

1 **Predicting landscape-scale CO<sub>2</sub> flux at a pasture and rice paddy with long-term**  
2 **hyperspectral canopy reflectance measurements**

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12 **Abstract**

13           Measurements of hyperspectral canopy reflectance provide a detailed snapshot of  
14 information regarding canopy biochemistry, structure and physiology. In this study, we collected  
15 five years of repeated canopy hyperspectral reflectance measurements for a total of over 100 site  
16 visits within the flux footprints of two eddy covariance towers at a pasture and rice paddy in  
17 Northern California. The vegetation at both sites exhibited dynamic phenology, with significant  
18 inter-annual variability in the timing of seasonal patterns that propagated into inter-annual  
19 variability in measured hyperspectral reflectance. We used partial least-squares regression  
20 (PLSR) modeling to leverage the information contained within the entire canopy reflectance  
21 spectra (400-900nm) in order to investigate questions regarding the connection between  
22 measured hyperspectral reflectance and landscape-scale fluxes of net ecosystem exchange (NEE)  
23 and gross primary productivity (GPP) across multiple timescales, from instantaneous flux to  
24 monthly-integrated flux. With the PLSR models developed from this large dataset we achieved a  
25 high level of predictability for both NEE and GPP flux in these two ecosystems, where the  $R^2$  of  
26 prediction with an independent validation dataset ranged from 0.24 to 0.69. The PLSR models  
27 achieved the highest skill at predicting the integrated GPP flux for the week prior to the  
28 hyperspectral canopy reflectance collection, whereas the NEE flux often achieved the same high  
29 predictive power at the daily- through monthly-integrated flux timescales. The high level of  
30 predictability achieved by PLSR regression in this study demonstrated the potential for using  
31 repeated hyperspectral canopy reflectance measurements to help partition NEE measurements  
32 into its component fluxes, GPP and ecosystem respiration, and for using quasi-continuous  
33 hyperspectral reflectance measurements to model regional carbon flux in future analyses.

34

## 35 **1. Introduction**

36           The development of remote sensing tools that bridge the scale of carbon flux  
37 measurements from individual eddy covariance towers to broader, continuous spatial scales has  
38 long been a goal of the earth systems science community (Bauer, 1975; Running et al., 1999;  
39 Ustin et al., 2004). This goal inspired the formation of the international research group SpecNet,  
40 developed to synthesize the collection of near-surface ground reflectance measurements at eddy  
41 covariance tower sites to provide a crucial link between the spatial scales of eddy flux towers and  
42 aircraft or satellite measurements (Gamon et al., 2010). Previous work in near-surface remote  
43 sensing has demonstrated that normalized canopy reflectance indices can yield important insights  
44 for understanding landscape-scale CO<sub>2</sub> flux measurements, particularly for understanding  
45 patterns in CO<sub>2</sub> uptake through photosynthesis (Gamon et al., 1997; Inoue et al., 2008). Recent  
46 work has also demonstrated the utility of using the entire reflectance spectrum to uncover new  
47 normalized near-surface reflectance indices that are correlated with ecosystem productivity and  
48 can be used to monitor canopy phenology with relatively inexpensive LED sensors (Ryu et al.,  
49 2010a). Metrics based on canopy reflectance can be used as proxies for biological processes at  
50 the surface when those biological processes have corresponding features that change the  
51 reflectance and absorption of energy in the plant canopy. The two most commonly used remote  
52 sensing metrics, the normalized difference vegetation index (NDVI) and the enhanced vegetation  
53 index (EVI), track ecosystem productivity by measuring energy absorption at the visible  
54 wavelengths where chlorophyll is active and comparing that to the reflectance or emission at  
55 near-infrared wavelengths where active plant canopies dissipate energy (Liu and Huete, 1995;  
56 Rouse et al., 1974). NDVI and EVI are widely used metrics since they can be calculated  
57 worldwide (although at coarse spatial resolution of about 250m) by reflectance measurements

58 from the Moderate-Resolution Imaging Spectroradiometer (MODIS) instruments. The  
59 widespread use of normalized indices has revolutionized the predictive power of global carbon  
60 flux measurements, as they act as important proxies for photosynthetic carbon dioxide uptake in  
61 plants that can be modeled through temporally quasi-continuous satellite imagery (Justice et al.,  
62 1985; Potter et al., 1993; Running and Nemani, 1988; Tucker et al., 1985).

63 While these normalized indices have wide utility for predicting landscape-scale carbon  
64 flux at spatial scales from that of near-surface sensors to satellite remote sensing, these indices  
65 necessarily leave out much of the information provided within the entire visual and near-infrared  
66 spectrum of canopy reflectance. Modeling techniques such as partial least-squares regression  
67 (PLSR) (Wold et al., 2001) that can leverage the entire information contained within the quasi-  
68 continuous canopy reflectance spectrum by reducing the regression variables to a set of fewer  
69 latent variables (i.e. modeled variables that capture information from many individual regression  
70 variables at once) are now widely used to predict traits at the leaf, plot, and canopy level.  
71 Hyperspectral reflectance measurements have been used with PLSR methods to successfully  
72 predict leaf-level traits like nitrogen (N) and carbon content, specific leaf area, protein, cellulose,  
73 and lignin content, and even leaf isotopic  $^{15}\text{N}$  content and  $V_{\text{cmax}}$ , the maximum rate of  
74 carboxylation during photosynthesis (Asner and Martin, 2008a; Bolster et al., 1996; Serbin et al.,  
75 2012, 2014). PLSR has also been used with near-surface canopy hyperspectral reflectance  
76 measurements to predict biomass and nitrogen content in wheat crops (Hansen and Schjoerring,  
77 2003) and to predict pasture forage quality (Kawamura et al., 2008). Airborne hyperspectral  
78 reflectance measurements have been used with PLSR to map canopy-level chemistry (Ollinger et  
79 al., 2002; Smith et al., 2002), to predict citrus yields in orchards (Ye et al., 2009), and to map  
80 floristic gradients in grasslands (Schmidtlein et al., 2007) and species diversity in tropical forests

81 (Asner and Martin, 2008b). This large range of studies across a diverse set of spatial scales, from  
82 the leaf- to canopy-level, demonstrates the utility of using hyperspectral reflectance  
83 measurements in conjunction with PLSR methods to increase the predictive power of remote  
84 sensing relationships with ecological variables compared with traditional normalized indices.  
85 Despite the proven utility of PLSR methods over a wide range of spatial scales, to our  
86 knowledge no studies have yet investigated the potential for using hyperspectral reflectance  
87 measurements to directly predict landscape-scale carbon fluxes through PLSR modeling.

88         The goal of this analysis was to investigate the ability of repeat canopy hyperspectral  
89 reflectance to directly predict landscape-scale carbon dioxide (CO<sub>2</sub>) fluxes at two short-  
90 structured plant canopies. We measured replicated near-surface hyperspectral canopy reflectance  
91 on 100 different sampling dates over the course of five years from 2010-2014 within the flux  
92 footprint of two nearby eddy covariance tower sites with similar structure but different canopy  
93 phenology in Northern California. The first site was a pasture where grasses grew over the winter  
94 and the invasive pepperweed plant (*Lepidium latifolium*) was active throughout the summer. The  
95 second site was an irrigated rice paddy with a simple phenology, where rice plants were present  
96 only from May through October following the typical growing season pattern for agricultural  
97 crops within this region. We combined the rich information contained within these repeated  
98 hyperspectral canopy reflectance measurements with PLSR methods to predict landscape-scale  
99 patterns in net CO<sub>2</sub> flux (net ecosystem exchange; NEE) and CO<sub>2</sub> uptake through canopy  
100 photosynthesis (gross primary productivity; GPP).

101         We used this five-year long-term dataset of near-surface hyperspectral canopy reflectance  
102 measurements collected at two sites in conjunction with landscape-scale eddy covariance CO<sub>2</sub>  
103 fluxes to answer the following four research questions:

- 104 1) How does canopy hyperspectral reflectance vary seasonally and inter-annually within and  
105 across sites during different phenological stages?
- 106 2) How well can the quasi-continuous 400-900nm canopy reflectance spectrum predict GPP  
107 and NEE at the two sites?
- 108 3) Are there significant differences in the ability to predict GPP and NEE at the pasture site  
109 compared with the rice paddy?
- 110 4) At what timescale are fluxes most strongly correlated with changes in measured  
111 hyperspectral canopy reflectance?

112 First, we examined the variability in measured hyperspectral reflectance within each site and  
113 between the two sites on individual sampling dates and across years. This provided insight into  
114 the dynamic nature of the canopy reflectance spectrum at these two study sites. The second two  
115 questions addressed the ability of the hyperspectral reflectance spectra to capture changes in GPP  
116 and NEE at the two sites, and tested whether the predictive power of hyperspectral reflectance  
117 modeling with PLSR is higher at the rice paddy site, where GPP and ER are more closely  
118 coupled than at the pasture, where GPP and ER are more decoupled due to different  
119 environmental drivers (Hatala et al., 2012; Knox et al., 2014). The final research question  
120 investigated the temporal scale at which the measured hyperspectral canopy reflectance  
121 integrated previous CO<sub>2</sub> fluxes. The canopy traits that control hyperspectral reflectance (e.g.  
122 chlorophyll, nitrogen, and water content in leaves, leaf abundance, etc.) are the emergent,  
123 integrated response to previous ecophysiological variability. We tested the ability of the canopy  
124 reflectance to predict instantaneous fluxes, and daily-, weekly-, and monthly-integrated carbon  
125 fluxes at each of the sites to quantify the timescale at which the canopy reflectance integrated  
126 prior ecophysiology, providing insight into the system memory of canopy reflectance. These

127 three integrated flux timescales represented the peaks in temporal autocorrelation due to daily  
128 fluctuations in the diurnal cycle of plants and solar radiation, weekly fluctuations in synoptic  
129 weather fronts, and monthly variability due to seasonal and phenological patterns, respectively  
130 (Baldocchi et al., 2001b; Stoy et al., 2009). Together, these research questions yielded key  
131 insights into the utility and limitations of using repeated hyperspectral canopy reflectance  
132 measurements to predict landscape-scale CO<sub>2</sub> fluxes.

133

## 134 **2. Methods**

### 135 **2.1 Site Characteristics**

136 We collected replicated hyperspectral ground reflectance measurements of plant canopies  
137 at two sites in Northern California with similarly structured, yet phenologically different, plant  
138 canopies. The first site was a drained peatland pasture (hereafter referred to as “Pasture”) located  
139 on Sherman Island in the Sacramento-San Joaquin Delta (latitude: 38.0373; longitude: -  
140 121.7536; elevation: -4m) with annual grasses growing during the winter and spring, and the  
141 invasive perennial pepperweed plant (*Lepidium latifolium*) active from spring through autumn  
142 (Figure 3). Pepperweed produces a dense canopy of white flowers each year from about the  
143 beginning of June through the end of August, creating increased complexity in canopy  
144 reflectance during this time (Sonnentag et al., 2011a, 2011b). The second site was a rice paddy  
145 (hereafter referred to as “Rice”) located on Twitchell Island in the Sacramento-San Joaquin Delta  
146 (latitude: 38.1055, longitude: -121.6521, elevation: -5m) with an active growing season from  
147 May through October and maintained as a fallow and flooded field for the remainder of the year  
148 (Figure 3).

