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Six-week time series of eddy covariance CO₂ flux at Mammoth Mountain,
California: performance evaluation and role of meteorological forcing

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20

21 **Abstract**

22

23 CO₂ and heat fluxes were measured over a six-week period (09/08/2006 to 10/24/2006)
24 by the eddy covariance (EC) technique at the Horseshoe Lake tree kill (HLTK),
25 Mammoth Mountain, CA, a site with complex terrain and high, spatially heterogeneous
26 CO₂ emission rates. EC CO₂ fluxes ranged from 218 to 3500 g m⁻² d⁻¹ (mean = 1346 g
27 m⁻² d⁻¹). Using footprint modeling, EC CO₂ fluxes were compared to CO₂ fluxes
28 measured by the chamber method on a grid repeatedly over a 10-day period. Half-hour
29 EC CO₂ fluxes were moderately correlated ($R^2 = 0.42$) with chamber fluxes, whereas
30 average-daily EC CO₂ fluxes were well correlated ($R^2 = 0.70$) with chamber
31 measurements. Average daily EC CO₂ fluxes were correlated with both average daily
32 wind speed and atmospheric pressure; relationships were similar to those observed
33 between chamber CO₂ fluxes and the atmospheric parameters over a comparable time
34 period. Energy balance closure was assessed by statistical regression of EC energy fluxes
35 (sensible and latent heat) against available energy (net radiation, less soil heat flux).
36 While incomplete ($R^2 = 0.77$ for 1:1 line), the degree of energy balance closure fell
37 within the range observed in many investigations conducted in contrasting ecosystems
38 and climates. Results indicate that despite complexities presented by the HLTK, EC can
39 be reliably used to monitor background variations in volcanic CO₂ fluxes associated with
40 meteorological forcing, and presumably changes related to deeply derived processes such
41 as volcanic activity.

42

43

44 **Keywords:** CO₂ emissions; volcano monitoring; eddy covariance; chamber method;

45 Mammoth Mountain

46

47 **1. Introduction**

48

49 The measurement of surface emissions of CO₂ has become an integral part of many
50 volcanic and geothermal monitoring programs, as temporal variations in emissions may
51 indicate changes at depth associated with volcanic activity or geothermal processes (e.g.,
52 Baubron et al., 1991; Farrar et al., 1995; Chiodini et al., 1998; Hernandez et al., 1998;
53 Klusman et al., 2000; McGee et al., 2000; Bergfeld et al., 2001; Hernandez et al., 2001;
54 Werner and Cardellini, 2006). Furthermore, it is important to understand the link
55 between temporal variations in deeply derived CO₂ emissions, and meteorologic and
56 hydrologic processes, as these near-surface processes can drive large changes in CO₂
57 emissions (e.g., Connor et al., 1993; McGee and Gerlach, 1998; Rogie et al., 2001;
58 Granieri et al., 2003; Lewicki et al., 2007) that may pose health and environmental
59 hazards or be misinterpreted to reflect changes at depth.

60

61 While the chamber method (e.g., Chiodini et al., 1998) has been reliably used to measure
62 spatial and temporal variations in surface CO₂ fluxes in many volcanic and geothermal
63 regions, limitations of the method include the measurement's small spatial scale (<1 m²),
64 alteration of the ground surface and gas flow during the measurement, and the ability to
65 continuously monitor temporal changes in CO₂ fluxes at only a single or limited number

66 of point locations within a study area. The eddy covariance (EC) method, a
67 micrometeorological technique traditionally used to measure CO₂ (and other trace gas
68 and heat) fluxes across the interface between the atmosphere and a plant canopy (e.g.,
69 Baldocchi, 2003 and references therein) has been proposed as a viable and
70 complementary technique to monitor volcanic CO₂ and heat fluxes in conjunction with
71 the chamber method (Werner et al., 2000; 2003; 2006; Anderson and Farrar, 2001). EC
72 provides the benefit of an automated flux measurement that does not interfere with the
73 ground surface and is averaged over both time and space, with the spatial scale
74 significantly larger (m²-km²) than that of the chamber method. Importantly, however, the
75 theory that underlies the EC method assumes spatial homogeneity of surface fluxes, flat
76 terrain, and temporal stationarity (e.g., Folken and Wichura, 1996), conditions that are
77 not typically met in volcanic and geothermal environments.

78

79 Work in mountain ecosystems has shown that under suitable atmospheric conditions, EC
80 can provide reliable CO₂ and heat flux measurements in complex terrain (e.g., Turnipseed
81 et al., 2003; 2004). Werner et al. (2000; 2003) deployed EC from 1 to 2.5 weeks in the
82 Yellowstone National Park hydrothermal system, USA and at Solfatara volcano, Italy,
83 sites with highly heterogeneous surface CO₂ and heat fluxes, yet relatively flat terrain.
84 Using footprint modeling, they showed general consistency between EC CO₂ fluxes and
85 chamber CO₂ fluxes measured on grids, indicating that EC yielded representative
86 measurements at these sites. However, Werner et al. (2003) suggested that the relative
87 difference observed between the two methods could have been derived in part by
88 incomplete characterization of the temporal variability of surface CO₂ fluxes within the

89 study area by the chamber method over the EC measurement period. Anderson and
90 Farrar (2001) performed EC measurements of CO₂ and heat fluxes for up to four days in
91 three pilot studies at the Horseshoe Lake tree kill (HLTK) on Mammoth Mountain, USA
92 (Figure 1). The HLTK is a site with complex terrain and highly heterogeneous, yet cold
93 volcanic CO₂ emissions, thus possessing distinctly different characteristics from the
94 Yellowstone and Solfatara areas. While they found average EC CO₂ flux measurements
95 to be generally similar to chamber measurements made in separate studies, footprint
96 modeling as performed by Werner et al. (2000; 2003) would have been required to
97 directly compare the results derived from these two methods.

98

99 We build on the work of Werner et al. (2000; 2003) and Anderson and Farrar (2001) by
100 presenting a six-week time series of EC CO₂ fluxes measured at the HLTK. We assess
101 the quality of EC CO₂ and heat flux measurements by comparing them to measurements
102 made by independent techniques. In particular, EC CO₂ fluxes were compared to
103 chamber CO₂ fluxes over a 10-day period when spatio-temporal variations in surface CO₂
104 fluxes were captured by repeated chamber measurements on a grid. Despite the
105 complexities presented by the study site, we show that under certain atmospheric
106 conditions, the EC method performs well relative to independent methods. Finally, the
107 multi-week time series of EC fluxes allowed us to establish relationships between
108 temporal variations in surface CO₂ fluxes and meteorological parameters on time scales
109 longer than a day.

