



## Supplement of

## On the relationship between ecosystem-scale hyperspectral reflectance and $\mathrm{CO}_2$ exchange in European mountain grasslands

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Figure S1. Selected grassland spectral signatures during the growing seasons. The figure legends indicates the corresponding leaf area index (LAI;  $m^2 m^{-2}$ ) and the day of year (in parenthesis).



Figure S2. Correlograms of  $R^2$  values for daily averaged GPP,  $\varepsilon$  and NEE and NSD-type indices for Amplero, Neustift, Monte Bondone (both study years pooled) and all sites pooled. The white dots indicate the position of paired band combinations corresponding to the maximum  $R^2$ .



Figure S3. Correlograms of  $R^2$  values for daily averaged GPP,  $\varepsilon$  and NEE and SR-type indices for Amplero, Neustift, Monte Bondone (both study years pooled) and all sites pooled. The white dots indicate the position of paired band combinations corresponding to the maximum  $R^2$ .



Figure S4. Correlograms of  $R^2$  values for daily averaged GPP,  $\varepsilon$  and NEE and SD-type indices for Amplero, Neustift, Monte Bondone (both study years pooled) and all sites pooled. The white dots indicate the position of paired band combinations corresponding to the maximum  $R^2$ .



Figure S5. Results of linear correlation analysis for  $\alpha$ , GPP<sub>max</sub> and midday averaged GPP,  $\varepsilon$  and NEE and selected best SR-type indices for (a) Amplero, (b) Neustift, (c) Monte Bondone (both study years pooled) and (d) all sites pooled. R<sup>2</sup>—Coefficient of determination; RMSE—Root Mean Square Error; R<sup>2</sup>cv—Cross-validated coefficient of determination; RMSEcv— Cross-validated root Mean Square Error. The solid red lines indicate the fitted models and the dotted red lines represent the 95% upper and lower confidence bounds.



Figure S6. Results of linear correlation analysis for  $\alpha$ , GPP<sub>max</sub> and midday averaged GPP,  $\varepsilon$  and NEE and selected SD-type indices for (a) Amplero, (b) Neustift, (c) Monte Bondone (both study years pooled) and (d) all sites pooled. R<sup>2</sup>—Coefficient of determination; RMSE—Root Mean Square Error; R<sup>2</sup>cv—Cross-validated coefficient of determination; RMSEcv— Cross-validated root Mean Square Error. The solid red lines indicate the fitted models and the dotted red lines represent the 95% upper and lower confidence bounds.



Figure S7. Results of linear correlation analysis for daily averaged GPP,  $\varepsilon$  and NEE and selected NSD-type indices for (a) Amplero, (b) Neustift, (c) Monte Bondone (both study years pooled) and (d) all sites pooled. R<sup>2</sup>—Coefficient of determination; RMSE—Root Mean Square Error; R<sup>2</sup>cv—Cross-validated coefficient of determination; RMSEcv— Cross-validated root Mean Square Error. The solid red lines indicate the fitted models and the dotted red lines represent the 95% upper and lower confidence bounds.



Figure S8. Results of linear correlation analysis for daily averaged GPP,  $\varepsilon$  and NEE and selected SR-type indices for (a) Amplero, (b) Neustift, (c) Monte Bondone (both study years pooled) and (d) all sites pooled. R<sup>2</sup>—Coefficient of determination; RMSE—Root Mean Square Error; R<sup>2</sup>cv—Cross-validated coefficient of determination; RMSEcv— Cross-validated root Mean Square Error. The solid red lines indicate the fitted models and the dotted red lines represent the 95% upper and lower confidence bounds.



Figure S9. Results of linear correlation analysis for daily averaged GPP,  $\varepsilon$  and NEE and selected SD-type indices for (a) Amplero, (b) Neustift, (c) Monte Bondone (both study years pooled) and (d) all sites pooled. R<sup>2</sup>—Coefficient of determination; RMSE—Root Mean Square Error; R<sup>2</sup>cv—Cross-validated coefficient of determination; RMSEcv— Cross-validated root Mean Square Error. The solid red lines indicate the fitted models and the dotted red lines represent the 95% upper and lower confidence bounds.