149           The two sites were located within 10km of each other in the Sacramento San-Joaquin  
150 Delta, and as such, they experienced the same Mediterranean climate with hot and dry summer  
151 months and rainy, cool winters. The 30-year mean annual air temperature (1981-2010) recorded  
152 at a nearby climate station in Antioch, CA was 16.4°C, and mean annual precipitation was  
153 335mm. Despite their similar climatology, the difference in hydrological and agricultural  
154 management between the two sites results in ecosystems with plant canopies that are quite  
155 different in phenology (Hatala et al., 2012; Knox et al., 2014). The water table at the Pasture was  
156 maintained at a level always below the soil surface at around 50-80cm throughout the year.  
157 While the phenology of grasses at the Pasture peaked during the springtime, the pepperweed  
158 plants at the site remained relatively active throughout the summer as their roots can tap the  
159 shallow water table, creating a biologically active canopy almost year-round (Sonntag et al.,  
160 2011a). The Rice was planted and flooded through irrigation management during the summer  
161 growing season only, and the plant canopy sustained high rates of productivity during the  
162 precipitation-free summer months. The field remained fallow and flooded during the remainder  
163 of the year. Differences in the canopy phenology at both sites propagated into differences in the  
164 peak periods of photosynthesis, where peak GPP at the Pasture occurs April-May and peak GPP  
165 at the rice occurs August-September (Hatala et al., 2012; Knox et al., 2014).

## 166 ***2.2 Hyperspectral canopy reflectance sampling***

167           At both the Pasture and Rice, hyperspectral canopy reflectance was collected with a fiber  
168 optic spectrometer (USB 2000; Ocean Optics, Dunedin, FL) with a detector range from 200-  
169 1100nm at a height of 1m above the mean canopy surface. The fiber optic sensor was filtered  
170 through a cosine corrector (CC-3-UV-S Spectralon) to ensure that the bi-hemispherical  
171 reflectance from the ground surface was measured at an angle normal to the sensor surface



172 (Nicodemus et al., 1977; Schaepman-Strub et al., 2006). We measured bi-hemispherical  
173 reflectance to minimize the contribution of background soil surfaces to the spectral signal, and  
174 we ensured that our reflectance signal was not comprised by low Sun zenith angles by sampling  
175 near midday (Meroni et al., 2011). For this analysis we constrained our data to 400-900nm due to  
176 large levels of noise at the detection edges of this instrument. The spectrometer was mounted on  
177 a tripod approximately one meter above the canopy and was connected via USB cable to a laptop  
178 computer running the OOBase32 software (USB 2000; Ocean Optics, Dunedin, FL) to capture  
179 spectra, which internally corrected for instrument-specific calibration parameters. Each field  
180 spectrum was collected and saved by OOBase32. At the start of each site visit, the integration  
181 time within OOBase32 was adjusted to the ambient light conditions and a reference dark  
182 spectrum measurement was collected by covering the fiber optic head with two layers of black  
183 electrical tape and orienting the sensor downward.

184         After this initial set-up, we collected a reflectance spectrum for each site replicate by first  
185 pointing the spectrometer directly skyward to record the spectrum of incoming energy, and  
186 within seconds, pointing the spectrometer directly at the ground surface to record the spectrum of  
187 reflected energy. Thus, we calculated the canopy reflectance for each replicate as the reflected  
188 spectrum normalized by the incoming spectrum. For each collection date at each site, we  
189 averaged the replicate spectra for this analysis to compute a single mean spectral reflectance per  
190 date at each site. The spectrometer records data at approximately 0.28nm intervals, and we  
191 smoothed each reflectance spectrum using a spline fit to 1nm intervals between 400-900nm in  
192 order to reduce instrumental noise in the data.

193         We measured canopy hyperspectral reflectance from July 2010 through September 2014  
194 at both sites, collecting measurements during the entire year at the Pasture and during the

195 growing season at the Rice, which amounted to 100 total sampling dates at the Pasture and 71  
196 total sampling dates at the Rice (Figure 1). On each sampling date, hyperspectral reflectance  
197 measurements were collected at each site with a spatial and temporal replicate frequency suited  
198 to the individual site heterogeneity. At the Pasture, where the canopy was spatially and  
199 temporally heterogeneous, we measured hyperspectral reflectance approximately weekly, bi-  
200 weekly, or monthly, with nine replicate canopy reflectances randomly sampled per visit. At the  
201 Rice, which had lower spatial variability, hyperspectral reflectance was collected weekly or bi-  
202 weekly during the growing season, with five replicate canopy reflectance spectra collected per  
203 visit. We occasionally collected up to ten additional replicates at each of the sites, in order to  
204 ensure that our smaller sampling sizes were capturing broad landscape-scale patterns in spatial  
205 heterogeneity. At each site we randomly sampled canopy reflectance at locations approximately  
206 10-20m within the flux tower footprint, the area most representative of the half-hourly flux  
207 measurements. For partial least-squared regression analysis, we averaged across the  
208 hyperspectral canopy reflectance replicates for each site and day. Because leaf geometry and  
209 clumping can critically impact the interpretation of canopy reflectance measurements (Colwell,  
210 1974), these two sites provide a useful first-case study for directly connecting hyperspectral  
211 canopy reflectance measurements to CO<sub>2</sub> flux because both ecosystems have an erectophile in  
212 leaf angle distribution for the majority of the year, minimizing shadow effects when field spectra  
213 are collected near solar noon.

### 214 ***2.3 CO<sub>2</sub> flux measurements***

215 Both sites are active AmeriFlux and FLUXNET sites (Baldocchi et al., 2001a) measuring  
216 fluxes of energy, water vapor, and CO<sub>2</sub> using standard eddy covariance methods and processing  
217 procedures described elsewhere in detail (Ameriflux site codes: US-Snd and US-Twt; Hatala et

218 al., 2012; Knox et al., 2014; Sonnentag et al., 2011a). The eddy covariance technique was used  
219 to measure the fluxes of CO<sub>2</sub> at each site by collecting simultaneous 10 Hz measurements of  
220 vertical turbulence ( $w$ , m s<sup>-1</sup>), measured with a sonic anemometer (Gill WindMaster Pro; Gill  
221 Instruments Ltd, Lymington, Hampshire, England), and CO<sub>2</sub> density ( $c$ , μmol m<sup>-3</sup>), measured  
222 with an infrared gas analyzer (LI-7500; Li-Cor Biosciences, Lincoln, NE). From these  
223 measurements we calculated the net half-hourly mean flux of CO<sub>2</sub> (NEE, μmol m<sup>-2</sup> s<sup>-1</sup>) between  
224 the surface and atmosphere by averaging the covariance between  $w$  and  $c$  over a half-hourly time  
225 period after applying a coordinate rotation and a set of standard air density and temperature  
226 corrections (Detto et al., 2010; Schotanus et al., 1983; Webb et al., 1980). To partition NEE into  
227 gross primary photosynthesis (GPP, μmol m<sup>-2</sup> s<sup>-1</sup>) and ecosystem respiration (ER, μmol m<sup>-2</sup> s<sup>-1</sup>),  
228 net CO<sub>2</sub> fluxes were first gap-filled using artificial neural network (ANN) techniques outlined in  
229 detail within Knox *et al.* [2014], driven by meteorological variables (Moffat et al., 2007; Papale  
230 et al., 2006). After the net CO<sub>2</sub> fluxes were gap-filled using the ANN technique, we separated the  
231 net flux into GPP and ER by modeling nighttime NEE measurements as ER, since GPP is  
232 assumed to be zero at night (Reichstein et al., 2005). We prescribed the nighttime temperature  
233 dependence of ER by an Arrhenius-type model (Lloyd and Taylor, 1994), and extrapolated this  
234 model to the daytime, calculating GPP as the difference between NEE and modeled ER. Net CO<sub>2</sub>  
235 flux data within this analysis are presented from the atmospheric convention, where a negative  
236 flux indicates ecosystem uptake, and a positive flux indicates release from the ecosystem to the  
237 atmosphere.

238           Within this analysis we examined the predictive power of hyperspectral canopy  
239 reflectance to explain patterns in instantaneous and daily-, weekly-, and monthly-integrated NEE  
240 and GPP flux. We tested these variables separately in order to determine whether the canopy

241 reflectance better predicted an instantaneous flux measurement at the time of collection, or a flux  
242 signal integrated over the previous day, week, or month. For instantaneous NEE and GPP flux,  
243 we matched the time of spectral collection with the nearest mean half-hourly flux measurement,  
244 where these values are presented in units of  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . For the daily-, weekly-, and monthly-  
245 integrated NEE and GPP fluxes, we integrated the net  $\text{CO}_2$  and GPP flux over the course of the  
246 previous day, week, or month for the date of spectral reflectance collection, where these values  
247 are presented in units of  $\text{g-C m}^{-2} \text{time}^{-1}$ . For reference regarding the magnitude and temporal  
248 dynamics of  $\text{CO}_2$  fluxes at the Pasture and Rice, the instantaneous GPP flux and daily NEE flux  
249 for both sites are plotted as Figure 2.

#### 250 ***2.4 Partial Least-Squares Regression Modeling***

251 Partial least-squares regression is a standard method in chemometrics for modeling the  
252 ability of a set of quasi-continuous spectral variables to predict a single response (Wold et al.,  
253 2001). In this analysis we used PLSR methods with the hyperspectral canopy reflectance dataset  
254 to model the response of instantaneous or integrated NEE or GPP. PLSR is similar to principle  
255 components analysis (PCA), in that the modeling algorithm reduces a large predictor matrix of  
256 spectral reflectance data to a reduced set of latent variables. In our study, the large predictor  
257 matrix is the measured hyperspectral reflectance at each wavelength between 400-900 nm during  
258 each sampling event, which in our analysis was reduced to a maximum of 10 latent variables that  
259 contained the most significant sets of variables from the larger matrix for predicting  
260 instantaneous or integrated NEE or GPP. PLSR typically outperforms PCA or standard step-wise  
261 linear regression for situations where there is high co-linearity within the predictor matrix, such  
262 as within narrow-band spectral reflectance and chemometrics (Wold et al., 2001). For this  
263 analysis we used the PLS package (Mevik et al., 2013) within the R statistical environment (R

264 Development Core Team 2014). All the R code used to conduct this analysis is freely available  
265 on GitHub at [http://github.com/jhmatthes/canreflectance\\_flux\\_plsr](http://github.com/jhmatthes/canreflectance_flux_plsr).

266 For PLSR model fitting and validation, our methods followed those of Serbin *et al.*  
267 (2014), which used PLSR regression modeling to determine the ability of hyperspectral  
268 reflectance data to predict a suite of leaf traits. However, in this analysis, we used repeated  
269 measurements to examine how well the repeated hyperspectral reflectance measurements could  
270 directly predict landscape-scale fluxes of NEE and GPP. We conducted one set of PLSR  
271 regression modeling for the entire spectral reflectance dataset that combined both the Pasture and  
272 Rice data, and then two additional PLSR modeling exercises with the only the Pasture data and  
273 only the Rice data, to examine whether there were significant differences between the two sites  
274 in the resulting PLSR models. For each of the three PLSR modeling exercises, we split the data  
275 into model calibration (80% of the data) and independent validation (20% of the data; hereafter  
276 referred to as “Independent Validation”), where the model calibration data were used to fit the  
277 model, and the independent validation data were used to evaluate the ability of the model to  
278 predict landscape-scale NEE and GPP outside of the PLSR model fitting exercise. As in Serbin  
279 *et al.* [2014], we randomly split the model calibration data into 70% for model fitting (hereafter  
280 referred to as “Calibration”) and 30% for model uncertainty evaluation (hereafter referred to as  
281 “Evaluation”) over 1000 iterations to evaluate the uncertainty in PLSR model development. So  
282 overall, we used 56% of the total data for Calibration, 24% of the data for Evaluation, and an  
283 unchanging 20% of the data for Independent Validation to test the predictive power of the final  
284 mean models. We conducted an initial optimization with a single set of Calibration data and  
285 Evaluation data to determine the total number of PLSR latent variables to include in each model  
286 by minimizing the prediction residual sum of squares, calculated through leave-one-out cross-

287 validation (Chen et al., 2004). We used the entire 400-900nm spectrum range with these PLSR  
288 methods to fit the instantaneous and daily-, weekly-, and monthly-integrated NEE and GPP flux  
289 data.