110

111 **2. Study Site**

112

113 Mammoth Mountain (3368 m) is a dormant dacitic volcano formed 200,000 to 50,000
114 years ago on the southwestern rim of Long Valley caldera, eastern California (Figure 1).
115 While lavas were last erupted ~50,000 years ago, phreatic eruptions occurred up to ~700
116 years ago (Bailey, 1989). Recent volcanic unrest associated with Mammoth Mountain
117 was first detected in 1979 and activity was subsequently expressed as ground
118 deformation, swarms of small earthquakes ($M \leq 3$), spasmodic bursts, long-period and
119 very long-period earthquakes, elevated $^3\text{He}/^4\text{He}$ ratios in fumarolic gases, and diffuse
120 surface CO_2 emissions (Hill and Prejean, 2005). An eleven-month-long seismic swarm
121 occurred at Mammoth Mountain in 1989, possibly related to dike intrusion and/or
122 magmatic fluid migration (Hill, 1996; Hill and Prejean, 2005). Tree kills then formed in
123 six general areas on Mammoth Mountain in 1990-1991 due to diffuse, non-thermal
124 emissions of volcanic CO_2 resulting in high CO_2 concentrations in the root zone (e.g.,
125 Farrar et al., 1995).

126

127 The HLTK is the largest ($\sim 120,000 \text{ m}^2$) tree kill on Mammoth Mountain and is located on
128 the northwest shore of Horseshoe Lake, on the southeast flank of the volcano (Figure 1).
129 It lies in the Lakes Basin, with terrain sloping upward to the west-northwest (Figures 1
130 and 2). Soils here are largely barren of vegetation, 1 to 3 m thick, and composed of 0.1 to
131 0.4 m of pumice overlying coarse sand with cobbles to boulders and low organic carbon
132 (McGee and Gerlach, 1998; Evans et al., 2001). Horseshoe Lake is perched, while the
133 water table here is located at ~40 m depth (HSL-1 well; Farrar et al., 1998).

134

135 Extensive monitoring of subsurface CO₂ concentrations and surface CO₂ fluxes has been
136 conducted at the HLTK (e.g., Farrar et al., 1995; Rahn et al., 1996; Gerlach et al., 1998;
137 McGee and Gerlach, 1998; McGee et al., 2000; Gerlach et al., 2001; Anderson and
138 Farrar, 2001; Rogie et al., 2001; Lewicki et al., 2007). Studies have reported large
139 diurnal to seasonal fluctuations in time series of soil CO₂ concentrations, surface CO₂
140 fluxes, and total CO₂ discharges that appear to be due to variations in meteorological and
141 hydrologic processes (e.g., McGee and Gerlach, 1998; McGee et al., 2000; Rogie et al.,
142 2001). Also, Lewicki et al., (2007) showed that large spatio-temporal variations in
143 surface CO₂ fluxes over multiple days can be driven by slow-moving cold fronts.
144 Furthermore, long-term monitoring suggests that emissions have markedly declined over
145 the past decade. For example, the average estimated CO₂ discharge from the tree kill
146 area was ~250 t d⁻¹ for 1995 to 1997 (Gerlach et al., 1998) and 93 t d⁻¹ for 1997 to 2000
147 (Rogie et al., 2001), whereas the average discharge measured in 2006 was 38 t d⁻¹
148 (Lewicki et al., 2007).

149

150 **3. Methods**

151

152 *3.1. Eddy covariance measurements*

153

154 An EC station (2.5 m high; see below) was deployed at the HLTK (Figure 2)
155 continuously from 09/08/2006 to 10/24/2006. The location of the station was chosen to
156 take advantage of the westerly prevailing winds and the absence of asphalt road and
157 parking lot to the west. The average surface slope to the west (from directions of 190 to

158 360°) and within 100 m of the station was 9% (range = 1 to 15%; Figure 2). Within 300
159 m of the station, the average slope was 13% (range = 1 to 18%). Widely distributed tree
160 stumps, rocks, and logs were located within about 50 m of the EC station. In addition,
161 foliage-free standing dead trees, which have lost the majority of fine branches, were
162 located from about 50 to 200 m from the EC station (Figure 1).

163

164 The EC station was similar in design to that described by Billesbach et al. (2004) and was
165 composed of fast-response and slow-response subsystems. The fast-response subsystem
166 included two sensors used to measure the variables necessary to calculate turbulent fluxes
167 of CO₂, H₂O, heat, and momentum. A Gill-Solent WindMaster Pro sonic three-
168 dimensional anemometer/thermometer (Gill Instruments, Ltd) measured wind speeds in
169 three directions and sonic temperature at 10 Hz. A LI-COR 7500 open-path CO₂-H₂O
170 infrared gas analyzer (LI-COR, Inc) measured CO₂ and water vapor densities at 10 Hz.
171 Both sensors were mounted to the top of a tripod tower at 2.5 m height.

172

173 The slow-response subsystem included sensors associated with a second tripod tower that
174 measured auxiliary variables used to compare with EC fluxes and establish relationships
175 between EC fluxes and environmental parameters. Atmospheric pressure was measured
176 using a Vaisala PTB101B barometer (Vaisala, Inc.). Atmospheric temperature and
177 relative humidity were measured using a Vaisala HMP50 humidity and temperature
178 probe. Mean horizontal wind speed and direction were measured by a Climatronics
179 CS800-12 wind set (Climatronics Corp.) at 2.5 m height. Net radiation, total insolation
180 and photosynthetically active radiation (PAR) were measured with a Kipp & Zonen

181 CNR-1 radiometer (Kipp & Zonen), LI-COR LI-200SA pyranometer, and LI-COR LI-
182 190SA quantum sensor, respectively, mounted to a horizontal bar extending from the
183 tripod tower at 2 m height. Mean precipitation was measured by a TE525 tipping bucket
184 rain gage (Texas Electronics). Soil moisture profiles (10 and 30 cm depth) were
185 measured at two locations using ECH2O (Decagon Devices) soil moisture probes. Soil
186 temperature profiles (10, 20, and 30 cm depth) were measured at two locations with
187 thermocouples. Soil heat flux was measured by four HFT3 soil heat flux plates
188 (Radiation and Energy Balance Systems) located at 5 cm depth near the radiometer.
189 Slow-response subsystem variables were measured every 5 seconds and averaged over 30
190 minutes for comparison with turbulent fluxes.

191

192 Carbon dioxide, latent heat (LE), sensible heat (H), and momentum fluxes (F_s) were
193 calculated as the temporal covariance of the scalar (s) and vertical wind velocity (w):

194

$$195 \quad F_s = \overline{w's'} \quad (1)$$

196

197 where the overbar denotes time averaging and primes denote deviations from a mean.

198 Fluxes were calculated for 30-minute periods. Equation 1 gives the mean vertical
199 turbulent flux of the scalar of interest over a horizontally homogeneous surface under
200 steady-state conditions. Details on the theory and assumptions of the EC method can be
201 found in Baldocchi et al. (1988); Foken and Wichura (1996); Aubinet et al. (2000);
202 Baldocchi (2003).

