in hysteresis curves. There is a clockwise hysteresis loop in the ET versus GPP relationship, and a counterclockwise loop for the ET versus VPD relationship (Figures 3a and 3b).



**Figure 3.** Typical diurnal hysteresis relationships between ET and (a) GPP, (b) VPD, (c) GPP · VPD, and (d) GPP · VPD<sup>0.5</sup> on 24 June 2002 at Station US-Ne1 (CRO).

Using the product of GPP and VPD, the effect of hysteresis is reduced (Figure 3c). With the product of GPP and VPD<sup>0.5</sup>, the effect of time lags is essentially eliminated, and the hysteresis curve disappears (Figure 3d), and the product of GPP and VPD<sup>0.5</sup> aligns very well with the diurnal variations in ET (Figure 2). It therefore follows that the higher correlation coefficient for the GPP · VPD<sup>0.5</sup> versus ET relationship in comparison to other combinations occurs because, with this product of GPP and VPD<sup>0.5</sup>, the effect of the time lags among GPP, ET, and VPD at the subdaily scale is largely removed.

During clear or slightly cloudy days when environmental conditions are favorable, the diurnal variations in ET, GPP, and VPD can be approximated by sinusoidal functions [Pita *et al.*, 2013; Zhang *et al.*, 2014a], as explained in Text S1 of the supporting information. There is a time lag ranging from 0.5 to 3 h between ET and GPP (average 1.68 h) and from 1 to 5 h between VPD and ET (average 3.04 h) for the 2685 site days examined in this paper (Table S2). As for the four individual vegetation types (CRO, DBF, ENF, GRA) with more than 30 site years, the average time lags range from 1.53 to 1.82 h between ET and GPP and from 2.87 to 3.20 h between VPD and ET, and the exponent  $k^*$  estimated from these time lags and equation (S5b) varies from 0.474 to 0.552 (Table S2). It is interesting to note that the magnitude of  $k^*$  is broadly similar to that of  $k^*$  empirically determined using subdaily data for site years, and the variations in  $k^*$  and  $k^*$  broadly follow the same pattern around 0.5 for all four vegetation types (cf. Figures 1d and S1a). The difference between the average  $k^*$  and 0.5 is less than 0.06 for the four vegetation types; thus, an exponent of 0.5 for VPD is appropriate for different vegetation types.

The highest correlation coefficient and the corresponding optimal  $k^*$  were calculated for each site day, using the same method for site years. A comparison of the correlation coefficient between GPP · VPD <sup>$k^*$</sup>  versus ET



and  $GPP \cdot VPD^{K^*}$  versus ET relationships shows that the differences in the correlation coefficient are less than 0.05 for 95% of all site days and less than 0.01 for 69% of all site days; only nine out of total 2685 site days have differences more than 0.1 (Figure S1b). The average correlation coefficient for the relationship using  $GPP \cdot VPD^{0.5}$  was 0.9192 for individual days, while that using  $GPP \cdot VPD^{K^*}$  was 0.9194, with a difference  $< 0.001$  in terms of the  $r$  values (Table S2). The data points in Figure S1c are evenly distributed around the 1:1 line, suggesting that using  $k = 0.5$  would lead to essentially the same correlation coefficient on average. The  $GPP \cdot VPD^{0.5}$  versus ET relationships are good for 71% of all the site days ( $r > 0.9$ ) (Figure S1c). These results show that the assumed sinusoidal functions and the resulting optimal exponent  $K^*$  are quite effective in minimizing the time lags between GPP and ET, and support the uWUE model with the exponent for VPD at 0.5 for the underlying water use efficiency at the subdaily time scale.

As for  $GPP \cdot VPD^{0.5}$  versus ET, the linear relationship for cropland is the best ( $r = 0.977$ ), followed by grassland ( $r = 0.938$ ) and deciduous broadleaf forest ( $r = 0.918$ ), and evergreen needle leaf forest ( $r = 0.871$ ) for individual site days (Table S2). The correlation coefficients greater than 0.95 were obtained for 90% of the 595 site days for cropland. In comparison, the linear relationship is not very good for deciduous broadleaf forest and evergreen needle leaf forest; only 36% (deciduous broadleaf forest) and 15% (evergreen needle leaf forest) of the correlation coefficients are larger than 0.95. It can also be seen from Figure S1b that the data points are closer to the 1:1 line for cropland, suggesting that  $K^*$  is essentially the optimal exponent in terms of the maximum  $r$  values for most of the 595 site days tested. For deciduous broadleaf forest and evergreen needle leaf forest, the  $r$  values were lower and suboptimal as the data points are away from the 1:1 line.

#### 4. Discussion

Testing of the uWUE and the hysteresis models indicates that the GPP and  $VPD^{0.5}$  combination would lead to a nearly optimal linear relationship with ET during the growth season and at the subdaily time scale. The uWUE was developed by taking into account the underlying relationship between VPD and  $c_i/c_a$ , which is related to equation (4). However, the uWUE may not be appropriate when the three critical assumptions are violated. For example, the first assumption would be invalid when the canopy is highly decoupled from the atmosphere and there is an obvious difference in temperature between leaves and the atmosphere [Jarvis and McNaughton, 1986], and the second assumption would be violated if there is a significant difference between canopy transpiration ( $T$ ) and ET when the leaf area index (LAI) is small.