290 To quantify the performance of each PLSR model we calculated the coefficient of  
291 determination ( $R^2$ ), the root mean square error (RMSE), and the model bias. We used the 1000  
292 iteration bootstrapping approach for each PLSR to quantify the model calibration performance as  
293 in Serbin *et al.* [2014]. From the random 70% to 30% split of the Calibration and Evaluation  
294 data, we generated new estimates for each iteratively removed sample. This allowed us to test the  
295 stability and generality of the models using different sets calibration data and to estimate robust  
296 errors for the prediction of flux measurements by representing the uncertainty across  
297 measurements, spectral data, and the PLSR modeling approach. For each set of 1000 modeling  
298 iterations over the random calibration/validation fit dataset split, we calculated the resulting  
299 mean PLSR model coefficients and the variable importance of projection (VIP) score associated  
300 with the reflectance measured at each wavelength. The VIP score represents the statistical  
301 contribution of each individual wavelength to the overall fitted PLSR model across all latent  
302 model components. In this way, the VIP score can be used to identify the wavelengths that  
303 contribute the most information for predicting the variable at hand (in this case, either NEE or  
304 GPP). Using the mean of the bootstrapped PLSR models, we tested each final mean model  
305 against the 20% of original data left aside for Independent Validation by linear regression.

### 306 ***2.5 Standardized vegetation indices for GPP and NEE prediction***

307 We analyzed the skill of standardized vegetation indices (SVIs) in predicting NEE and  
308 GPP flux at the Pasture and Rice, and compared the utility of these models to our PLSR  
309 modeling results. Due to their wide use in other studies, we tested the normalized difference

310 vegetation index (NDVI;  $[R_{800} - R_{680}] / [R_{800} + R_{680}]$ ; Rouse et al., 1974), NDVI calculated with  
311 the wavelengths from the Moderate Resolution Imaging Spectroradiometer satellite (NDVI<sub>MOD</sub>;  
312  $[R_{841-876} - R_{620-670}] / [R_{841-876} + R_{620-670}]$ ), green NDVI (NDVI<sub>g</sub>;  $[R_{800} - R_{550}] / [R_{800} + R_{550}]$ ;  
313 Gitelson et al., 1996), red-edge NDVI (NDVI<sub>re</sub>;  $[R_{800} - R_{700}] / [R_{800} + R_{700}]$ ; Gitelson and  
314 Merzlyak, 1994), and the photochemical reflectance index (PRI;  $[R_{531} - R_{570}] / [R_{531} + R_{570}]$ ;  
315 Gamon et al., 1992), where R indicates reflectance in the subscripted wavelengths in nanometers.  
316 For all SVIs except NDVI<sub>MOD</sub>, we averaged the measured reflectance for a 10nm window  
317 centered on the reflectance value to reduce measurement noise.

318 We assessed the ability of SVI measurements to predict NEE and GPP fluxes for All  
319 data, the Rice only, and the Pasture only by randomly selecting 80% of the reflectance spectra  
320 for calibration, leaving 20% of the data for prediction. For GPP fluxes, we assessed the fit and  
321 prediction of SVIs with a log-linear model as this model best fit the data, and for NEE we used a  
322 simple linear model, which fit the data better than a log-linear model. To assess the ability of the  
323 SVIs to predict GPP and NEE, we performed an iterative calibration/prediction analysis where  
324 we randomly parsed the data into 80% calibration and 20% prediction for 100 iterations, and  
325 present the mean statistics for comparative analysis with the PLSR modeling results.

326

### 327 **3. Results**

#### 328 ***3.1 Spatiotemporal variability in hyperspectral canopy reflectance***

329 There was significant seasonal, inter-annual, and site-level variability across the  
330 hyperspectral canopy reflectance measurements collected over the course of five years at both  
331 sites. Intra-site variability within canopy reflectance changed due to the phenological stage of the  
332 ecosystem, whereas inter-annual variability was driven by changes in the timing of these

333 phenological events. The Pasture tended to be more spatially heterogeneous than the Rice,  
334 observed through the higher intra-site variability during an individual sampling event,  
335 particularly in the infrared reflectance (Figure 3). This intra-site variability at the Pasture is  
336 caused by higher spatial heterogeneity in canopy structure compared with the Rice, which is a  
337 monoculture with a simpler crop phenological cycle. During the green leaf-out stage at both the  
338 Pasture and Rice, the patterns of hyperspectral reflectance were quite similar, with a peak at the  
339 green wavelengths, absorption in the red wavelengths, and high reflectance in the near-infrared  
340 wavelengths (Figure 3a,b). Intra-site variability across the spectrum was high across at the  
341 Pasture during periods of white pepperweed flowering that produced a much higher albedo than  
342 the green canopy and obscured reflectance patterns in the green and red wavelengths, despite  
343 relatively high plant productivity during this time (Figure 3c). The closest analogous  
344 phenological stage to this period at the Rice was during the time at which the rice has seeded and  
345 the plants have dried in preparation for harvest, when the Rice experienced similar trends in  
346 increased albedo through the visible wavelengths (Figure 3d). However, the magnitude of the  
347 senescing Rice reflectance was not as large as the white pepperweed canopy at the Pasture, and  
348 in addition the reflectance spectra were not obfuscated during this time since the rice  
349 productivity was quite low at this point in the growing season.

350         The seasonal and inter-annual patterns in narrow-band reflectance in the green ( $550\pm 5$   
351 nm), red ( $640\pm 5$  nm), and near-infrared (NIR;  $800\pm 5$  nm) wavelengths also highlighted intra-site  
352 and inter-annual variability. At the Pasture, there was low intra-site variability and inter-annual  
353 variability in green reflectance from January through the end of May, when the grass canopy was  
354 present at the site (Figure 4a). However, when pepperweed became the dominant canopy plant at  
355 the Pasture during the summer growing season, both replicate and inter-annual variability



356 increased as the pepperweed created a more heterogeneous cover than the grass due to its white  
357 flowers and more spatially variable structure than the winter grass canopy. The same pattern was  
358 evident in the red reflectance at the Pasture, with low variability in the second half of winter and  
359 spring, and a large increase in variability during the summer growing season and autumn (Figure  
360 4c). At the Rice, there was also large inter-annual variability in the timing of the seasonal pattern  
361 green and red reflectance, however there was a more discernible seasonal pattern of reflectance  
362 that tracks within years across the entire growing season (Figures 4b,d). For example, each year  
363 green reflectance and red reflectance started high, decreased as the growing season progressed,  
364 then eventually increased again as the rice straw dried before harvest. The NIR reflectance at the  
365 Pasture had a stable mean through the year with little inter-annual variability but large intra-site  
366 variability across the year (Figure 4e). The Rice NIR reflectance had a consistent seasonal  
367 pattern between years, with low reflectance in the early growing season and increasing NIR  
368 reflectance as the canopy developed due to the change in the rice canopy closure as the growing  
369 season progressed (Figure 4f). Although there was a consistent phenological trend in NIR  
370 reflectance at the Rice each year, there remained inter-annual variability in the timing of the NIR  
371 minimum and larger intra-site variability compared with reflectance in the visible wavelengths.

### 372 ***3.2 Calibrated PLSR models for predicting NEE and GPP***

373 We fit PLSR models to the hyperspectral data to predict landscape-scale NEE and GPP at  
374 four integrated flux timescales: instantaneous flux measurements, and daily-, weekly-, and  
375 monthly-integrated flux measurements for the period preceding the time of hyperspectral canopy  
376 reflectance collection. In this analysis we determined the optimal number of latent variables to  
377 include for each model by minimizing the predictive residual sum of squares. The number of  
378 optimal latent variables included in the PLSR models ranged from 2-8, which indicated that

379 some models could achieve the best predictive statistical fit for NEE and GPP with a much lower  
380 number of components than other models (Table 1). For the PLSR models that included the  
381 entire canopy reflectance dataset for both sites, the optimal number of latent variables was stable  
382 at six components, except for the instantaneous GPP model, which included seven components.  
383 The number of optimal components was more variable across the PLSR models for the Pasture  
384 reflectance data (2-8 components) compared with those from the Rice reflectance data (4-6  
385 components).

386 As expected, across all models, the  $R^2$  for the PLSR Calibration was higher than the  $R^2$   
387 for the PLSR Evaluation fit, and the RMSE was lower for the Calibration and higher for the  
388 Evaluation during the model calibration step (Table 1). The fit statistics presented within Table 1  
389 show the mean fit statistics for the 1000 iterations of random 70% Calibration, 30% Validation  
390 data selection from the 80% total data used during the model development fitting process. For  
391 each PLSR model, the 1000 iterated fit statistics followed a normal distribution with low  
392 variance, which indicated only a low bias to selecting the Calibration and Evaluation data so only  
393 the mean results are presented within Table 1. Across almost all of the  $\text{CO}_2$  flux prediction  
394 variables, the PLSR models for the Rice dataset achieved the highest fit for both the Calibration  
395 ( $R^2 = 0.77-0.92$ ) and Evaluation ( $R^2 = 0.58-0.68$ ) exercises, the PLSR models with the dataset  
396 including both sites achieved a slightly lower overall fit for Calibration ( $R^2 = 0.63-0.87$ ) and  
397 Evaluation ( $R^2 = 0.24-0.69$ ), and the PLSR models for the Pasture had the lowest overall fit for  
398 Calibration ( $R^2 = 0.38-0.97$ ) and Evaluation ( $R^2 = 0.29-0.56$ ) (Table 1).

399 For each set of 1000 modeling iterations over the random calibration/validation fit dataset  
400 split, we calculated the resulting mean PLSR model coefficients and the variable importance of  
401 projection (VIP) statistic associated with each wavelength. Across all fitted PLSR models, as the

402 timescale of the fitted integrated flux increased from instantaneous to daily-, weekly-, and  
403 monthly-integrated values, the VIP statistic in the visible wavelengths (400-700nm) decreased  
404 and the VIP statistic in the near-infrared wavelengths (700-900nm) increased (Figure 5). This  
405 indicated that for flux measurements on short timescales, the reflectance in the visible  
406 wavelengths contributed the highest explanatory power to the PLSR model components, but at  
407 longer timescales structural changes in the canopy that are correlated with the NIR range became  
408 more important for predicting GPP and NEE flux. This pattern was especially apparent for the  
409 VIP scores of the GPP model using the dataset with both sites (Figure 5a), where there was a  
410 dramatic shift in VIP scores between the weekly- and monthly-integrated flux models. For the  
411 weekly-integrated GPP flux model and those at shorter timescales, the highest VIP scores were  
412 contributed by the visible wavelengths, with a peak in the red wavelengths near 700nm. However  
413 for the monthly-integrated GPP flux model, there was a dramatic difference where the highest  
414 VIP scores shifted from the visible to the NIR range, indicating that structural components of the  
415 plant canopy correlated with NIR reflectance contributed higher predictive power than  
416 reflectance in the visible part of the spectrum. There is a lower shift in VIP scores across  
417 integrated flux timescales in the models developed with only the Rice dataset (Figure 5e-f)  
418 compared against the models developed with only the Pasture dataset (Figures 5c-d), likely  
419 reflecting the increased spatial and phenological complexity of the Pasture ecosystem compared  
420 with the relatively homogeneous Rice.