203

204 For each half-hour of data, the mean lateral (\bar{v}) and then the mean vertical (\bar{w}) wind
205 velocities were rotated to zero (Kaimal and Finnigan, 1994). The Webb correction for the
206 effects of fluctuation in heat and water vapor on the density of air (Webb et al., 1980)
207 was applied. Raw signals from the infrared gas analyzer and sonic anemometer were
208 evaluated for voltage spikes and all points more than ten standard deviations (thereby
209 accepting a non-Gaussian tail to the data) away from a 60 s moving average were
210 removed from the data. Turbulent fluxes measured during periods of insufficient
211 turbulent mixing are typically underestimated. To filter data for this effect, friction
212 velocities (u_*) were calculated as the square root of the momentum flux. Figure 3 shows
213 a plot of EC CO₂ flux versus u_* for all EC measurements corresponding to mean wind
214 directions from 190 to 360° (i.e., hereafter, only EC measurements corresponding to
215 mean wind directions from the tree kill area will be considered). EC CO₂ fluxes increase
216 sharply with u_* until $u_* \sim 0.25 \text{ m s}^{-1}$, above which EC fluxes remain relatively constant
217 (Figure 3). We eliminated all EC (CO₂ and heat) fluxes corresponding to $u_* \leq 0.25 \text{ m s}^{-1}$.
218 A test for stationarity was conducted according to Foken and Wichura (1995). Each 30-
219 minute EC flux measurement was divided into six five-minute segments. If the
220 difference between the average of the six five minute segments and the 30-minute
221 measurement was greater than 30%, the measurement was considered non-stationary and
222 discarded. Specific details of data filtering are also shown on each of the following
223 figures.

224

225 3.2. Chamber measurements

226

227 Surface CO₂ flux was measured using a WEST Systems fluxmeter (WEST Systems)
228 based on the chamber method, with repeatability of ±10% (Chiodini et al., 1998). Evans
229 et al. (2001) conducted laboratory measurements of imposed CO₂ fluxes over a range
230 typical of Mammoth Mountain tree kill areas through a synthetic “soil” similar in
231 properties to surficial deposits in the tree kill areas, and showed that chamber
232 measurements were negatively biased, on average by 12.5%. Collars were not used for
233 chamber measurements, due to due to the potential alteration of soil properties and gas
234 flow (e.g., Gerlach et al., 2001). Surface CO₂ flux was measured at 170 grid points at 27-
235 m spacing in the HLTK (Figure 2). Flux measurements were repeated in the same order
236 along the grid each day from 09/12/2006 to 09/21/2006 between 07:00 and 15:00, with
237 the exception of 09/15/2006 when no measurements were made. For the purpose of
238 comparison with EC CO₂ fluxes, the negative bias in chamber measurements was
239 corrected for by increasing each flux measurement by 12.5%. A map of surface CO₂ flux
240 was then produced for each day of grid measurements using nearest neighbor
241 interpolation at 5 x 5 m resolution, chosen for its simplicity in the comparison of chamber
242 to EC CO₂ flux measurements. Surface CO₂ flux maps produced using the sequential
243 Gaussian simulation method and corresponding total CO₂ discharges from the study area
244 are presented in Lewicki et al. (2007). For reference, Lewicki et al. (2005) presented a
245 comparison of a range of geostatistical interpolation and simulation methods that were
246 applied to chamber CO₂ fluxes measured in a volcanic environment.

247

248 **4. Results**

249

250 4.1. Meteorology

251

252 Atmospheric temperatures ranged from -8.3 to 20.8°C and winds were dominantly from
253 the west (Figure 4) over the study period. The highest wind speeds were measured from
254 westerly directions, while easterly winds typically corresponded to relatively low wind
255 speeds (Figure 4). Precipitation (typically light snow) occurred on six days during
256 October (10/01/2006, 10/02/2006, 10/10/2006, 10/11/2006, 10/14/2006, and 10/17/2006)
257 (Figures 5b and 7). Average daily wind speeds and atmospheric pressures varied from
258 1.1 to 3.5 m s^{-1} and 725 to 740 mbar , respectively from 09/08/2006 to 10/24/2006 (Figure
259 5a). A cold front occurred on 09/14/2006 to 09/15/2006 (Lewicki et al., 2007) and was
260 accompanied by high average daily wind speeds and low atmospheric pressures (see zone
261 I on Figure 5a). Over the entire measurement period (09/08/2006 to 10/24/2006),
262 average daily wind speeds and atmospheric pressures were moderately inversely
263 correlated (correlation coefficient = -0.43). From 09/08/2006 to 09/22/2006 (zone I,
264 Figure 5a), average daily wind speed and pressure were strongly inversely correlated
265 (correlation coefficient = -0.80). Relationships between meteorological parameters and
266 chamber CO_2 fluxes over this time period were examined in Lewicki et al. (2007). We
267 therefore selected this time frame to analyze relationships between meteorological
268 parameters and EC CO_2 fluxes for comparison. From 09/24/2006 to 10/10/2006 (zone II,
269 Figure 5a), average daily wind speed and pressure were poorly correlated (correlation
270 coefficient = 0.14). We selected zone II to examine correlations between average daily
271 wind speed, pressure, and EC CO_2 fluxes because of different meteorological conditions

272 (i.e., lack of a cold front) from zone I, and a sufficient number of EC data to perform the
273 analysis.

274

275 *4.2. Chamber fluxes*

276

277 Large spatio-temporal variations in surface CO₂ fluxes were measured using the chamber
278 method from 09/12/2006 to 09/21/2006 (Figures 5b and 6). During the first two days of
279 measurements (09/12/2006 and 09/13/2006), the spatial distribution of surface CO₂
280 fluxes remained relatively stable (Figure 6a-b). Then, on 09/14/2006 surface CO₂ fluxes
281 decreased and the region of relatively high flux began to contract in size (Figures 5b and
282 6c). On 09/16/2006, surface CO₂ fluxes continued to decrease and the region of elevated
283 flux further contracted in size (Figures 5b and 6d). CO₂ fluxes then increased and the
284 region of elevated CO₂ flux expanded outwards on 09/17/2006 to 09/18/2006 (Figures 5b
285 and 6e-f). With the exception of on 09/19/2006, surface CO₂ fluxes continued to increase
286 over the remainder of the measurement period (Figures 5b and 6g-i). Further details on
287 the spatio-temporal variations in chamber CO₂ fluxes are found in Lewicki et al. (2007).

288

289 *4.3. Eddy covariance CO₂ fluxes*

290

291 EC CO₂ fluxes measured from 09/08/2006 to 10/24/2006 ranged from 218 to 3500 g m⁻²
292 d⁻¹ (Figure 7), with a mean and standard deviation of 1346 and 575 g m⁻² d⁻¹,
293 respectively. Large gaps in the time series of CO₂ fluxes were present due to filtering for
294 mean horizontal wind direction, u_* , and stationarity. For example, 47% of the EC CO₂

295 fluxes corresponding to wind directions from 190 to 360° were lost due to filtering for u_*
296 and stationarity.

