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BACKGROUND

Using proton transfer reaction mass spectrometry (PTR-MS) equipped with a quadrupole mass analyser to quantify the biosphere-atmosphere exchange of **volatile organic compounds (VOC)**, concentrations of different VOC are measured sequentially. Depending on how many VOC species are targeted and their respective integration times, each VOC is measured at repeat rates on the order of a few seconds. This represents an order of magnitude longer sample interval compared to the standard eddy covariance method, where repeat rates of ten to twenty times a second are commonly used. Here we simulate the effect of **disjunct sampling** on eddy covariance flux estimates by progressively decreasing the time resolution of CO₂ and H₂O fluxes measured at 20 Hz above a temperate mountain grassland in the Stubai Valley (Austria).

Fluxes for one month are calculated with the standard eddy covariance method and compared to fluxes calculated based on the disjunct data (1, 3 and 5s sampling rates) using three different approaches.



Neustift, Stubai Valley

METHODS

Fluxes have been calculated using the original, 20Hz-data and three different gap-filling (GF) methods:

i) **GFs**: gap-filling method after Spirig et al. (2005). The disjunct concentration measurements were filled up to the time resolution of the wind components (20 Hz) by repeating each disjunct concentration in time half of the sampling interval before and after the disjunct measurement.

ii) **GFI**: gaps between disjunct measurements were filled using linear interpolation.

iii) **vDEC**: virtual disjunct eddy covariance (vDEC) as suggested by Karl et al. (2002). Fluxes were calculated without filling the gaps between the disjunct concentration measurements.

Fig. 1 shows the resulting time series of the three methods in comparison to the **original data**.

RESULTS & CONCLUSION

Our cross-correlation analyses used for lag determination (**Fig. 2**) show **smoothing of the peak**, and an ~ 0.7 s and 1 s lag for the original CO₂ and H₂O data, respectively. The vDEC sampling approach shows a similar effect (insets in **Fig. 2**), but with **more noise**. In contrast, the **GFs** and **GFI** methods both show a **longer lag time** (as shown in the frequency distribution of observed lag times; **Fig. 2**), and additional **reduction in the peak correlation magnitude**.

Table 1 shows the results of a linear regression analysis of fluxes calculated with the original 20 Hz data against the three methods. Increasing the disjunct sampling interval **increased flux loss** (defined here as slopes < unity) and variability (i.e. decreased the r^2). The choice of the integration time had little influence on this general pattern. Flux loss was least for the vDEC method, where a maximum flux loss of 7 and 11 % ($\Delta T = 5$ s) was observed for CO₂ and H₂O, respectively. For the **GFs** and **GFI** methods flux loss increased up to 24 (28) and 29 (33) % for CO₂ (H₂O), respectively, with $\Delta T = 5$ s.

In search for the cause of the considerable flux loss with the **GFs** and **GFI** methods we performed a co-spectral analysis, which showed that these two methods suffered from additional low-pass filtering (**Fig. 3**).

Using the cut-off frequencies shown in **Fig. 4** and implementing an additional empirical transfer-function based correction proposed by Aubinet et al. 2000 allowed us to correct **GFs** and **GFI** for their respective flux losses, resulting in **cGFs** and **cGFI**.

In conclusion, all approaches investigated in this study yielded reasonable results (as compared to the original 20 Hz data), provided that the appropriate corrections for flux loss were applied. The vDEC method involved **fewer empirical corrections** and may thus be regarded as the best choice for dealing with disjunct data from a theoretical point of view, even though the noisy nature of the cross-correlations poses problems with lag determination using the maximum cross-correlation method.