421         Across all models, the visible wavelengths that contributed the most information to the  
422 PLSR models, as determined by the magnitude of the VIP score, were within the red portion of  
423 the visible spectrum (Figure 5). Most PLSR models had VIP scores above 1.0 that correlated  
424 with reflectance at 642 and 662 nm, the wavelengths of chlorophyll absorption. Across most

425 PLSR models there was also a peak in the VIP score near 673 nm, the wavelength of chlorophyll  
426 fluorescence. However, the second band of chlorophyll fluorescence at 726nm, exhibited low  
427 VIP scores across all models. For both of the PLSR models developed using only the Pasture  
428 dataset, there were also high VIP scores within the violet and blue range of the visible spectrum,  
429 from 400-450nm. These high VIP scores in the violet-blue portion of the spectrum could be  
430 partly explained by the chlorophyll a and b absorption peaks at 430nm and 460nm, because  
431 slightly higher VIP scores were also observed at the Rice site for these wavelengths (Figure 5e-  
432 f). However, this part of the spectrum at the Pasture site was particularly significant compared  
433 with the other models, and this could correspond to white reflectance of the pepperweed flowers  
434 at the site. When the pepperweed canopy was blooming, the bright white flowers reflected light  
435 across the entire visible spectrum, a unique characteristic to this site, where the high visible  
436 albedo in this spectral range might also have contributed to the high VIP scores within this  
437 portion of the spectrum (Figure 5c-d).

### 438 ***3.3 Independent Validation of PLSR models for NEE and GPP***

439 After we fit the PLSR models to 80% of the entire dataset through 1000 iterations of  
440 different random sets of Calibration and Evaluation data, we tested the mean fitted models  
441 against the Independent Validation data (the 20% of the original dataset left out of the PLSR  
442 model fitting process). In general, the fitted PLSR models achieved a good fit with the  
443 measurements for this Independent Validation dataset, where the  $R^2$  fit between the predicted  
444 and actual NEE and GPP ranged from 0.26 to 0.69 (Table 2). As was the case for the calibration  
445 and validation  $R^2$  fits during the PLSR calibration process, the Rice dataset achieved the highest  
446  $R^2$  values (0.40-0.69), the dataset with both sites achieved the second-highest set of  $R^2$  (0.27-  
447 0.62), and the Pasture dataset had the lowest  $R^2$  (0.27-0.54). As in the previous discussion for the

448 Calibration and Evaluation fits to these three sets of data, we believe that the lower level of  
449 predictability at the Pasture is due to the higher level of spatial heterogeneity and phenological  
450 complexity compared with the Rice.

451 Although all models achieved a statistically significant fit between the predicted and  
452 measured CO<sub>2</sub> fluxes with the Independent Validation dataset with relatively high R<sup>2</sup> values, the  
453 uncertainty in the prediction was significantly lower for the models that included all the data  
454 compared with the models that included only either the Pasture or Rice data. This pattern is  
455 clearly observed within the Independent Validation fit for the daily GPP and NEE data (Figure  
456 6). For the daily prediction of both GPP and NEE, the dataset that included all the data had a  
457 smaller range for both the 95% confidence interval and 95% prediction interval for the  
458 relationship between predicted and actual GPP and NEE. This trend likely represented an  
459 increase in predictive power achieved by including a larger dataset with a wider range of values  
460 both for NEE and GPP and for the measured hyperspectral reflectance. As the datasets that  
461 included either the Pasture and Rice data only had a lower amount of data overall as well as a  
462 narrower range of values, the confidence in the ability to predict NEE and GPP at these  
463 individual sites was lower compared with the power of using the entire combined dataset.

#### 464 ***3.4 Prediction of NEE and GPP fluxes with standardized vegetation indices***

465 We compared the ability of a suite of commonly used SVIs to predict GPP and NEE with  
466 the skill of the mean PLSR models developed within this study. Overall, the suite of NDVI SVIs  
467 performed reasonably well at predicting both GPP and NEE, and models tested with all the  
468 reflectance data for both sites achieved predictive R<sup>2</sup> values that ranged from 0.18 to 0.59 (Table  
469 3; Supplementary Table 1), where red-edge NDVI was the SVI that achieved the highest skill for  
470 predicting GPP and NEE for the sites in this study. PRI was not well suited to predicting CO<sub>2</sub>

471 fluxes at these sites, and models for this SVI achieved predictive  $R^2$  fits that ranged from 0.02 to  
472 0.22.

473 For models that fit all the data from both sites, the predictive fit from PLSR modeling  
474 outperformed the red-edge NDVI (the best-fit SVI) at the instantaneous and weekly timescales,  
475 the two models were not significantly different at the daily timescale, and red-edge NDVI  
476 outperformed PLSR modeling at the monthly timescale (Table 3). PLSR modeling outperformed  
477 SVIs across all timescales for models that fit the Pasture data only. The performance of red-edge  
478 NDVI and PLSR models were not significantly different at instantaneous, daily, and weekly  
479 timescales when fit with the Rice data only, however red-edge NDVI was a better predictor of  
480 monthly  $\text{CO}_2$  fluxes than the PLSR models (Table 3).

### 481 ***3.5 Prediction of NEE and GPP fluxes across different timescales***

482 We investigated the ability of PLSR modeling with the hyperspectral canopy reflectance  
483 measurements to predict instantaneous GPP and NEE fluxes from the same half hour of spectral  
484 measurement, in addition to fluxes integrated over the previous day, week, and month. Previous  
485 work determined that sampling errors in eddy covariance flux measurements diminished when  
486 the fluxes were integrated over the course of many days (Moncrieff et al., 1996). We expected  
487 that the instantaneous flux would achieve the lowest correlation with the measured canopy  
488 reflectance since reflectance changes more slowly compared with  $\text{CO}_2$  flux, and that the fluxes  
489 integrated over longer timescales would provide a stronger signal with a higher predictive  
490 capacity. For the Calibration and Evaluation during the initial PLSR model fitting, there was no  
491 strong evidence that one timescale (instantaneous, daily, weekly, or monthly flux) was  
492 particularly better fit with the hyperspectral canopy reflectance than the other timescales (Table  
493 1). However, during the evaluation of the predictive power of the PLSR models with the

494 Independent Validation data, most models achieved the highest predictive  $R^2$  with GPP flux at  
495 the weekly-integrated timescale, and we found no clear optimal timescale for predicting NEE  
496 with measured hyperspectral reflectance data (Table 2; Figure 7).

497

## 498 **4. Discussion**

### 499 *4.1 Sources of variability in measured reflectance*

500 Variation across the measured hyperspectral canopy reflectance was dominated by inter-  
501 annual variability in the timing of canopy phenology (Figures 3,4). At the Rice, transitions were  
502 typical for an agricultural crop, where canopy reflectance incorporated portions of the  
503 background flooded soil in conjunction with the emerging green plants early the in growing  
504 season, with canopy closure achieved by early July (Beget and Di Bella, 2007). After flooding  
505 when the Rice canopy closed, there was less intra-site variability in measured reflectance, until  
506 the end of the growing season when the rice plants started to senesce and dry before harvest  
507 (Figure 4). At the Pasture, canopy phenology was more complicated, marked by a transition from  
508 a green grass canopy to a green pepperweed canopy in April, followed by the white flowering of  
509 the pepperweed canopy from June through August, which increased intra-site variability in  
510 measured reflectance (Figure 4). Both the Rice and Pasture experienced significant inter-annual  
511 variability in the start and end dates of these phenological patterns, but despite this variability the  
512 sites experienced relatively low variability in the overall  $CO_2$  flux (Figure 2). The primary driver  
513 of inter-annual variability at the Pasture was the timing of summer drought in the Mediterranean  
514 climate, and canopy management (Sonntag et al., 2011a). These primary controls agreed with  
515 the results from European syntheses of FLUXNET sites where water was a key driver of inter-  
516 annual variability in NEE (Reichstein et al., 2007). At the Rice, inter-annual variability was

517 driven by changes in the start and end dates of canopy phenology that were driven by changes  
518 agricultural management of the planting and harvesting dates each year and smaller changes in  
519 fertilizer management (Hatala et al., 2012; Knox et al., 2014). The timing of the planting and  
520 harvest at the Rice is controlled by logistical environmental drivers, as the field must be dry  
521 enough to drive farm equipment through the soil, and warm enough to ensure seedling survival.  
522 Differences in these variables from year to year created variability in the planting dates, and  
523 subsequent variability in the seasonal trajectory of hyperspectral canopy reflectance (Figures  
524 3,4). There are also important differences between PLSR methods using the complete spectrum  
525 and standardized vegetation indices (SVIs) that may lead to differences in interpreting which  
526 bands are best suited for correlation with CO<sub>2</sub> fluxes. Because SVIs are normalized by a  
527 reference band, they may be better suited to reducing noise within temporal trends in reflectance  
528 time series, particularly at sites that experience a wide range of illumination conditions. While  
529 the PLSR methods used in this analysis benefit from the large information content that results  
530 from using the entire reflectance spectrum, the measurements represent relative reflectance  
531 values rather than normalized reflectance ratios, and thus likely include more noise in the  
532 measurement time series than SVIs. This is an important trade-off when considering whether to  
533 use the entire reflectance spectrum or SVIs to understand how canopy reflectance tracks CO<sub>2</sub>  
534 fluxes, but the simple canopy structure at the sites in this analysis and the collection of  
535 measurements during ideal illumination conditions limits the overall noise within the reflectance  
536 time series.

#### 537 ***4.2 Predicting NEE & GPP with PLSR models***

538 Along with the inter-annual variability experienced at both sites, there were also  
539 differences in the intra-site variability of measured reflectance within the two flux tower



540 footprints. The Pasture site was more spatially heterogeneous than the Rice, driving increased  
541 variability among replicate hyperspectral reflectance spectra at the site (Figure 4). The increased  
542 spatial variability at the Pasture was reflected in the lower predictive power of the PLSR models  
543 in predicting GPP and NEE with only the Pasture dataset (Tables 1,2). The lower overall fit  
544 between the hyperspectral measurements and CO<sub>2</sub> flux at the Pasture can be explained through  
545 three possible mechanisms: 1) the hyperspectral canopy reflectance measurements at the Pasture  
546 are less representative of the entire flux footprint than the Rice data, 2) white pepperweed  
547 flowers in the Pasture canopy during summertime create an obstruction for reflectance that  
548 degrades the representativeness of measured spectra (Hestir et al., 2008; Sonnentag et al.,  
549 2011b), 3) the lack of irrigation at the Pasture compared with the Rice could create conditions of  
550 water stress during which reflectance becomes temporally decoupled from CO<sub>2</sub> flux. It is likely  
551 that all of these factors contributed to the lower PLSR predictive power at the Pasture, and in  
552 particular the obstruction by white canopy flowers presented a challenge that is somewhat  
553 unavoidable for canopy reflectance studies in complex ecosystems. Changes to future sampling  
554 efforts that address the footprint representativeness, for example increasing the number and  
555 spatial distribution of hyperspectral reflectance collected at the Pasture or flying an unmanned  
556 aerial vehicle (UAV) with a mounted hyperspectral sensor, might help to further improve the  
557 future PLSR predictive power.