Figure S10. Results of validation of linear regression models between VIs ((a) NSD-type; (b) SR-type; (c) SD-type) and daily average  $\varepsilon$  and CO<sub>2</sub> fluxes (NEE and GPP). R<sup>2</sup> – coefficients of determination. Different colours represent results of the validation performed applying to the three new sites the model for Amplero (in magenta), Neustift (in red) and Monte Bondone (in blue) and a model parameterized grouping Monte Bondone and Neustift (M.Bondone&Neustift; in black). The black lines are 1:1 lines. Statistical significance is indicated as \* (p < 0.05), \*\* (p < 0.01), and \*\*\* (p < 0.001).



Figure S11. Correlation between selected (a) NSD-, (b) SR- and (c) SD-type indices and the total chlorophyll content for daily average  $\varepsilon$  and CO<sub>2</sub> fluxes (NEE and GPP) for Monte Bondone in 2013. R<sup>2</sup>— coefficient of correlation for daily average of  $\varepsilon$  and CO<sub>2</sub> fluxes (NEE and GPP); RMSE—root mean square error; R<sup>2</sup>cv— cross-validated coefficient of correlation; RMSEcv— cross-validated root mean square error. The solid red lines indicate the fitted models and the dotted red lines represent the 95% upper and lower confidence bounds. The selected bands to compute NSD-, SR- and SD-type indices are reported in brackets.

## <u>Tables</u>

Table S1. Description of  $CO_2$  flux measurements at the study sites.

Parameter	Amplero	Neustift	Monte Bondone
Futurneter	(IT-Amp)	(AT-Neu)	(IT-MBo)
Sonic anemometer model	R3, Gill, Gill Instruments Ltd., Lymington, UK	R3, Gill, Instruments Ltd., Lymington, UK	R3, Gill Instruments Ltd., Lymington, UK
Infrared gas analyser model	Li-7500, Li-Cor Inc., Lincoln, Nebraska, USA	Li-7500, Li-Cor Inc., Lincoln, Nebraska, USA	Li-7500, Li-Cor Inc., Lincoln, Nebraska, USA
Data acquisition frequency (Hz)	20	20	20
Post-processing software	Developped by University of Viterbo (IT)	EdiRE (Version 1.4.3.1021, R. Clement, University of Edinburgh)	EdiRE (Version 1.4.3.1021, R. Clement, University of Edinburgh)
Outlier removal (method)	Wickers and Mahrt (1997)	-	-
CO <sub>2</sub> /H <sub>2</sub> O signal lag removal	Covariance maximization	Covariance maximization	Covariance maximization
Coordinate rotation (method) <sup>1</sup>	3D	3D	3D
Detrending of time series (method)	Linear detrending	-	-
Density corrections applied <sup>2</sup>	x	x	x
Sonic buoyancy to sensible heat flux conversion and cross-wind correction <sup>3</sup>	x	x	x

Low- and high-pass filtering corrected for (method)	Aubinet et al. (2000)	Moore (1986)	Aubinet et al. (2000)
Iterative calculation of fluxes <sup>4</sup>	-	X	-

<sup>1</sup> according to Wilczak et al. (2001); <sup>2</sup> according to Webb et al. (1980); <sup>3</sup> according to Schotanus et al. (1983); <sup>4</sup> according to Mauder et al. (2008)

Table S2. Description of the validation study sites and period.