297

298 4.4. Comparison of eddy covariance to chamber CO₂ fluxes

299

300 The vertical scalar flux (e.g., of CO₂; F_{CO_2}) measured by EC at point (x_m, y_m, z_m) is the
301 integral of the contributions from all upwind surface CO₂ emissions. The relative weight
302 of each surface point source emission on F_{CO_2} depends on its location relative to the EC
303 instrumentation. F_{CO_2} is related to the distribution of source CO₂ fluxes at the surface $(x',$
304 $y', z' = z_0)$ with strength Q_{CO_2} by the footprint function or source weight function, $f(x_m -$
305 $x', y_m - y', z_m - z_0)$:

306

$$307 F_{CO_2}(x_m, y_m, z_m) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q_{CO_2}(x', y', z' = z_0) \cdot f(x_m - x', y_m - y', z_m - z_0) \cdot dx' \cdot dy' \quad (2)$$

308

309 (e.g., Horst and Weil, 1992; Schmid, 1997). The value of the footprint function generally
310 rises to a maximum some distance upwind of the EC sensors, then smoothly falls off in
311 all directions. The total surface influence on F_{CO_2} , or the source area, is the integral
312 beneath the footprint function.

313

314 Similar to the methods of Werner et al. (2000; 2003), we compared EC with chamber
315 measurements of CO₂ flux by modeling the footprint function for each half-hour EC
316 measurement from 09/12/2006 to 09/21/2006. The Flux Source Area Model (FSAM) of
317 Schmid (1997), based on analytic solutions of the advection-diffusion equation (Horst

318 and Weil, 1992) was used to model footprint functions using the following inputs: (1) z_m
319 = 2.5 m; (2) surface roughness height, $z_0 = 0.03$ m, in accordance with Anderson and
320 Farrar (2000); (3) measured mean horizontal wind direction; (4) cross-wind turbulence
321 near the surface characterized by calculated σ_v/u_* , where σ_v is the standard deviation of
322 the wind speed in the cross-wind direction; (5) calculated Monin-Obukhov length, L , if
323 corresponded to unstable atmospheric conditions (i.e., only measurements corresponding
324 to $L < 0$ were considered) (Table 1). We calculated f at the center of each 25-m² grid
325 block in Figure 6. The source area was defined here as the area within which 90% of the
326 measured EC flux was derived from. Results indicated that the source area was located
327 within ~100 m upwind of the EC station for all of the 73 footprint functions modeled
328 (mean = 86 m, range = 26 to 108 m; Figure 8). In other words, the source area was
329 contained within the tree kill area for all modeled footprint functions.

330

331 On each day from 09/12/2006 to 09/21/2006, Q_{CO_2} was assumed equal to the chamber
332 CO₂ flux in Figure 6. The product of Q_{CO_2} and f was then calculated for each 25-m² grid
333 block and summed over the source area, yielding the “footprint CO₂ flux”. Figure 9
334 shows a histogram of the relative difference between the measured EC CO₂ flux and the
335 footprint CO₂ flux, expressed as a percent of the EC flux. The mean relative difference
336 was -0.3%, with a standard error = 2.7%. The standard deviation of the relative
337 difference was 23% and the mode was offset positively from zero. No systematic
338 relationship was observed between the relative difference and L , u_* , time of day, or wind
339 direction for the ranges of values considered. A plot of EC versus footprint CO₂ flux
340 (Figure 10a) shows that the data were moderately correlated ($R^2 = 0.42$ for 1:1 line). At

341 CO₂ flux up to ~1300 g m⁻² d⁻¹, the data clustered around the 1:1 line, while at higher
342 flux, EC CO₂ fluxes tended to be biased high relative to footprint CO₂ fluxes. Mean
343 vertical wind velocities (\bar{w}) corresponding to the modeled footprints ranged from -0.43
344 to 0.03 m s⁻¹ (mean and standard deviation = -0.17 and 0.12 m s⁻¹, respectively). \bar{w} was
345 negatively correlated (correlation coefficient = -0.37) with the relative difference between
346 the EC and footprint CO₂ fluxes, such that EC CO₂ fluxes were typically greater than
347 footprint fluxes when \bar{w} was more negative.

348

349 The correlation of average daily EC and average daily footprint CO₂ flux increased
350 substantially ($R^2 = 0.70$ for 1:1 line) relative to half-hour measurements, while the
351 positive bias at flux >1300 g m⁻² d⁻¹ was reduced (Figure 10b). Furthermore, the
352 correlation between average daily \bar{w} (Table 1) and the relative difference between EC
353 and footprint CO₂ fluxes was reduced (correlation coefficient = 0.24) relative to half-hour
354 measurements.

355

356 *4.5. Relationships between temporal variations in EC CO₂ fluxes and meteorology*

357

358 To assess the relationships between temporal variations in meteorological parameters and
359 EC CO₂ fluxes, we calculated average daily EC CO₂ fluxes from 09/08/2006 to
360 10/24/2006 using fluxes corresponding to a narrow range of mean horizontal wind
361 directions (250 to 290°; Figure 5b). Since the source area changes for each EC flux
362 measurement depending on atmospheric conditions, a time series of EC fluxes is
363 influenced by both temporal variations in, and spatial heterogeneity of, surface fluxes.
364 This spatial component can complicate comparison of temporal variations in EC CO₂

365 fluxes to meteorological (or deep volcanic, hydrothermal) processes. Therefore, to limit
366 the effects of spatial heterogeneity of surface fluxes on the evaluation of temporal
367 variability of EC CO₂ fluxes, we only considered fluxes corresponding to a narrow range
368 of mean horizontal wind directions (250 to 290°) in the calculation of average daily EC
369 CO₂ fluxes (Figure 5b). However, in this simple analysis, it was not possible to assess
370 changes in the same flux source area over time.

371

372 No systematic relationship was observed between average daily EC CO₂ flux and average
373 daily atmospheric or soil temperature. A decrease in average daily and half-hour EC CO₂
374 fluxes was observed during precipitation events on 10/01/2007-10/02/2007 and
375 10/10/2007-10/11/2007 and in half-hour measurements on 10/17/2007 (Figures 5b and
376 7). Changes in EC flux associated with snowfall on 10/14/2007 were not possible to
377 assess due to gaps in the time series of EC flux. From 09/08/2006 to 10/24/2006, average
378 daily EC CO₂ flux was most strongly positively correlated with average daily
379 atmospheric pressure (correlation coefficient = 0.52) and inversely correlated with
380 average daily wind speed (correlation coefficient = -0.33) at one-day time lag (Figure 5a
381 and b). From 09/08/2006 to 09/22/2006 (zone I, Figure 5a and b), average daily EC CO₂
382 flux was more strongly correlated with average daily wind speed (correlation coefficient
383 = -0.70) than with average daily atmospheric pressure (correlation coefficient = 0.57).
384 However, from 09/24/2006 to 10/10/2006 (zone II, Figure 5a and b), EC CO₂ flux was
385 more strongly correlated with atmospheric pressure (correlation coefficient = 0.64) than
386 with wind speed (correlation coefficient = -0.39).

387

388 4.6. Eddy covariance heat fluxes

389

390 Measured H from 09/08/2006 to 10/24/2006 ranged from -91.9 to 466 W m^{-2} , with a
391 mean and standard deviation of 52.2 and 106.2 W m^{-2} , respectively. Measured LE ranged
392 from -99.9 to 176.4 W m^{-2} , with a mean and standard deviation of 19.3 and 34.7 W m^{-2} ,
393 respectively.