558         The most important wavelengths for the PLSR modeling with the GPP and NEE flux data  
559 in this study fell in line with previous work that has examined correlations between reflectance  
560 and traits of photosynthetic uptake (Main et al., 2011). However, we were initially surprised to  
561 find that the green wavelengths were not dominant components for prediction of either NEE or  
562 GPP across the suite of calibrated PLSR models (Figure 5). These results do parallel recent work

563 in oak forests that demonstrated a temporal mismatch between peak greenness and peak leaf  
564 chlorophyll content (Yang et al., 2014). This temporal mismatch could be the cause for the  
565 insignificant correlation in narrow-band green reflectance, because at both sites vegetation is a  
566 lighter green early in the growing season and develops into a darker green as the season  
567 progresses. There were particularly high VIP scores in the blue visible wavelength range, from  
568 400-450 nm, at the Pasture site (Figure 5c,d), which could be partly explained by the chlorophyll  
569 a and b absorption peaks at 430nm and 460nm since the Rice also experienced slightly higher  
570 VIP scores in this region (Figure 5e-f). However, the magnitude of the VIP scores in this region  
571 at the Pasture far exceeded those at the Rice. There are two possible explanations for this marked  
572 increase in the importance of the blue visible wavelengths at the Pasture: 1) white reflectance of  
573 the pepperweed flowers at the site could be increasing the albedo within this portion of the  
574 spectrum; 2) the more complex phenology at the site with annual grass and pepperweed  
575 senescence is periodically driving reflectance near 420 nm in response to these periods of stress  
576 (Carter and Miller, 1994). While the Pasture shifted toward much higher reflectivity across the  
577 visible wavelengths during the brief period of white flowering in late spring (Figure 3a), this site  
578 also experienced more dynamic phenology overall, with browning of the grass in early summer  
579 and of the pepperweed in late summer.

580         Almost all of the PLSR models predicting instantaneous and daily- and weekly-integrated  
581 NEE and GPP had a peak in the VIP score at red wavelengths (Figure 5). Reflectance features  
582 within this portion of the spectrum include absorption in the red wavelengths at 642 and 662 nm  
583 correlated with chlorophyll absorption, and reflectance in the chlorophyll a fluorescence  
584 wavelengths that occurs near 673 nm. The maximum VIP score in the visible wavelengths across  
585 nearly all of the PLSR models occurred near the end of the red portion of the spectrum between

586 670-680 nm, indicating that these wavelengths provided critical information to the latent  
587 variables that comprised most of the PLSR models (Figure 5). This result paralleled previous  
588 work that demonstrated the importance of narrow-band reflectance at 670-680 nm for predicting  
589 chlorophyll absorption features across a diverse suite of plant canopies (Carter and Miller, 1994;  
590 Dawson et al., 1999; Gitelson and Merzlyak, 1997; Main et al., 2011).

591         The differences among the predictive power of the PLSR models that included all the  
592 data compared with the models developed at individual sites highlighted important  
593 considerations for future work in this area. The predictive models with the smallest 95%  
594 prediction intervals originated from the models that included all of the data from both sites  
595 (Table 2), demonstrating the power of using larger datasets, with a wider range of values, to  
596 develop the predictive capacity of PLSR models. Further improvements in PLSR predictive  
597 power might be achieved by building upon this data to include paired hyperspectral-eddy flux  
598 datasets from additional sites that can expand and refine the connection between reflectance and  
599 CO<sub>2</sub> flux. This approach has particular promise for sites with automated hyperspectral sensing  
600 systems in conjunction with eddy covariance measurements (Balzarolo et al., 2011; Hilker et al.,  
601 2007; Leuning et al., 2006; Rossini et al., 2010). However, we do emphasize that changes in the  
602 canopy complexity and clumping are important consideration for such work at other sites,  
603 compared with the short-statured canopies with low clumping indices (Ryu et al., 2010b)  
604 included in this study. In canopies with more complex leaf and branch clumping, hyperspectral  
605 canopy reflectance measurements will need to be combined with radiative transfer modeling in  
606 order to accurately model the energy reflectance spectrum (Knyazikhin et al., 2013; Verhoef and  
607 Bach, 2007).

608 In testing the ability of common SVIs used in the literature to predict GPP and NEE, the  
609 skill of some NDVI models were on par with that of the PLSR models when developed using all  
610 the data from both sites or the Rice data only (Table 3). We believe that SVIs well-predicted  
611 GPP and NEE at the Rice due to its simple annual phenology and corresponding seasonal pattern  
612 in CO<sub>2</sub> flux. However, PLSR modeling significantly outperformed SVI models for predicting  
613 GPP and NEE flux when developed using only the Pasture data, due to the increased canopy  
614 complexity at the Pasture site. At the Pasture, the PLSR approach captured more variance within  
615 the dataset through its ability to model more complex relationships across the entire spectrum  
616 compared with SVIs, which focus only on two spectral areas. This highlights the improved utility  
617 for PLSR modeling compared with the use of SVIs to predict ecosystem CO<sub>2</sub> fluxes from  
618 canopies with complex phenological shifts.

#### 619 ***4.3 CO<sub>2</sub> flux prediction at various timescales***

620 Across all sets of PLSR models, there was an interesting shift in VIP scores from the  
621 visible wavelengths to the NIR wavelengths as the timescale of NEE and GPP integration  
622 increased (Figure 5). An increase in structural complexity drives higher NIR reflectivity (Main et  
623 al., 2011), and the VIP scores across the suite of PLSR models showed that this structural  
624 components of the canopy driving NIR reflectance became increasingly important to predicting  
625 both NEE and GPP as the integrated timescale increased. This demonstrated that reflectance in  
626 visible wavelengths correlated with chlorophyll content was most important for short-term flux  
627 prediction, but canopy structural changes in the NIR wavelengths was most important for longer-  
628 term flux prediction. These results are analogous with those from a modeling study across a  
629 network of European grassland sites that found a strong correlation between GPP and NIR  
630 reflectance indicative of phenological shifts in structural canopy components independent of

631 changes in chlorophyll reflectance (Balzarolo et al., 2015). An important constraint of our  
632 analysis is that the field spectrometer used only measured wavelengths up to 900 nm reliably,  
633 making analysis at longer wavelengths in the infrared area correlated with leaf structural  
634 components such as fiber, lignin, and cellulose content impossible (Serbin et al., 2014).  
635 However, this same approach of canopy-level PLSR modeling could be used in conjunction with  
636 a spectrometer capable of making wider spectral reflectance measurements at eddy covariance  
637 sites to evaluate longer wavelength areas of the short-wave IR (SWIR) spectrum, for example  
638 with the newly developed WhiteRef automated sensor for quasi-continuous SWIR hyperspectral  
639 measurements (Sakowska et al., 2015).

640         Comparing the predictive fit achieved with the PLSR models across different CO<sub>2</sub> flux  
641 timescales with the Independent Validation dataset provided important insights into the temporal  
642 scale of CO<sub>2</sub> flux integration represented by the hyperspectral canopy reflectance collection at a  
643 moment in time. Almost all of the final PLSR models achieved the highest predictive fit with the  
644 weekly-integrated GPP fluxes (Figure 7). The changes in the PLSR predictive power for NEE  
645 and GPP at different timescales provided important information for considering what exactly is  
646 represented by measured hyperspectral reflectance in the field, as canopy biochemistry is in fact  
647 an emergent response to biological and environmental drivers that are integrated through time.  
648 The fact that all three models achieved the best predictive fit with the Independent Validation  
649 data for GPP at the weekly timescale yielded support for modeling efforts that determine carbon  
650 fluxes from MODIS satellite reflectance, which is aggregated into an 8-day timescale. The  
651 results of this flux timescale analysis are congruous with those from previous work, which found  
652 a good correlation between gross CO<sub>2</sub> flux and the 8-day MODIS data timescale (Sims et al.,  
653 2005). While there was a clear signal in the higher predictive power for estimating the weekly-

654 integrated GPP flux compared with other timescales, there was less consistency within the best  
655 predictive timescale for estimating NEE (Figure 7). This is likely due to the fact that NEE is a  
656 combination of both GPP and ER, which change on different timescales in response to different  
657 environmental drivers and are more highly coupled at the Rice than they are at the Pasture  
658 (Hatala et al., 2012; Knox et al., 2014). The fact that NEE achieved a good fit with canopy  
659 hyperspectral reflectance through the monthly timescale for the models developed with all the  
660 data (Figure 7a) could indicate that the system memory in carbon flux at these sites is integrated  
661 over a longer timescale than was tested in this analysis, and that canopy biochemistry collected at  
662 one moment reflects at least the previous month of integrated NEE flux.

663

## 664 **5. Conclusions**

665 This analysis demonstrated that using PLSR modeling with repeated near-surface  
666 hyperspectral canopy reflectance created reliable predictive models of NEE and GPP flux for  
667 two short-structured plant canopies with different phenology and significant intra-site and inter-  
668 annual variability in canopy reflectance. The PLSR models developed from hyperspectral canopy  
669 reflectance collected during 100 site visits from 2010-2014 at a Pasture and a Rice paddy  
670 achieved a high level of predictability for both NEE and GPP flux where the predictive  $R^2$   
671 ranged from 0.24 to 0.69 using an independent validation dataset. The higher variability in  
672 measured hyperspectral reflectance at the Pasture did decrease the predictive power of the PLSR  
673 models when compared against those developed at the Rice site with a more homogeneous  
674 canopy. The PLSR models were most skilled at predicting the GPP flux for the integrated week  
675 prior to the collection of canopy reflectance. Although the use of PLSR methods with  
676 hyperspectral field reflectance such as those presented within this analysis need to be rigorously

677 tested with a much larger dataset and in more diverse ecosystems, the results from this analysis  
678 showed promise for using repeated hyperspectral canopy reflectance to directly predict  
679 landscape-scale carbon flux. Use of this method, particularly if developed with large datasets  
680 collected over several years, might help to constrain GPP estimates through the integration of  
681 additional datasets into the modeling efforts that partition NEE into GPP and ER at flux sites  
682 (Hilker et al., 2014). The development of PLSR models to predict NEE and GPP from  
683 hyperspectral canopy reflectance collected within flux tower footprints is a promising avenue of  
684 future research, particularly with the development and deployment of hyperspectral satellite  
685 sensors such as NASA's Hyperspectral and InfraRed Imager (HyspIRI; [http://](http://http://hyspiri.jpl.nasa.gov)  
686 <http://hyspiri.jpl.nasa.gov>), which will provide continuous spatial coverage of measured  
687 hyperspectral reflectance.

688

## 689 **6. Author Contributions**

690 D.D.B., J.H.M., and O.S. designed the experiment, all co-authors collected, processed, and  
691 analyzed the reflectance and eddy covariance measurements, J.H.M. designed and conducted  
692 PLSR modeling, and J.H.M. wrote the manuscript with input from all co-authors.