The simple hysteresis model effectively reduces the time lag between  $GPP \cdot VPD^k$  and ET in order to develop an optimal combination of GPP and VPD to minimize the hysteresis effect on ET. The hysteresis model is adequate when environmental conditions are favorable and the three variables can be approximated by sinusoidal functions. The model may not be appropriate on cloudy days when these variables do not increase monotonically from sunrise to their maxima then decrease monotonically to sunset. Intermittent clouds can disrupt the linear relationship during daytime, but the nonlinear relationship between  $GPP \cdot VPD^{0.5}$  and ET can be remarkably weakened at larger time scales. Daily GPP  $\cdot$  VPD versus ET relationship (IWUE) and monthly GPP versus ET relationship (WUE) have been investigated in Beer *et al.* [2009] and Yang *et al.* [2013], respectively. Their results showed that both IWUE and WUE perform well at certain time scales, and upscaling may further improve the linear relationship because variations and fluctuations at the subdaily time scale can be reduced through averaging. It would be interesting to further test the  $GPP \cdot VPD^{0.5}$  versus ET relationship at different time scales.

Comparison of the  $GPP \cdot VPD^{0.5}$  versus ET relationship for the four vegetation types using the two models shows consistently that cropland has the highest correlation coefficient, followed by grassland and deciduous broadleaf forest, and the lowest is evergreen needle leaf forest (Tables 1 and S2). These results indicate that  $GPP \cdot VPD^{0.5}$  relates to ET weakly for evergreen needle leaf forest at the subdaily time scale. In spite of the weaker correlation between  $GPP \cdot VPD^{0.5}$  and ET for the evergreen needle leaf forest, more than 50% of optimal exponents, i.e.,  $k^*$ s, still lie within 0.4–0.6 with an average of 0.49. The difference in the correlation coefficients for the  $GPP \cdot VPD^{0.5}$  versus ET and  $GPP \cdot VPD^{K^*}$  versus ET relationships is only 0.005 (Table 1). These results suggest that the  $GPP \cdot VPD^{0.5}$  versus ET relationship is still the optimal combination of GPP and VPD for evergreen needle leaf forest, and the relatively low correlation coefficient may indicate the additional nonlinearity, likely to result from violation of assumptions. In particular, the second assumption could be easily violated when soil evaporation makes up a large proportion of ET. Partition of evaporation

and transpiration should be implemented to further improve uWUE for the evergreen needle leaf forest. The uWUE model could be revised based on a hybrid dual-source model [Guan and Wilson, 2009].

The two models indicate a linear relationship between  $GPP \cdot VPD^{0.5}$  and ET for various vegetation types, resulting in a robust uWUE at the subdaily time scale during the growth season; thus, uWUE can be used to estimate ecosystem ET or GPP more effectively or to identify the impact of CO<sub>2</sub> fertilization and other environmental controls on the photosynthesis/transpiration balance. In Beer et al. [2009] and Yang et al. [2013], IWUE and WUE were modeled as functions of soil water content and leaf area index (LAI) to explore variations in water use efficiency among different ecosystems. According to equation (7), uWUE does vary for different vegetation types or when atmospheric conditions change in the long run. Important factors affecting uWUE at a large spatial scale and in the long term are  $\lambda_{cf}$  and  $C_a$ .  $\lambda_{cf}$  is a parameter related to vegetation type and environmental condition [Lloyd and Farquhar, 1994]. It can be used to explain the variations in uWUE among different ecosystems, which means that high  $\lambda_{cf}$  of a specific ecosystem is related to low uWUE at the same level of  $(C_a - \Gamma)$ . As uWUE increases proportionally to the square root of  $(C_a - \Gamma)$ , "CO<sub>2</sub> fertilization" effect might result in an increase of uWUE in the long term due to an increase in  $C_a$  in the atmosphere [Donohue et al., 2013].

## 5. Conclusions

Linear correlation analysis for 184 site years from 42 AmeriFlux sites among seven vegetation types shows that the  $GPP \cdot VPD^{0.5}$  versus ET relationship, which takes into account the effect of VPD on  $c_i/c_a$ , is much stronger than GPP versus ET and  $GPP \cdot VPD$  versus ET relationships at the subdaily time scale during the growth season. Furthermore, a hysteresis model that minimizes the time lags among GPP, ET, and VPD further provides support for the  $GPP \cdot VPD^{0.5}$  versus ET relationship. These empirical findings indicate that the underlying water use efficiency (i.e.,  $GPP \cdot VPD^{0.5}/ET$ ) is suitable for estimating ecosystem GPP and ET and identifying the photosynthesis/transpiration balance and water use efficiency variations among different vegetation types in the long term. As uWUE is proportional to the square root of the atmosphere CO<sub>2</sub> concentration, it may be an ideal indicator to estimate the effects of CO<sub>2</sub> fertilization on the ecosystem water loss and carbon assimilation.

## Acknowledgments

Half-hourly data used for the paper (see the supporting information) were available at the AmeriFlux network (<http://public.ornl.gov/ameriflux>). This paper is financially supported by the National Natural Science Foundation of China (91125018), National Key Science and Technology Project Fund from the Ministry of Science and Technology (MOST) during the Twelfth Five-year Project (2013BAB05B03), and the Research and Development Special Fund for Public Welfare Industry of the Ministry of Water Research in China (201301081).

The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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