394

395 Neglecting the heat stored in the air beneath the sensors and horizontal advection, the
396 one-dimensional energy balance for the tree kill can be written as:

397

$$398 \quad Rn - G = LE + H, \quad (3)$$

399

400 where Rn and G are the net radiation and heat flux into the soil, respectively. Their
401 difference represents the available energy. Figure 11 shows $LE + H$ versus $Rn - G$
402 measured at the HLTK from 09/08/2006 to 10/24/2006. Data were categorized based on
403 time of day using PAR measurements and atmospheric stability using the stability
404 parameter ξ

405

$$406 \quad \xi = \frac{z_m - d}{L} \quad (4)$$

407

408 (Garrat, 1992). d is the zero-plane displacement, estimated as 63% of canopy height,
409 which we assumed to equal zero based on absence of a canopy within the much of the
410 source areas. Measured turbulent heat fluxes were well correlated with available energy

411 ($R^2 = 0.77$ for 1:1 line). We calculated the relative difference between $H + LE$ and $Rn -$
412 G , expressed as percent of $H + LE$. Systematic energy imbalances were observed,
413 depending on time of day and atmospheric stability. The mean relative difference for
414 energy fluxes measured at night was 44.1%. For fluxes measured during the day during
415 neutral and stable conditions ($\xi > -0.1$), the mean relative difference was -47.3%, whereas
416 it was -34.8% for fluxes measured during unstable-daytime ($\xi \leq -0.1$) periods. No
417 systematic relationships were observed between \bar{w} and the relative difference between H
418 $+ LE$ and $Rn - G$.

419

420 **5. Discussion**

421

422 *5.1. Performance evaluation of eddy covariance*

423

424 The average CO_2 flux ($1346 \text{ g m}^{-2} \text{ d}^{-1}$) measured by EC from 09/08/2006 to 10/24/2006 at
425 the HLTK (Figure 7) fell within the range of average fluxes (691 to $1382 \text{ g m}^{-2} \text{ d}^{-1}$)
426 measured by Anderson and Farrar (2001) during their three sampling campaigns in 1996-
427 1998. While the general similarity of measured values is encouraging, direct comparison
428 of the two studies is not possible due to the different flux source areas that were sampled
429 in the two studies. For example, the EC stations in the Anderson and Farrar (2001) study
430 were located north of our EC station (Figure 2); thus, portions of asphalt parking lot were
431 likely located within their flux source areas. In addition, comparison of EC fluxes
432 measured in the different studies will also be complicated by the large spatial-temporal

433 variations in surface CO₂ fluxes that occur within the tree kill on diurnal to inter-annual
434 timescales (e.g., Gerlach et al., 1998; Rogie et al., 2001; Lewicki et al., 2007).
435
436 We used footprint modeling to compare EC to chamber measurements of CO₂ fluxes at
437 the HLTK. With a mean relative difference of $-0.3 \pm 2.7\%$ between half-hour EC and
438 footprint CO₂ fluxes (Figure 9), the measurements were on average nearly unbiased. At
439 relatively high flux, half-hour EC CO₂ fluxes tended to be biased high, relative to
440 footprint CO₂ fluxes. Also, datasets for the HLTK were moderately correlated (Figure
441 10a), with a variance in the relative difference of 23%. Table 2 shows relative
442 differences between EC and chamber CO₂ fluxes in volcanic and hydrothermal systems.
443 Using footprint models to compare chamber to EC CO₂ fluxes, the Werner et al. (2000;
444 2003) investigations are most analogous to this study. Our results for the HLTK were
445 similar to those reported by Werner et al. (2003) for diffusely degassing areas of
446 Solfatara volcano, Italy (Figure 10a; Table 2). On average, a larger relative difference
447 was observed between EC and chamber CO₂ fluxes for the Yellowstone National Park
448 data, likely due in part to the presence of hydrothermal features within the EC source
449 areas (Werner et al., 2000). Also, a larger dataset would be required for Yellowstone for
450 closer comparison with other studies. While Anderson and Farrar (2001) did not directly
451 compare EC to chamber CO₂ fluxes at the HLTK based on footprint modeling, they
452 reported relative differences between average EC CO₂ fluxes calculated for the duration
453 of their pilot studies and average chamber CO₂ fluxes measured in independent studies.
454 Based on this analysis, they reported significantly larger negative bias in EC relative to
455 chamber flux measurements than reported in other studies (Table 2).

456

457 Several factors may account for the differences observed between half-hour EC and
458 footprint CO₂ fluxes (Figures 9 and 10a). First, both the EC method and the analytic
459 footprint model assume homogeneous surface fluxes, flat terrain, and uniform surface
460 roughness. However, systematic errors associated with violations to these assumptions
461 could be difficult to diagnose because they will depend on interactions between terrain,
462 wind direction and speed, and atmospheric stability. EC fluxes were on average
463 unbiased relative to footprint fluxes and no systematic relationship was observed when
464 comparing the relative difference between the EC and footprint CO₂ fluxes and the
465 ranges of L , u_* , time of day, or wind direction considered in the analysis. However, we
466 observed positive bias of EC relative to footprint CO₂ fluxes at relatively high flux. Also,
467 the relative difference between EC and footprint CO₂ fluxes increased as \bar{w} became
468 more negative. Non-zero \bar{w} values can be indicative of advective flux (e.g., Lee, 1998;
469 Turnipseed et al., 2003), but interpretations of their effect on EC fluxes vary. Lee (1998)
470 suggested that horizontal flow divergence below the EC measurement height caused
471 negative \bar{w} and loss of CO₂ flux at night under stable conditions over a deciduous forest.
472 However, over a coniferous forest in mountainous terrain, Turnipseed et al. (2003)
473 interpreted positive \bar{w} values and loss of CO₂ flux at night under stable stratification to
474 reflect flow convergence near the EC tower due to local changes in terrain. We only
475 deployed a single EC station, and so we cannot assess the horizontal advective fluxes
476 necessary to close the conservation of mass equations that would be required to
477 understand the sign and cause of the bias we observe. We suspect that the negative bias
478 in \bar{w} and positive bias in EC CO₂ flux at high flux we observe under unstable conditions

479 likely result from air flow changes as wind interacts with the complicated terrain of the
480 study area. Presumably, a planar-fit coordinate rotation (Wilczak et al., 2001) could be
481 used to reduce vertical-wind bias. Finally, the effects of wind drag on downhill
482 horizontal flows would likely only subtly affect wind speed gradients, since standing
483 dead wood within the EC source areas was sparsely distributed and free of foliage and
484 fine branches. In fact, the observed negative bias in \bar{w} is opposite to what we might
485 expect if wind drag slowed airflow and forced up-flow near the EC station.