693

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941 **Table 1. Fit statistics for the bootstrapped PLSR model.** The mean  $R^2$  and root mean squared  
942 error (RMSE) is provided for the PLSR Calibration fitting (Cal) and the calibration Evaluation  
943 (Eval) during the PLSR model development, conducted with 80% of the total dataset. Units for  
944 instantaneous fluxes are  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , and for daily, weekly, and monthly values are  $\text{g-C m}^{-2}$ . In  
945 general, models with daily-integrated GPP and NEE had the best fit compared with models that  
946 fit the flux data from other timescales. The PLSR fit for GPP using the hyperspectral reflectance  
947 data tended to outperform the fit of NEE across the datasets and models. The statistical fit of the  
948 PLSR models was higher at the Rice site compared with the Pasture.

		$R^2$ Cal	$R^2$ Eval	RMSE Cal	RMSE Eval	Components
Both sites	GPP inst	0.87	0.64	3.34	4.74	7
	GPP daily	0.87	0.69	1.42	1.96	6
	GPP wkly	0.86	0.69	10.35	13.82	6
	GPP mthly	0.63	0.24	45.47	44.75	6
	NEE inst	0.84	0.64	3.30	4.39	6
	NEE daily	0.84	0.66	1.43	1.87	6
	NEE wkly	0.83	0.65	10.34	13.21	6
	NEE mthly	0.81	0.64	42.11	51.88	6
Pasture	GPP inst	0.94	0.49	1.36	3.49	7
	GPP daily	0.97	0.56	0.43	1.53	8
	GPP wkly	0.53	0.38	11.64	10.15	3
	GPP mthly	0.91	0.42	22.96	52.43	7
	NEE inst	0.43	0.33	3.56	2.52	2
	NEE daily	0.38	0.30	1.40	0.91	2
	NEE wkly	0.44	0.29	8.47	6.42	3
	NEE mthly	0.79	0.36	22.81	30.49	6
Rice	GPP inst	0.85	0.61	4.34	5.92	5
	GPP daily	0.92	0.65	1.34	2.58	6
	GPP wkly	0.84	0.67	13.32	17.06	4
	GPP mthly	0.89	0.68	10.96	16.95	5
	NEE inst	0.77	0.58	4.88	5.66	4
	NEE daily	0.86	0.60	1.68	2.52	5
	NEE wkly	0.85	0.59	11.82	17.88	5



949

	NEE mthly	0.80	0.64	56.50	67.93	4
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950 **Table 2. Independent validation dataset fit for mean PLSR models.** We calculated the  $R^2$  and  
 951 bias between the predicted  $\text{CO}_2$  flux variables with the mean PLSR models and the actual  
 952 measurements from the 20% of data left for Independent Validation. Units for instantaneous  
 953 fluxes are  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , and for daily, weekly, and monthly values are  $\text{g-C m}^{-2}$ . The highest  
 954 predictive fit for the PLSR models was achieved with the dataset that included the Rice data  
 955 only.

		$R^2$		Bias	
		NEE	GPP	NEE	GPP
<b>Both sites</b>	Inst	0.51	0.42	-1.63	3.89
	Daily	0.52	0.52	-0.41	1.60
	Weekly	0.55	0.62	-3.31	9.75
	Monthly	0.57	0.27	-11.92	31.51
<b>Pasture</b>	Inst	0.53	0.24	-2.28	5.10
	Daily	0.44	0.45	-0.56	2.79
	Weekly	0.51	0.54	-1.96	15.94
	Monthly	0.43	0.47	-14.18	76.86
<b>Rice</b>	Inst	0.51	0.40	-1.41	2.73
	Daily	0.65	0.50	-0.89	0.58
	Weekly	0.69	0.62	-2.35	0.21
	Monthly	0.41	0.45	-18.56	4.60

956

957

958 **Table 3. Comparison of SVIs and PLSR model skill.** We evaluated the ability of the  
 959 commonly used standardized vegetation indices (SVIs) to predict GPP and NEE in comparison  
 960 with the PLSR models. Here we show results for the widely used MODIS NDVI (NDVI<sub>MOD</sub>) and  
 961 the red-edge NDVI (NDVI<sub>re</sub>), which was the SVI that achieved the highest skill at predicting  
 962 GPP and NEE. Results from all SVIs tested in this study are included as Supplementary Table 1.

Site	Flux	NDVI <sub>MOD</sub> fit	NDVI <sub>re</sub> fit	PLSR fit	NDVI <sub>MOD</sub> pred	NDVI <sub>re</sub> pred	PLSR pred
All	GPP_inst	0.50	0.57	0.87	0.18	0.22	0.42
All	GPP_day	0.55	0.65	0.87	0.44	0.53	0.52
All	GPP_week	0.56	0.64	0.86	0.42	0.50	0.62
All	GPP_month	0.49	0.56	0.63	0.32	0.38	0.27
All	NEE_inst	0.49	0.57	0.84	0.50	0.57	0.51
All	NEE_day	0.45	0.54	0.84	0.51	0.58	0.52
All	NEE_week	0.48	0.56	0.83	0.53	0.59	0.55
All	NEE_month	0.53	0.58	0.81	0.54	0.59	0.57
Pasture	GPP_inst	0.29	0.38	0.94	0.09	0.13	0.24
Pasture	GPP_day	0.35	0.45	0.97	0.26	0.34	0.45
Pasture	GPP_week	0.29	0.38	0.53	0.22	0.30	0.54
Pasture	GPP_month	0.18	0.25	0.91	0.13	0.19	0.47
Pasture	NEE_inst	0.31	0.40	0.43	0.30	0.39	0.53
Pasture	NEE_day	0.31	0.41	0.38	0.26	0.35	0.44
Pasture	NEE_week	0.29	0.36	0.44	0.25	0.31	0.51
Pasture	NEE_month	0.20	0.25	0.79	0.17	0.22	0.43
Rice	GPP_inst	0.46	0.54	0.85	0.48	0.49	0.4
Rice	GPP_day	0.56	0.69	0.92	0.57	0.62	0.5
Rice	GPP_week	0.60	0.72	0.84	0.62	0.65	0.62
Rice	GPP_month	0.59	0.68	0.89	0.60	0.63	0.45
Rice	NEE_inst	0.47	0.56	0.77	0.49	0.52	0.51
Rice	NEE_day	0.49	0.60	0.86	0.51	0.55	0.65
Rice	NEE_week	0.54	0.64	0.85	0.56	0.58	0.69
Rice	NEE_month	0.60	0.69	0.8	0.63	0.64	0.41

963

964 **Figure captions**

965 **Figure 1. Canopy hyperspectral field collection dates.** This analysis synthesized canopy  
966 hyperspectral reflectance measurements collected from 2010-2014 at Pasture and Rice sites in  
967 the Sacramento-San Joaquin Delta in Northern California. On each sampling date we collected  
968 nine individual canopy hyperspectral reflectance replicates at the Pasture site and five individual  
969 reflectance replicates at the Rice site.

970  
971 **Figure 2. Instantaneous gross primary productivity (GPP) and daily net CO<sub>2</sub> flux on the**  
972 **hyperspectral canopy reflectance sampling dates.** Both the Pasture and the Rice exhibited  
973 strong seasonal patterns with peak CO<sub>2</sub> uptake mid-year. However, the Pasture experienced peak  
974 CO<sub>2</sub> uptake that preceded the peak for the Rice, where the maximum CO<sub>2</sub> uptake occurred in  
975 March-April for the Pasture and in July-August for the Rice.

976  
977 **Figure 3. Daily variability in measured canopy hyperspectral reflectance during**  
978 **phenological events. a-b)** Daily measured hyperspectral canopy reflectance for the Pasture and  
979 Rice sites when the canopy was closed and green, at the Pasture on 10 April 2014 and the Rice  
980 on 31 July 2013. Reflectance was very low in the visible wavelengths due to canopy absorption,  
981 but quite large in the near infrared reflectance with a high amount of variability. Both sites had  
982 spectral peaks that corresponded to green reflectance (~550 nm) and troughs that corresponded to  
983 spectral absorption in red reflectance (~675 nm). **c)** During the white flowering of the  
984 pepperweed plants, the measured reflectance changed significantly, due to the higher albedo of  
985 the bright white flowers. There was much higher reflectance across the spectrum during this  
986 time, and the white flowers obfuscated reflectance in the wavelengths that corresponded to plant

987 productivity. **d)** There was a similar but not as dramatic shift in increased albedo particularly  
988 across the visible wavelengths from green to red reflectance during the rice seeding and  
989 senescence as the canopy dried before harvest. However an important distinction between this  
990 phenological event and the white flowering at the Pasture is that the productivity of the rice  
991 plants was quite low at this time, in contrast with the higher productivity of the pepperweed  
992 during flowering.

993

994 **Figure 4. Inter-annual and daily variability at narrow-band green, red, and near-infrared**

995 **(NIR) reflectance. a-b)** Inter-annual variability in measured canopy green reflectance at  $550\pm 5$

996 nm, where the points are the site mean and the bars represent one standard deviation for each

997 sampling date. The green reflectance at the Pasture was relatively uniform throughout the year,

998 due to the presence of either grass or pepperweed canopy for most of the year. There was more

999 intra-site variability in reflectance during the summer when the pepperweed canopy was active,

1000 since at some locations the white flowers of the pepperweed plant can complicate the green

1001 reflectance spectrum. The green reflectance at the Rice had more inter-annual variability but a

1002 more discernible seasonal pattern within each year, where the trough in green reflectance tended

1003 to occur mid-summer. **c-d)** These plots show red reflectance at  $662\pm 5$  nm at each site, which

1004 corresponds to the absorption wavelength of chlorophyll b. Both sites demonstrated a seasonal

1005 pattern, where the minimum in red reflectance occurred in late spring at the Pasture and in late

1006 summer at the Rice, corresponding to the times of peak plant growth at each site. Again, the

1007 Pasture had more intra-site variability, particularly during the summer months when pepperweed

1008 is active. **e-f)** Here we plot the near infrared (NIR) reflectance at  $800\pm 5$  nm for the two sites. NIR

1009 reflectance at the Pasture had no strong seasonal pattern, with a constant mean throughout the

1010 year and across years. The rice demonstrated a stronger pattern across the season, with less NIR  
1011 reflectance early in the growing season when the canopy was developing, with higher NIR  
1012 reflectance as the crop achieved a full canopy later in the summer. At both sites, intra-site  
1013 variability in NIR reflectance was much higher than the variability in the reflectance in the  
1014 visible spectrum.

1015

1016 **Figure 5. Variable importance of projection (VIP) statistics for bootstrapped partial least-**  
1017 **squared regression (PLSR) modeling coefficients.** Here we show the variable importance of  
1018 projection (VIP) statistics for the mean bootstrapped PLSR models, fitted to the GPP and NEE  
1019 flux datasets. The VIP statistic describes the relative contribution of each wavelength to the  
1020 predictive power of the PLSR model across all final PLSR model components. Across all  
1021 models, the visible wavelengths (400-700nm) were most important for prediction at shorter  
1022 timescales of integrated flux, while the infrared wavelengths (700-900nm) became increasingly  
1023 important at longer integrated flux intervals. This pattern is particularly apparent within the  
1024 PLSR model for GPP fitted across All the data (Figure 5a), where there was a dramatic shift in  
1025 the VIP statistics between the weekly- and monthly-integrated flux prediction and the infrared  
1026 wavelengths become much more important for prediction at longer timescales. This pattern was  
1027 also apparent with the PLSR models developed using the Pasture data only. The PLSR models  
1028 developed for the Rice data only (Figures 5e-f) had the least variation for fluxes integrated at  
1029 different timescales.