		Integration period														
		50 ms				250 ms				500 ms						
		ΔT	k	d	r^2	k	d	r^2	k	d	r^2	k	d	r^2		
CO ₂	vDEC	0.96	0.18	0.99	0.96	0.17	0.99	0.95	0.18	0.99	0.95	0.18	0.99	0.95	0.18	0.99
		0.85	0.09	1.00	0.86	0.10	1.00	0.85	0.14	1.00	0.85	0.14	1.00	0.85	0.14	1.00
		1.01	0.04	1.00	1.02	0.07	1.00	1.02	0.11	1.00	1.02	0.11	1.00	1.02	0.11	1.00
		0.83	0.11	1.00	0.83	0.14	1.00	0.83	0.17	1.00	0.83	0.17	1.00	0.83	0.17	1.00
	cGFI	1.01	0.06	1.00	1.02	0.09	1.00	1.02	0.13	1.00	1.02	0.13	1.00	1.02	0.13	1.00
		0.96	0.04	0.98	0.97	0.16	0.99	0.95	0.07	0.99	0.95	0.07	0.99	0.95	0.07	0.99
		0.84	0.26	0.98	0.84	0.29	0.98	0.84	0.33	0.98	0.84	0.33	0.98	0.84	0.33	0.98
		1.01	0.17	1.00	1.02	0.20	1.00	1.03	0.25	1.00	1.03	0.25	1.00	1.03	0.25	1.00
	GFI	0.80	0.31	0.98	0.80	0.34	0.98	0.80	0.38	0.98	0.80	0.38	0.98	0.80	0.38	0.98
		1.01	0.21	0.99	1.02	0.24	0.99	1.03	0.29	0.99	1.03	0.29	0.99	1.03	0.29	0.99
		0.95	0.16	0.97	0.95	0.07	0.97	0.95	0.11	0.98	0.95	0.11	0.98	0.95	0.11	0.98
		1.01	0.23	0.99	1.02	0.28	0.99	1.01	0.32	0.99	1.01	0.32	0.99	1.01	0.32	0.99
cGFI	0.71	0.41	0.96	0.71	0.43	0.96	0.71	0.44	0.96	0.71	0.44	0.96	0.71	0.44	0.96	
	1.00	0.28	0.99	1.02	0.31	0.99	1.01	0.33	0.99	1.01	0.33	0.99	1.01	0.33	0.99	
	0.95	2.35	0.99	0.95	2.02	0.99	0.94	2.09	1.00	0.94	2.09	1.00	0.94	2.09	1.00	
	0.96	1.56	1.00	0.96	1.65	1.00	0.95	1.89	1.00	0.95	1.89	1.00	0.95	1.89	1.00	
H ₂ O	vDEC	1.01	0.50	1.00	1.01	0.47	1.00	1.00	0.84	1.00	1.00	0.84	1.00	1.00	0.84	1.00
		0.93	2.01	1.00	0.93	2.20	1.00	0.93	2.39	1.00	0.93	2.39	1.00	0.93	2.39	1.00
		1.01	0.49	1.00	1.01	0.68	1.00	1.01	0.76	1.00	1.01	0.76	1.00	1.01	0.76	1.00
		0.97	1.18	0.98	0.93	0.99	0.96	0.85	1.60	0.98	0.85	1.60	0.98	0.85	1.60	0.98
	cGFI	0.83	4.20	0.99	0.83	4.18	0.99	0.82	4.29	0.99	0.82	4.29	0.99	0.82	4.29	0.99
		1.00	1.11	1.00	1.01	1.01	1.00	1.01	1.07	1.00	1.01	1.07	1.00	1.01	1.07	1.00
		0.78	4.46	0.98	0.78	4.54	0.98	0.77	4.70	0.98	0.77	4.70	0.98	0.77	4.70	0.98
		1.00	0.69	0.99	1.00	0.77	0.99	1.01	0.79	0.99	1.01	0.79	0.99	1.01	0.79	0.99
	vDEC	0.96	1.68	0.96	0.95	1.77	0.96	0.94	2.45	0.97	0.94	2.45	0.97	0.94	2.45	0.97
		0.72	5.89	0.96	0.72	5.94	0.96	0.72	5.95	0.96	0.72	5.95	0.96	0.72	5.95	0.96
		0.98	2.03	0.99	0.98	2.06	0.99	0.97	2.20	0.99	0.97	2.20	0.99	0.97	2.20	0.99
		0.67	5.71	0.95	0.67	5.81	0.95	0.67	5.89	0.95	0.67	5.89	0.95	0.67	5.89	0.95
cGFI	0.98	0.96	0.99	0.99	0.99	0.99	0.99	1.18	0.99	0.99	1.18	0.99	0.99	1.18	0.99	