486

487 Second, aspects of the chamber method can lead to underestimation or overestimation of
488 soil CO₂ fluxes. For example, fluxes measured by vented chambers can be systematically
489 high during windy times due to Venturi effects (e.g., Conen and Smith, 1998). While we
490 cannot rule this effect out for all measurements, we did not find evidence for systematic
491 overestimation of chamber CO₂ fluxes at the HLTK. In addition, some infiltration of
492 atmospheric air into the chamber during windy periods could have occurred, biasing
493 chamber CO₂ fluxes low. However, this effect would not account for the spatially
494 systematic decrease in soil CO₂ flux that was observed on 09/14/2007 with high average
495 daily wind speed, and then following the passage of the cold front on 09/16/2007 when
496 low average daily wind speed was observed (Figure 6; Lewicki et al., 2007). Rather, we
497 would expect wind-driven air infiltration into the chamber to affect chamber flux
498 measurements randomly over the study area. Placement of the chamber on the soil
499 surface disturbs the soil properties and gas flow during the time of measurement, which
500 can lead to systematically low flux measurements when advective soil gas flow occurs
501 (Welles et al., 2000; Evans et al., 2001). While we attempted to correct chamber

502 measurements for this effect prior to the footprint analysis, it is possible that chamber
503 fluxes were under-corrected at relatively high flux, thus potentially contributing to the
504 high EC relative to footprint CO₂ fluxes.

505

506 Third, we demonstrated that large variations occur in the spatial distribution and
507 magnitude of surface CO₂ fluxes over relatively short periods of time within the tree kill
508 area (Figure 6), which are difficult to characterize with the chamber method, even when
509 measurements are repeated on a daily basis. As a result, our assumption that on any
510 given day, over the entire day, the distribution of source CO₂ fluxes is equal to the
511 measured chamber fluxes on that day probably introduced error into the comparison.

512 Finally, random errors associated with both the EC and chamber methods (e.g., Chiodini
513 et al., 1998; Baldocchi, 2003) were likely important sources of variability in the
514 comparison. Nonetheless, given all of the complexities of the HLTK site, it is
515 encouraging that relatively small biases exist in our dataset, which reinforces our
516 assertion that the EC method may be used with some success in such environments.

517

518 When the half-hour EC and footprint CO₂ fluxes were averaged over daily timescales, the
519 correlation improved substantially (Figure 10b). Also, the positive bias observed at
520 relatively high flux in half-hour EC relative to footprint CO₂ fluxes was reduced in the
521 average daily fluxes. Since each grid of chamber measurements was typically completed
522 over ~8 hours on a given day, averaging EC and footprint CO₂ fluxes over day-long
523 periods allowed us to evaluate the measurements over more comparable timescales. This
524 likely contributed to the improved correlation observed between average daily EC and

525 footprint CO₂ fluxes. Our results suggest that if monitoring variations in surface CO₂
526 fluxes over timescales longer than a day is adequate for the investigation of interest (e.g.,
527 volcano monitoring), then the EC technique can perform well under certain complex site
528 conditions.

529

530 Average *H* and *LE* values measured from 09/08/2006 to 10/24/2006 fell within the range
531 of average values measured by Anderson and Farrar (2001) during their three sampling
532 campaigns at the HLTK. These values were lower than those measured by Werner et al.
533 (2006) at Solfatara volcano, which is expected due to the relatively high soil temperatures
534 and steam condensation in soils in the Solfatara hydrothermal area. Also, Werner et al.
535 (2006) found that measurements of *H* and *LE* were positively correlated with EC CO₂
536 fluxes in the Solfatara hydrothermal area, reflecting a large volcanic component in all
537 fluxes. We found no systematic relationship between these parameters at the HLTK, due
538 to the different sources of heat (non-volcanic) and CO₂ (volcanic).

539

540 We further assessed the performance of EC at the HLTK by comparing EC heat flux
541 measurements to measurements made by independent methods. While the degree of
542 energy balance closure obtained in the field is directly applicable to evaluation of *H* and
543 *LE*, its utility in the evaluation of CO₂ fluxes will depend on whether sources of error are
544 associated with the EC method or in determining the available energy terms (e.g., Wilson
545 et al., 2002). The degree of energy balance closure observed (Figure 11) fell within the
546 range of that observed at FLUXNET sites, where energy fluxes were measured over a
547 wide range of ecosystems and climates, typically with more ideal terrain and surface flux

548 characteristics than observed at the HLTK (Wilson et al., 2002). Turbulent heat fluxes at
549 the tree kill were typically underestimated relative to available energy during daytime
550 hours, whereas during nighttime hours, turbulent heat fluxes were overestimated relative
551 to available energy.

552

553 Lack of complete energy balance closure can result from a range of issues, including
554 systematic and random sampling errors, lack of complete estimation of heat stored
555 beneath the EC sensors, inherent low and high pass filtering associated with the EC
556 method, and advection of heat induced by horizontal heterogeneity of surface fluxes and
557 complex terrain (e.g., Wilson et al., 2002). While it is not possible to unequivocally
558 determine the sources of error and their relative importance in the energy balance
559 assessment, one or more issues could be relevant to the HLTK area. First, the source
560 areas sampled by the soil heat flux plates (cm^2 scale), net radiometer (m^2 scale), and EC
561 vary between one another by up to several orders of magnitude. Therefore, variations in
562 the surface conditions (e.g., slope geometry and sun facing angle, presence of rocks and
563 standing/fallen deadwood) and climate within the different source areas likely induced
564 systematic biases in the energy balance calculation. Second, while the poorer energy
565 balance closure observed during neutral-and-stable-daytime relative to unstable-daytime
566 periods could be due in part to heat storage in the air beneath the EC sensors, this effect
567 was unlikely to be substantial because of the short height of the EC system and either
568 near-absence of a canopy in the EC system source areas. Third, advection associated
569 with wind speed gradients could, in principal, bias EC heat fluxes similarly to CO_2 .
570 Since we observed (1) no systematic relationship between \bar{w} and the relative difference

571 between $H + LE$ and $Rn - G$ and (2) substantially greater bias in EC heat flux versus
572 available energy measurements than in EC versus footprint CO_2 fluxes, it is likely that
573 the role of advection is minor relative to other factors such as difference in source area in
574 the lack of energy balance closure at the HLTK.

575

576 *5.2. Influence of meteorological forcing on surface CO_2 fluxes*

577

578 Lewicki et al. (2007) showed that large spatio-temporal variations in surface CO_2 fluxes
579 measured by the chamber method at the HLTK from 09/12/2006 to 09/21/2006 were
580 meteorologically driven. They calculated total CO_2 discharge rates for the study area
581 based on chamber measurements and found them to be positively correlated with average
582 daily atmospheric pressure and inversely correlated with average daily wind speed, most
583 strongly at one-day time lag. While the processes driving these relationships likely
584 involved complex interactions between meteorology, topography, and vadose zone gas
585 flow, Lewicki et al. (2007) suggested that spatio-temporal changes in surface CO_2 fluxes
586 may have been primarily due to dynamic coupling between the flow of volcanic CO_2 at
587 depth within the vadose zone and wind.