1030

1031 **Figure 6. Predictive ability of PLSR models on independent validation dataset.** The mean  
1032 PLSR models determined through the bootstrapping routine were tested on the Independent

1033 Validation dataset, which was composed of 20% of the original data that was separated from the  
1034 model calibration process. Here the independent validation is presented for instantaneous and  
1035 daily NEE and GPP flux for the exercises with all the data, Pasture only, and Rice only. The  
1036 regression line between the predicted and actual variables is black, the 1:1 line is dashed, the  
1037 95% credible interval of the regression are the curved dotted lines, and the 95% prediction  
1038 interval are the grey lines.

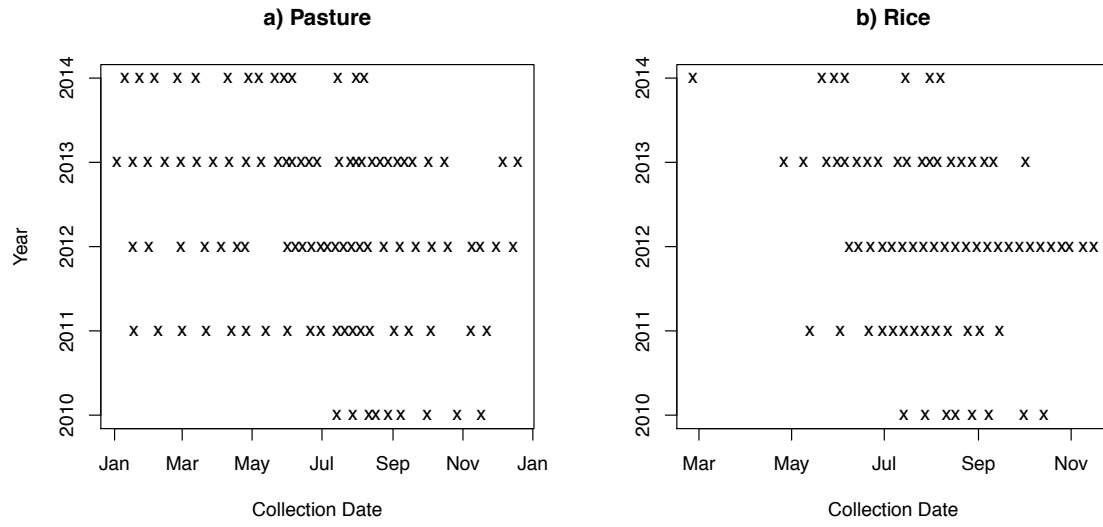
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1040 **Figure 7. Predictive power of measured hyperspectral reflectance at increasing CO<sub>2</sub> flux**  
1041 **integration intervals.** We examined the ability of PLSR modeling with the hyperspectral  
1042 reflectance data to predict instantaneous and daily-, weekly-, and monthly-integrated NEE and  
1043 GPP at **a)** both sites with the entire dataset, **b)** the Pasture only, and **c)** the Rice only. For all three  
1044 cases, the measured hyperspectral reflectance had the highest correlation with weekly-integrated  
1045 GPP flux. The time interval with the highest predictive power for NEE flux was less variable  
1046 across different timescales within each modeling exercise, and there was not a strong  
1047 improvement to using one particular timescale to model NEE with the hyperspectral reflectance  
1048 data.

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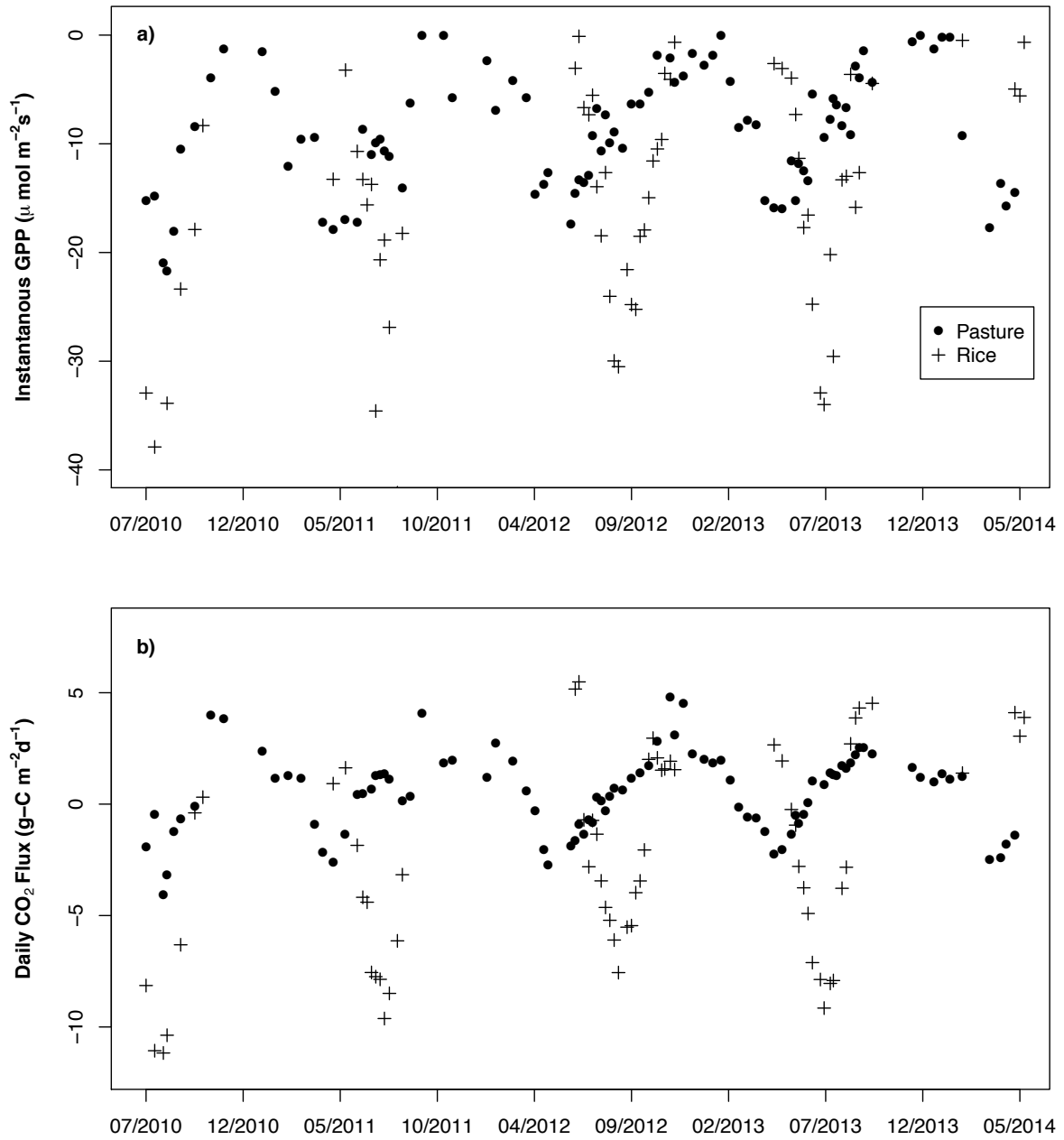
1051 **FIGURE 1**