	Längenfeld	Leutasch	Scharnitz
Site characteristics	(AT-Lan)	(AT-Leu)	(AT-Sch)
Latitude	47.0612	47.3780	47.3873
Longitude	10.9634	11.1627	11.2479
Elevation (m)	1180	1115	964
Mean annual temperature (°C)	5.8	4.8	6.4
Mean annual precipitation (mm)	733	1309	1418
Vegetation type	Phyteumo-Trisetion	Astrantio-Trisetetum	Arrenatherum montanum
Study period <sup>1</sup>	163, 2006 (1)	227, 2006 (1)	184-284, 2006 (5)
Sonic anemometer model	R3, Gill Instruments Ltd., Lymington, UK	R3, Gill Instruments Ltd., Lymington, UK	R3, Gill Instruments Ltd., Lymington, UK
nfrared gas analyser model	Li-7500, Li-Cor Inc., Lincoln, Nebraska, USA	Li-7500, Li-Cor Inc., Lincoln, Nebraska, USA	Li-7500, Li-Cor Inc., Lincoln, Nebraska, USA
Data acquisition frequency (Hz)	20	20	20
Post-processing software	EdiRE (Version 1.4.3.1021, R. Clement, University of Edinburgh)	EdiRE (Version 1.4.3.1021, R. Clement, University of Edinburgh)	EdiRE (Version 1.4.3.1021, R. Clement, University of Edinburgh)
Dutlier removal (method)	-	-	-
CO <sub>2</sub> /H <sub>2</sub> O signal lag removal	Covariance maximization	Covariance maximization	Covariance maximization
Coordinate rotation (method) <sup>2</sup>	3D	3D	3D
Detrending of time series (method)	-		
Density corrections applied <sup>3</sup>	х	x	x
sonic buoyancy to sensible heat flux conversion and cross-wind correction <sup>4</sup>	x	x	x
.ow- and high-pass filtering corrected for (method)	Moore (1986)	Moore (1986)	Moore (1986)

<sup>1</sup> from-to DOY, year (number of hyperspectral measurement dates); <sup>2</sup> according to Wilczak et al. (2001); <sup>3</sup> according to Webb et al. (1980); <sup>4</sup> according to Schotanus et al. (1983); <sup>5</sup> according to Mauder et al. (2008).

	3					GPP						NEE												
	Am	plero	Ne	ustift	Mor	nte Bondone		All	Am	plero	Neus	stift	Monte	Monte Bondone All		Am	Amplero Neustift		ustift	Monte Bondone			All	
	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE	R <sup>2</sup>	RMSE
	-	µmol <sub>cc</sub>	02 -	µmol <sub>co</sub>	02 -	$\mu mol_{CO2}$	-	$\mu mol_{CO2}$	-	$\mu mol_{CO2}$	-	$\mu mol_{CO2}$	-	$\mu mol_{CO2}$	-	$\mu mol_{CO2}$	-	µmol <sub>co:</sub>	2 -	$\mu mol_{CO2}$		$\mu mol_{CO2}$	-	
VI		$\mu mol_{ph}$	ot	µmol <sub>ph</sub>	ot	$\mu mol_{phot}$		$\mu mol_{phot}$		$m^2s$		$m^2s$		$m^2s$		$m^2s$		$m^2s$		$m^2s$		$m^2s$		
SR	0.66	0.01	0.33	0.04	0.33	0.04	0.13	0.04	0.95	0.73	0.25	2.63	0.71	2.30	0.26	4.92	0.91	0.90	0.25	1.96	0.69	1.60	0.24	3.40
GRI	0.39	0.01	0.74	0.02	0.43	0.04	0.39	0.04	0.81	1.39	0.16	2.64	0.75	2.12	0.07	5.51	0.83	1.23	0.16	2.06	0.67	1.65	0.09	3.72
WI	0.60	0.01	0.17	0.04	0.36	0.04	0.19	0.04	0.93	0.85	0.04	2.26	0.47	3.10	0.22	5.05	0.88	1.04	0.04	2.21	0.43	2.18	0.17	3.55
NDVI	0.51	0.01	0.31	0.04	0.48	0.04	0.29	0.04	0.88	1.09	0.30	2.60	0.73	2.19	0.35	4.60	0.88	1.02	0.30	1.89	0.77	1.39	0.34	3.16
SIPI	0.41	0.01	0.27	0.04	0.55	0.03	0.28	0.04	0.75	1.60	0.09	2.58	0.66	2.48	0.48	4.14	0.75	1.47	0.09	2.15	0.76	1.42	0.48	2.80
CI	0.54	0.01	0.70	0.02	0.38	0.04	0.25	0.04	0.94	0.76	0.13	2.65	0.73	2.22	0.14	5.29	0.95	0.65	0.13	2.11	0.77	1.38	0.16	3.57
PRI	0.49	0.01	0.14	0.04	0.32	0.04	0.36	0.04	0.44	2.37	0.06	2.44	0.17	3.86	0.12	5.36	0.44	2.21	0.06	2.19	0.21	2.56	0.07	3.76
EVI	0.53	0.01	0.42	0.03	0.51	0.03	0.28	0.04	0.86	1.17	0.12	2.63	0.60	2.69	0.32	4.71	0.87	1.05	0.12	2.11	0.66	1.67	0.27	3.33
NPQI	0.07	0.01	0.43	0.03	0.18	0.04	0.16	0.04	0.03	3.12	0.00	2.64	0.12	3.98	0.22	5.04	0.12	2.78	0.00	2.25	0.12	2.69	0.17	3.55
NPCI	0.45	0.01	0.13	0.04	0.00	0.05	0.01	0.04	0.60	2.01	0.01	2.47	0.18	3.83	0.38	4.51	0.67	1.71	0.01	2.25	0.26	2.47	0.36	3.11
SRPI	0.47	0.01	0.11	0.04	0.00	0.05	0.01	0.04	0.55	2.13	0.01	2.47	0.19	3.80	0.34	4.64	0.62	1.82	0.01	2.25	0.27	2.46	0.32	3.21
RedEdgeNDVI	0.52	0.01	0.72	0.02	0.42	0.04	0.29	0.04	0.93	0.82	0.12	2.65	0.73	2.20	0.18	5.20	0.95	0.67	0.12	2.11	0.78	1.35	0.19	3.50