588

589 Despite the complications introduced into the EC CO_2 flux time series by the temporally
590 varying flux source area, we observed similar relationships between average daily EC
591 CO_2 fluxes and average daily wind speed and atmospheric pressure from 09/08/2006 to
592 09/22/2006 (zone I, Figure 5a and b) to those observed by Lewicki et al. (2007) for
593 chamber measurements over a similar time period. The relatively high degree of

594 correlation observed between average daily EC CO₂ flux and wind speed from
595 09/08/2006 to 09/22/2006 was likely due to the cold front that passed through the region
596 during that time bringing high winds that could have modulated vadose zone gas flow
597 (Lewicki et al., 2007). However, from 09/24/2006 to 10/10/2006 (zone II, Figure 5), EC
598 CO₂ flux was more strongly correlated with atmospheric pressure and more weakly
599 correlated with wind speed. This was probably due to the lower magnitude variations in
600 average daily wind speed over this time period having less influence on subsurface gas
601 flow to the atmosphere. Overall, our results indicate that similar to the chamber method,
602 EC can be used to monitor background changes in volcanic CO₂ fluxes driven by
603 meteorological forcing, and presumably changes related to deeply derived processes such
604 as volcanic activity.

605

606 It is likely that precipitation events, and associated increases in soil moisture content also
607 affected surface CO₂ fluxes at the HLTK. However, it was only possible to assess the
608 relationship between EC CO₂ fluxes and precipitation in a limited fashion due to gaps in
609 the time series of EC flux caused by data filtering for wind direction, u_* , and stationarity.
610 This emphasizes the issue that potentially large gaps in time series of EC flux data must
611 be tolerated, particularly at a site such as the HLTK. For example, we lost about half of
612 the half-hour EC CO₂ flux data for the given wind direction range of interest (190 to
613 360°) due to insufficient turbulence and non-stationarity in the data. Automated and
614 continuous chamber measurements at a fixed location within the study area (e.g., Rogie et
615 al., 2001; Werner et al., 2003) would be valuable to supplement EC data.

616

617 **6. Summary and Conclusions**

618

619 We measured a six-week time series of EC CO₂ and heat fluxes at the HLTK on
620 Mammoth Mountain, a site with heterogeneous distribution of source fluxes and complex
621 terrain that challenged the underlying assumptions of EC theory.

622

623 1. Half-hour EC CO₂ fluxes were compared with chamber fluxes measured repeatedly on
624 a daily basis using footprint modeling. EC CO₂ fluxes were moderately correlated with,
625 and on average unbiased relative to, footprint CO₂ fluxes. The average relative
626 difference between HLTK EC and footprint CO₂ fluxes was similar to that reported for
627 diffusely degassing areas at Solfatara volcano, Italy (Werner et al., 2003). Even though
628 HLTK chamber CO₂ fluxes were measured on a daily basis, it was not possible to
629 completely characterize spatio-temporal variations in source CO₂ fluxes on the time scale
630 of the EC measurements. This factor, as well as advection of CO₂ due to topographic
631 variations and the inherent random errors associated with both the EC and chamber
632 methods likely contributed to the differences observed between CO₂ fluxes measured by
633 the two techniques.

634

635 2. Average daily EC CO₂ fluxes were well correlated with average daily footprint CO₂
636 fluxes, indicating that when random error is reduced in CO₂ flux measurements by
637 temporal averaging, the EC technique can perform well under certain complex site
638 conditions. However, potential volcanic and geothermal sites for deployment of EC must
639 be evaluated on an individual basis to assess viability of the method.

640

641 3. Turbulent heat fluxes were well correlated with available energy at the HLTK and the
642 degree of energy balance closure fell within the range observed in many investigations
643 conducted in contrasting ecosystems and climates with more ideal terrain and surface flux
644 characteristics.

645

646 4. Average daily EC CO₂ fluxes were correlated with both average daily wind speed and
647 atmospheric pressure over the observation period, the degree to which depended on the
648 magnitude of the fluctuations in the atmospheric parameters. The relationships between
649 EC CO₂ fluxes and wind speed and atmospheric pressure were similar to those observed
650 between chamber CO₂ fluxes and the atmospheric parameters over a comparable time
651 period. Similar to the chamber method, EC can be used to monitor background changes
652 in volcanic CO₂ fluxes driven by meteorological forcing, and presumably changes related
653 to deeply derived processes such as volcanic activity.

654

655 5. EC provides the benefit over the chamber method of a time and space-averaged
656 measurement of surface CO₂ flux that is essentially fully automated. However,
657 potentially large gaps in time series of data must be tolerated with EC, depending on site
658 characteristics and atmospheric conditions. Also, the spatial distribution of surface CO₂
659 fluxes cannot be mapped in detail by EC, as it can by the chamber method. The chamber
660 and EC methods are therefore best used together, providing complementary information
661 in volcanic gas surveillance programs.

662

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673

674

675 **References**

- 676 Anderson, D.E., Farrar, C.D., 2001. Eddy covariance measurement of CO₂ flux to the
677 atmosphere from an area of high volcanogenic emissions, Mammoth Mountain,
678 California. *Chemical Geology*, 177, 31–42.
- 679 Aubinet, M., Grelle, A., Ibrom, A., et al., 2000. Estimates of the annual net carbon and
680 water exchange of European forests: the EUROFLUX methodology. *Advances in*
681 *Ecological Research*, 30, 113–175.
- 682 Bailey, R.A., 1989. Geologic map of the Long Valley Caldera, Mono-Inyo Craters
683 volcanic chain and vicinity, eastern California, scale 1:62,500. U.S. Geological
684 Survey Miscellaneous Investigations Map, I-1933.
- 685 Baldocchi, D.D., 2003. Assessing the eddy covariance technique for evaluating carbon
686 dioxide exchange rates of ecosystems: past, present, and future. *Global Change*
687 *Biology*, 9, 479–492.
- 688 Baldocchi, D.D., Hicks, B.B., Meyers, T.P., 1988. Measuring biosphere-atmosphere
689 exchanges of biologically related gases with micrometeorological methods.
690 *Ecology*, 69, 1331–1340.
- 691 Baubron, J.-C., Allard, P., Sabroux, J.-C., Tedesco, D., Toutain, J.P., 1991. Soil gas
692 emanations as precursory indicators of volcanic eruptions. *Journal of the*
693 *Geological Society*, 148, 571–576.
- 694 Bergfeld, D., Goff, F., Janik, C.J., 2001. Elevated carbon dioxide flux at the Dixie Valley
695 geothermal field, Nevada; relations between surface phenomena and the
696 geothermal reservoir. *Chemical Geology*, 177, 43–66.

697 Billesbach, D.P., Fischer, M.L., Torn, M.S., Berry, J.A., 2004. A portable eddy
698 covariance system for the measurement of ecosystem-atmosphere exchange of
699 CO₂, water vapor, and energy. *Journal of Atmospheric and Oceanic Technology*
700 21, 639–650.

701 Chiodini, G., Cioni, G. R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO₂ flux
702 measurements in volcanic and geothermal areas. *Applied Geochemistry*, 13, 543–
703 552.