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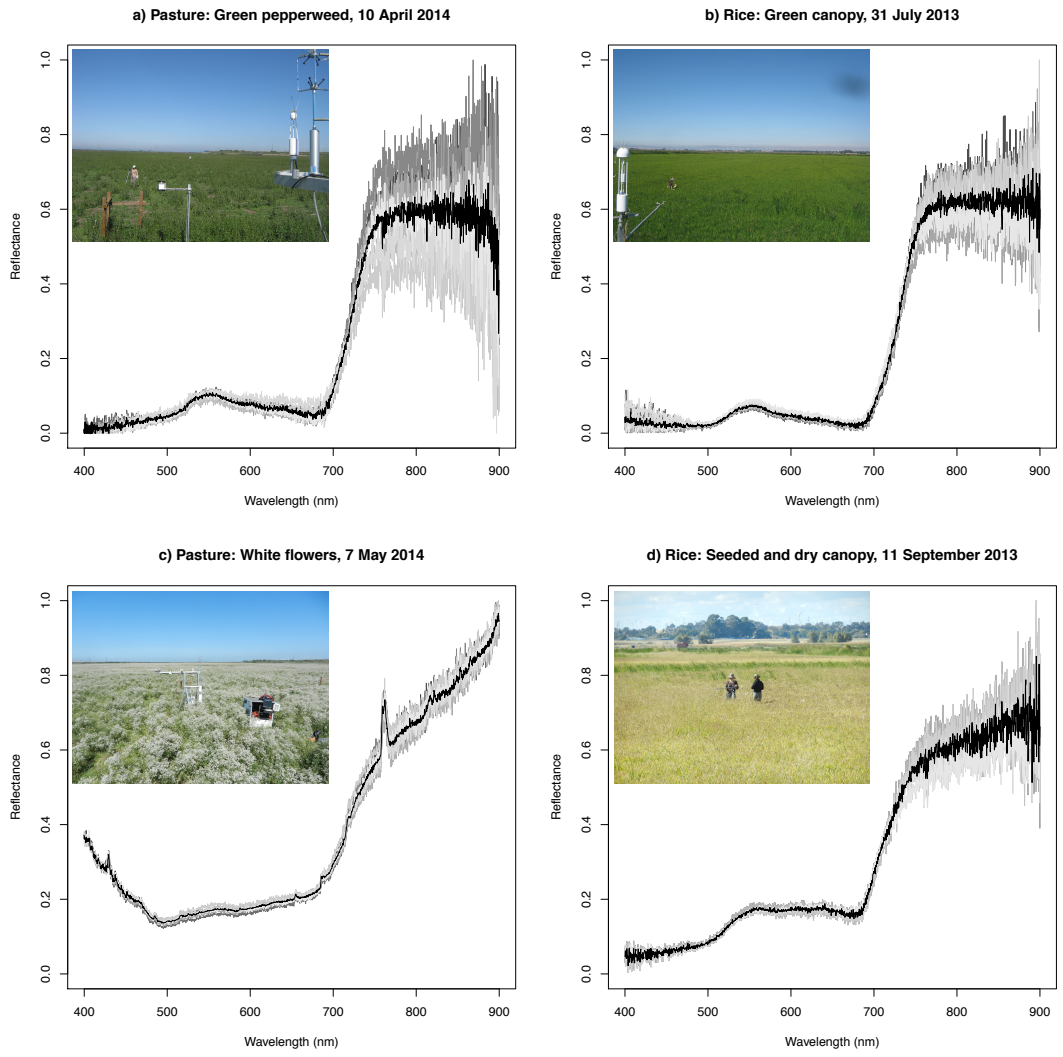
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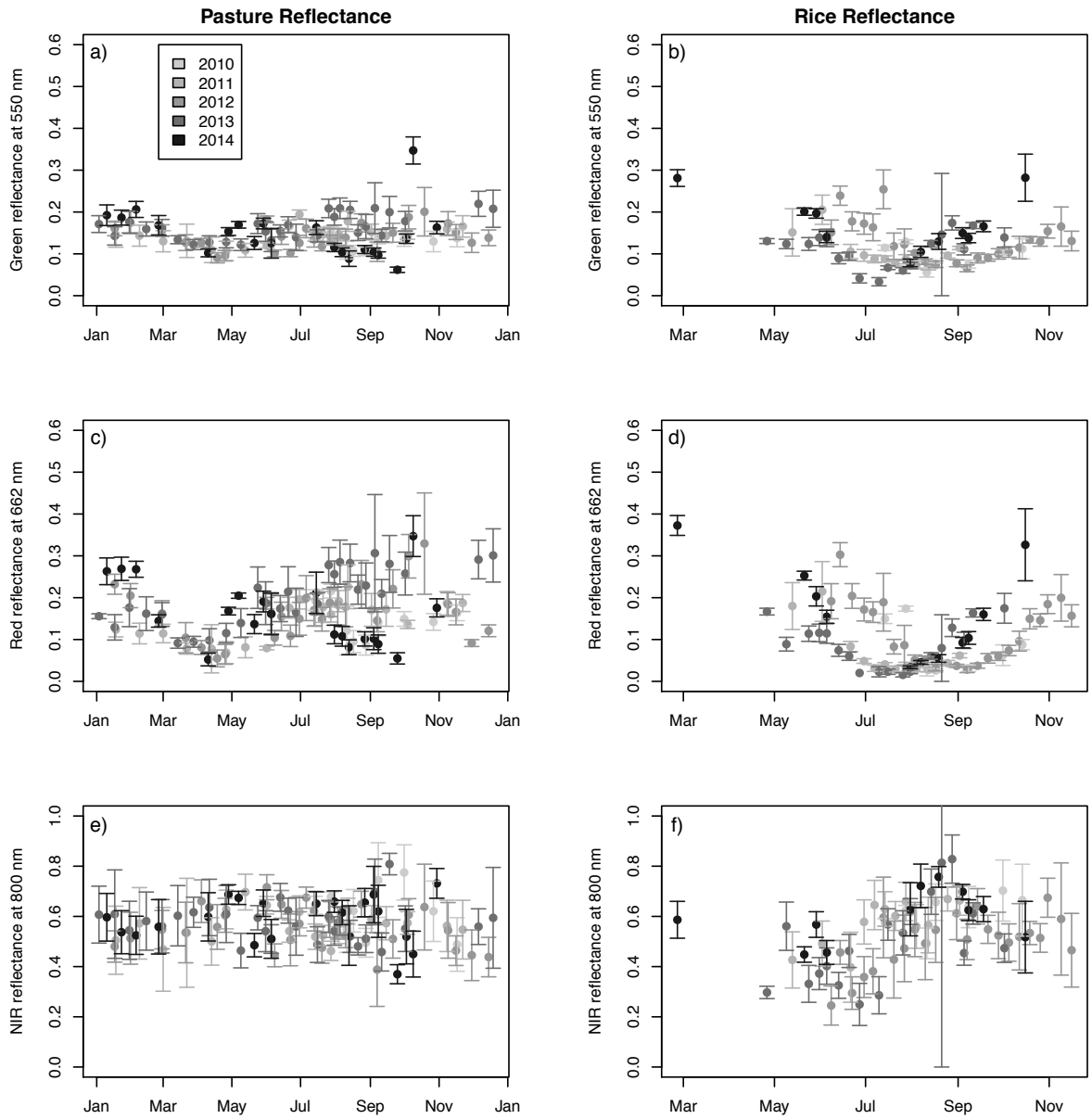
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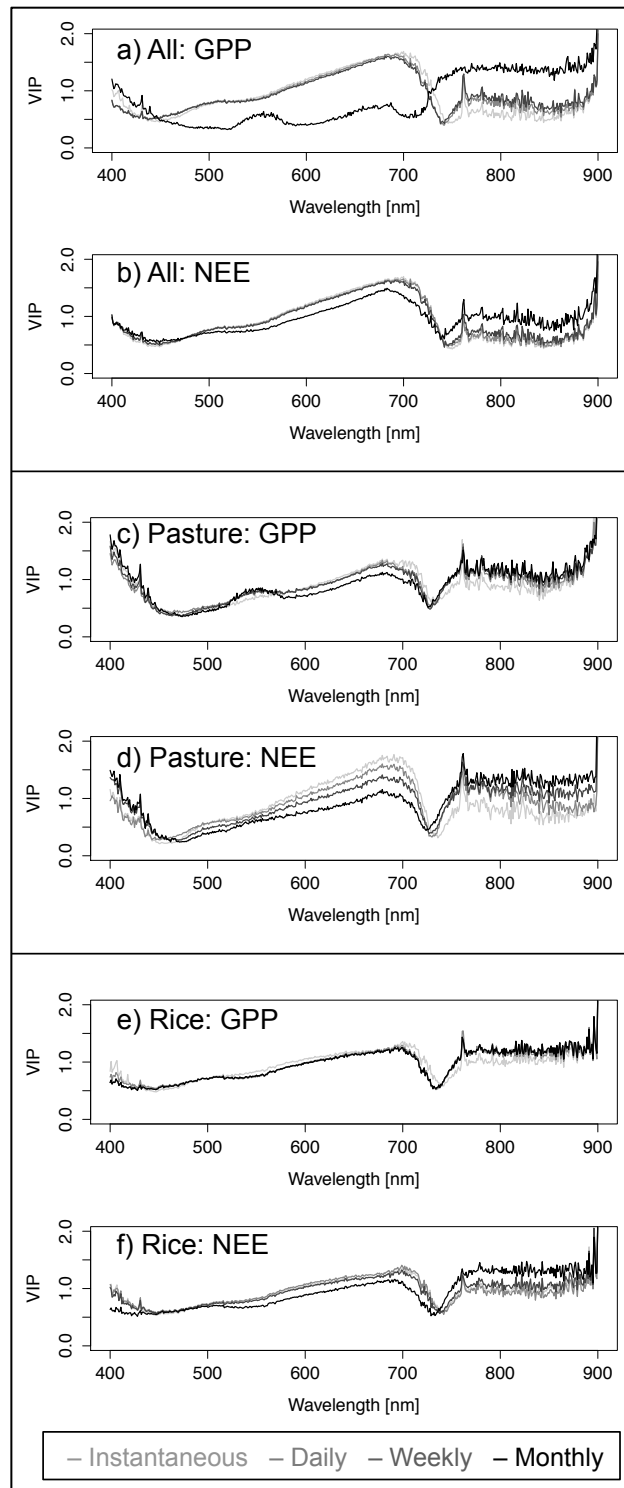
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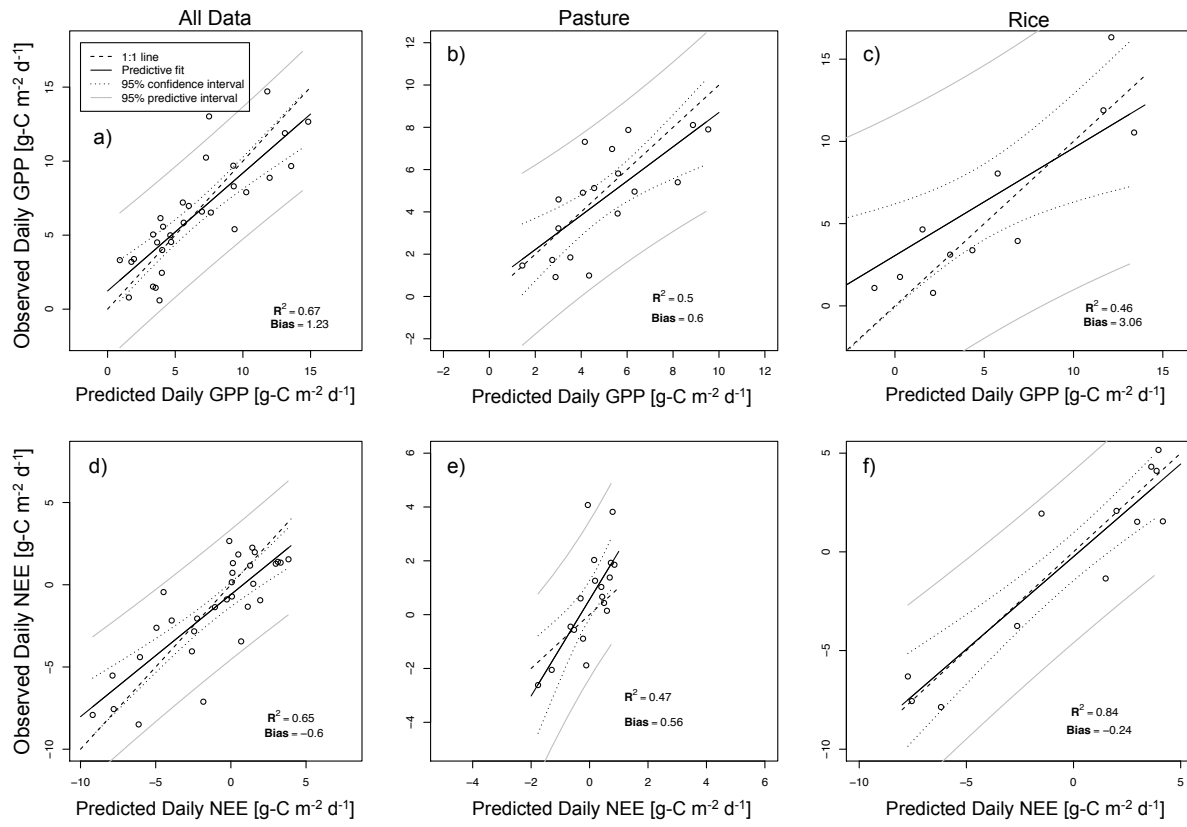


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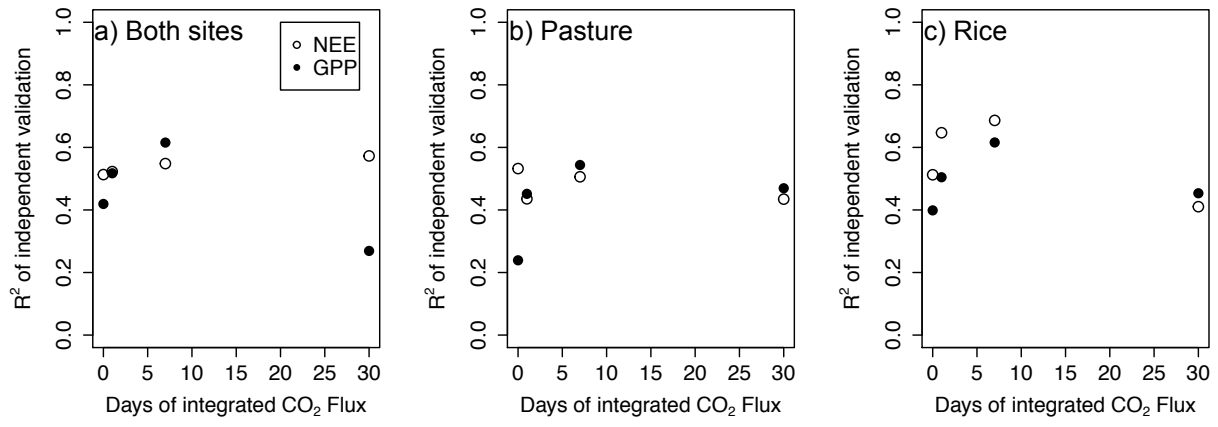
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1075 **FIGURE 7**



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