Table S3. Results of statistic of linear regression models between VIs and daily average of ecophysiological parameters:  $\epsilon$ , GPP and NEE. R<sup>2</sup>—Coefficient of determination and RMSE—Root Mean Square Error. Bold letters indicate the best fitting model.

Table S4. Results of validation of linear regression models between VIs ((a) NSD-type; (b) SR-type; (c) SD-type) and ecophysiological parameters:  $\alpha$ ,  $\varepsilon$  (midday average), GPP<sub>max</sub> and midday average CO<sub>2</sub> fluxes (NEE and GPP). Validation was performed by applying the three different models for Amplero, Neustift, Monte Bondone and a model parameterized grouping Neustift and Monte Bondone (M.Bondone&Neustift). slope—slope of linear model; y-int—intercept of linear model, and RMSE—Root Mean Square Error.

	α			GPPmax				GPP			3		_	NEE				
Madal	slope	y-int	RMSE	slope	y-int	RMSE	slope	y-int	RMSE	slope	y-int	RMSE	slope	y-int	RMSE			
woder	-	$\mu mol_{CO2}$	$\mu mol_{CO2}$	-	µmol <sub>CO2</sub>	$\mu mol_{CO2}$	-	µmol <sub>c02</sub>	$\mu mol_{CO2}$	-	µmol <sub>CO2</sub>	$\mu mol_{CO2}$	-	µmol <sub>co2</sub>	µmol <sub>CO2</sub>			
		$\mu mol_{phot}$	µmol <sub>phot</sub>		$m^2s$	$m^2s$		$m^2s$	$m^2s$		µmol <sub>phot</sub>	$\mu mol_{phot}$		$m^2s$	$m^2s$			
(a) NSD-type																		
Amplero	0.22	0.01	0.03	0.24	5.69	9.37	0.67	-5.30	11.51	-1.99	0.05	0.02	0.06	-0.89	11.78			
Neustift	-2.63	0.16	0.17	0.66	10.13	4.80	0.75	7.59	3.64	-7.37	0.15	0.06	0.28	-9.74	9.00			
Monte Bondone	-0.15	0.05	0.02	0.51	12.69	5.19	0.88	6.20	4.81	-1.88	0.10	0.06	0.54	-11.78	8.17			
M.Bondone&Neustift	2.94	-0.05	0.04	0.67	10.88	6.59	0.63	7.40	4.78	-4.25	0.10	0.08	0.24	-9.02	9.00			
(b) SR-type																		
Amplero	0.22	0.01	0.03	0.24	5.71	9.37	0.67	-5.25	11.52	-1.96	0.05	0.02	0.06	-0.90	11.77			
Neustift	-2.59	0.16	0.17	0.67	9.99	4.77	0.74	7.85	3.69	-7.37	0.15	0.06	0.27	-9.79	8.99			
Monte Bondone	-0.14	0.05	0.02	0.56	11.43	5.23	0.99	4.60	5.26	-1.88	0.10	0.06	0.46	-12.30	8.36			