Table 1 Results of a linear regression analysis of fluxes (CO₂: $\mu\text{mol m}^{-2} \text{s}^{-1}$, H₂O: $\text{J m}^{-2} \text{s}^{-1}$) calculated with the original 20 Hz data against the three methods (vDEC, **GFs**, **GFI**). **cGFs/cGFI** ... corrected method of the respective gap-filling approach; k ... slope of linear regression (dimensionless); d ... y-intercept of linear regression ($\mu\text{mol m}^{-2} \text{s}^{-1}$ and $\text{J m}^{-2} \text{s}^{-1}$ for CO₂ and H₂O, respectively); r^2 ... coefficient of determination, ΔT ... disjunct sampling interval (s)

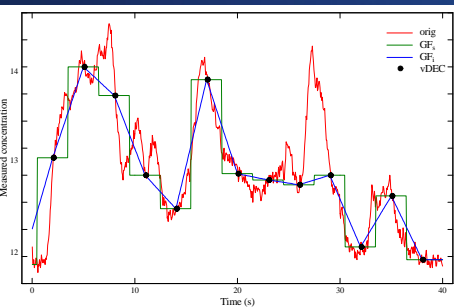


Figure 1 Example concentration time series illustrating disjunct sampling (vDEC, $\Delta T = 3$ s) of the original 20 Hz data and the **GFs** and **GFI** methods for filling gaps in the concentration time series.

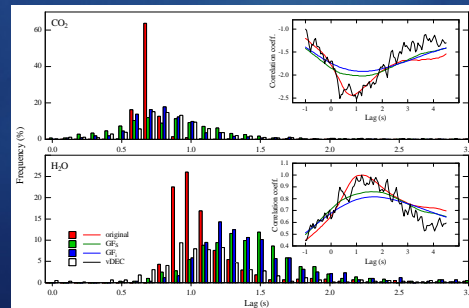


Figure 2 Frequency distribution of lag times calculated with the maximum cross-correlation method for the original data 20 Hz data and the vDEC, **GFs** and **GFI** methods. Insets show results of the cross-correlation analysis for one typical half-hourly period.

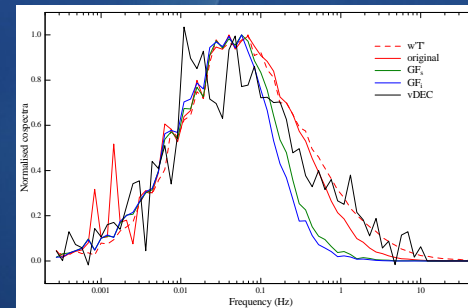


Figure 3 Average cospectra for unstable conditions of the vertical wind component (w') and concentrations of CO₂ for the vDEC, **GFs** and **GFI** methods in comparison with the original 20 Hz data. Sensible heat (wT') cospectra are shown as a reference.

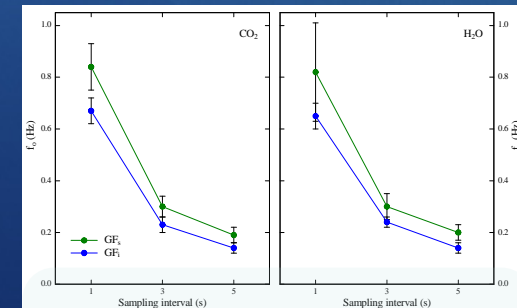


Figure 4 Parameter f_0 describing the additional low-pass filtering effect induced by the **GFs** and **GFI** methods. Error bars refer to ± 1 standard deviation.