M.Bondone&Neustift	0.93	0.05	0.05	0.67	10.81	6.58	0.67	6.75	4.81	-3.61	0.12	0.05	0.25	-8.97	9.01			
(c) SD-type																		
Amplero	0.11	0.01	0.03	-0.18	12.80	10.74	0.65	-5.09	11.73	2.52	-0.03	0.02	-0.08	-13.04	9.48			
Neustift	2.71	0.04	0.15	-0.48	28.93	9.75	0.53	12.63	5.57	0.30	0.01	0.07	-0.33	-21.85	13.17			
Monte Bondone	0.07	0.04	0.02	0.77	8.39	5.39	0.62	12.75	7.23	-0.89	0.09	0.06	0.40	-14.56	9.85			
M.Bondone&Neustift	-0.05	0.06	0.03	0.68	11.36	6.39	0.67	10.70	5.59	-0.86	0.09	0.06	0.39	-13.66	8.92			

Table S5. Results of validation of linear regression models between VIs ((a) NSD-type; (b) SR-type; (c) SD-type) and ecophysiological parameters: for the daily averaged GPP,  $\varepsilon$  and NEE. Validation was performed by applying the three different models for Amplero, Neustift, Monte Bondone and a model parameterized grouping Neustift and Monte Bondone (M.Bondone&Neustift). slope—slope of linear model; y-int—intercept of linear model, and RMSE—Root Mean Square Error.

		GPP			3			NEE	
Madal	slope	y-int	RMSE	slope	y-int	RMSE	slope	y-int	RMSE
wodel	-	$\mu mol_{CO2}$	µmol <sub>CO2</sub>	-	$\mu mol_{CO2}$	$\mu mol_{CO2}$	-	µmol <sub>CO2</sub>	µmol <sub>CO2</sub>
		$m^2s$	$m^2s$		$\mu mol_{phot}$	$\mu mol_{phot}$		$m^2s$	$m^2s$
(a) NSD-type									
Amplero	0.11	4.80	13.04	-0.18	0.02	0.01	0.26	-0.74	9.39
Neustift	0.25	13.90	5.07	-2.59	0.05	0.08	-0.04	-11.91	9.06
Monte Bondone	0.32	9.00	5.38	-1.44	0.11	0.07	0.24	-7.12	6.27
M.Bondone&Neustift	0.21	12.18	5.70	-3.90	0.10	0.08	0.13	-8.59	6.88
(b) SR-type									
Amplero	0.11	4.80	13.04	-0.18	0.02	0.01	0.26	-0.76	9.40
Neustift	-0.34	19.60	9.94	-2.76	0.05	0.07	-0.05	-11.79	9.09
Monte Bondone	0.36	7.89	5.65	-1.45	0.11	0.07	0.24	-7.13	6.27
M.Bondone&Neustift	0.22	12.12	5.67	-3.92	0.10	0.08	0.12	-8.78	6.98
(c) SD-type									
Amplero	0.35	-0.61	13.13	0.88	0.00	0.01	-0.02	-5.40	9.79
Neustift	0.24	14.09	5.06	0.33	0.02	0.07	0.07	-9.68	7.38
Monte Bondone	0.50	6.00	5.67	-1.47	0.10	0.05	0.32	-6.51	5.78
M.Bondone&Neustift	0.26	12.69	4.51	-0.70	0.04	0.06	0.27	-9.25	6.37

Table S6. Results of the correlation ( $R^2$ —Coefficient of determination) between the best NDS, SR and SD-type indices selected for the daily averaged GPP,  $\varepsilon$  and NEE and dry phytomass, nitrogen and water content for Amplero, Neustift, Monte Bondone and all sites pooled. Statistical significance is indicated as \* (p < 0.05), \*\* (p < 0.01), and \*\*\* (p < 0.001).

			GPP	3	NEE
Index	Site	Parameter	R <sup>2</sup>	R <sup>2</sup>	R <sup>2</sup>
			(-)	(-)	(-)
NSD-type	Amplero	Dry phytomass (g m <sup>-2</sup> )	0.67**	0.79**	0.69**
	Amplero	Nitrogen content (%)	0.38	0.29	0.31
	Amplero	Water content (%)	0.66**	0.28	0.72**
	Neustift	Dry phytomass (g m <sup>-2</sup> )	0.02	0.29	0.06
	Neustift	Nitrogen content (%)	0.07	0.83**	0.02
	Neustift	Water content (%)	0.04	0.64*	0.00
	Monte Bondone	Dry phytomass (g m <sup>-2</sup> )	0.56***	0.48***	0.27*
	Monte Bondone	Nitrogen content (%)	0.50***	0.44***	0.25*
	Monte Bondone	Water content (%)	0.45	0.37	0.18
	All	Dry phytomass (g m <sup>-2</sup> )	0.02	0.04	0.00
	All	Nitrogen content (%)	0.04	0.46***	0.10*
	All	Water content (%)	0.01	0.13*	0.01
SR-type	Amplero	Dry phytomass (g m <sup>-2</sup> )	0.67**	0.81*	0.69**
	Amplero	Nitrogen content (%)	0.37	0.30	0.31
	Amplero	Water content (%)	0.66**	0.28	0.72**
	Neustift	Dry phytomass (g m <sup>-2</sup> )	0.02	0.29	0.06
	Neustift	Nitrogen content (%)	0.00	0.85**	0.03

	Neustift	Water content (%)	0.15	0.64*	0.00
	Monte Bondone	Dry phytomass (g m <sup>-2</sup> )	0.55***	0.49***	0.27*
	Monte Bondone	Nitrogen content (%)	0.49***	0.45***	0.24*
	Monte Bondone	Water content (%)	0.45***	0.38	0.18*
	All	Dry phytomass (g m <sup>-2</sup> )	0.01	0.05	0.00
	All	Nitrogen content (%)	0.03	0.45***	0.10
	All	Water content (%)	0.01	0.14*	0.01
SD-type	Amplero	Dry phytomass (g m <sup>-2</sup> )	0.66**	0.79**	0.71**
	Amplero	Nitrogen content (%)	0.24	0.26	0.31*
	Amplero	Water content (%)	0.58*	0.35	0.71**
	Neustift	Dry phytomass (g m <sup>-2</sup> )	0.02	0.20	0.01
	Neustift	Nitrogen content (%)	0.11	0.81**	0.45
	Neustift	Water content (%)	0.06	0.64*	0.09
	Monte Bondone	Dry phytomass (g m <sup>-2</sup> )	0.32**	0.52***	0.22*
	Monte Bondone	Nitrogen content (%)	0.31**	0.45***	0.30**
	Monte Bondone	Water content (%)	0.32**	0.40***	0.23
	All	Dry phytomass (g m <sup>-2</sup> )	0.08	0.19**	0.03
	All	Nitrogen content (%)	0.02	0.31***	0.00
	All	Water content (%)	0.02	0.03	0.00