704 Conen, F., Smith, K.A., 1998. A re-examination of closed flux chamber methods for the
705 measurement of trace gas emissions from soils to the atmosphere. *European*
706 *Journal of Soil Science*, 49, 701-707.

707 Connor, C.B., Clement, B.M., Song, X.D., Lane, S.B., Westthomas, K., 1993.
708 Continuous monitoring of high-temperature fumaroles on an active lava dome,
709 Volcan Colima, Mexico- Evidence of mass-flow variation in response to
710 atmospheric forcing. *Journal of Geophysical Research*, 98, 19,713–19,722.

711 Evans, W. C., Sorey, M. L., Kennedy, B. M., Stonestrom, D. A., Rogie, J. D., Shuster,
712 D.L., 2001. High CO₂ emissions through porous media: Transport mechanisms
713 and implications for flux measurement and fractionation. *Chemical Geology*, 177,
714 15–29.

715 Farrar, C.D., Sorey, M.L., Evans, W.C., Howle, J.F., Kerr, B.D., Kennedy, B.M., King,
716 Y., Southon, J.R., 1995. Forest-killing diffuse CO₂ emission at Mammoth
717 Mountain as a sign of magmatic unrest. *Nature*, 376, 675–678.

718 Farrar, C.D., Neil, J.M., Howle, J.F., 1998. Magmatic carbon dioxide emissions at
719 Mammoth Mountain, California. U.S. Geological Survey Water Resources
720 Investigation Report 98-4217, 34 pp.

721 Folken, Th., Wichura, B., 1996. Tools for quality assessment of surface-based flux
722 measurements. *Agricultural and Forest Meteorology*, 78, 83-105.

723 Garrat, 1992. *The Atmospheric Boundary Layer*. Cambridge University Press,
724 Cambridge, 316 p.

725 Gerlach, T.M., Doukas, M.P., McGee, K.A., Kessler, R., 1998. Three-year decline of
726 magmatic CO₂ emissions from soils of a Mammoth Mountain tree kill: Horseshoe
727 Lake, CA, 1995-1997. *Geophysical Research Letters*, 25, 1947-1950.

728 Gerlach, T.M., Doukas, M.P., McGee, K.A., Kessler, R., 2001. Soil efflux and total
729 emission rates of magmatic CO₂ at the Horseshoe Lake tree kill, Mammoth
730 Mountain, California, 1995-1999. *Chemical Geology*, 177, 101-116.

731 Granieri, D., Chiodini, G., Marzocchi, W., Avino, R., 2003. Continuous monitoring of
732 CO₂ soil diffuse degassing at Phlegrean Fields (Italy): influence of environmental
733 and volcanic parameters. *Earth and Planetary Science Letters*, 212, 167-179.

734 Hernandez, P.A., Perez, N., Salazar, J.M., Nakai, S., Notsu, K., Wakita, H., 1998.
735 Diffuse emissions of carbon dioxide, methane, and helium-3 from Teide volcano,
736 Tenerife, Canary Islands. *Geophysical Research Letters*, 25, 3311-3314.

737 Hernandez, P.A., Notsu, K., Salazar, J.M., Mori, T., Natale, G., Okada, H., Virgilli, G.,
738 Shimoike, Y., Sato, M., Perez, N.M., 2001. Carbon dioxide degassing by
739 advective flow from Usu volcano, Japan. *Science*, 2001, 83-86.

740 Hill, D.P., 1996. Earthquakes and carbon dioxide beneath Mammoth Mountain,
741 California. *Seismological Research Letters*, 67, 8–15.

742 Hill, D.P., Prejean, S.G., 2005. Volcanic unrest beneath Mammoth Mountain, California.
743 *Journal of Volcanology and Geothermal Research*, 146, 257–283.

744 Horst, T.W., Weil, J.C., 1992. Footprint estimation for scalar flux measurements in the
745 atmospheric surface-layer. *Boundary-Layer Meteorology*, 59, 279-296.

746 Kaimal, J.C., Finnigan, J.J., 1994. *Atmospheric Boundary Layer Flows: Their Structure*
747 *and Measurement*. Oxford University Press, Oxford.

748 Klusman, R.W., Moore, J.N., LeRoy, M.P., 2000. Potential for surface gas
749 measurements in exploration and surface evaluation of geothermal resources.
750 *Geothermics*, 29, 637–670.

751 Lee, X., 1998. On micrometeorological observations of surface-air exchange above tall
752 vegetation. *Agricultural and Forest Meteorology*, 91, 39-49.

753 Lewicki, J.L., Bergfeld, D., Cardellini, C., Chiodini, G., Granieri, D., Varley, Werner, C.,
754 2005. Comparative soil CO₂ flux measurements and geostatistical estimation
755 methods on Masaya volcano. *Nicaragua, Bulletin of Volcanology*, 68, 76-90, doi:
756 10.1007/s00445-005-0423-9.

757 Lewicki, J.L., Hilley, G.E., Toshi, T., Aoyagi, R., Yamamoto, K., Benson, S.M., 2007.
758 Dynamic coupling of volcanic CO₂ flow and wind at the Horseshoe Lake tree kill,
759 Mammoth Mountain, California. *Geophysical Research Letters*, 34, L03401,
760 doi:10.1029/2006GL028848.

761 McGee, K.A., Gerlach, T.M., 1998. Annual cycle of magmatic CO₂ in a tree-kill soil at
762 Mammoth Mountain, California: Implications for soil acidification. *Geology*, 26,
763 463–466.

764 McGee, K.A., Gerlach, T.M., Kessler, R., Doukas, M.P., 2000. Geochemical evidence for
765 a magmatic CO₂ degassing event at Mammoth Mountain, California, September-
766 December 1997. *Journal of Geophysical Research*, 105, 8447–8456.

767 Rahn, T.A., Fessenden, J.E., Wahlen, M., 1996. Flux chamber measurements of
768 anomalous CO₂ emission from the flanks of Mammoth Mountain, California.
769 *Geophysical Research Letters*, 23, 1861–1864.

770 Rogie, J.D., Kerrick, D.M., Sorey, M.L., Chiodini, G., Galloway, D.L., 2001. Dynamics
771 of carbon dioxide emission at Mammoth Mountain, California. *Earth and*
772 *Planetary Science Letters*, 188, 535–541.

773 Schmid, H.P., 1997. Experimental design for flux measurements: matching scales of
774 observations and fluxes. *Agricultural and Forest Meteorology*, 87, 179–200.

775 Turnipseed, A.A., Anderson, D.E., Blanken, P.D., Baugh, W.M., Monson, R.K., 2003.
776 Airflows and turbulent flux measurements in mountainous terrain Part 1. Canopy
777 and local effects. *Agricultural and Forest Meteorology*, 119, 1–21.

778 Turnipseed, A.A., Anderson, D.E., Burns, S., Blanken, P.D., Monson, R.K., 2004.
779 Airflows and turbulent flux measurements in mountainous terrain Part 2.
780 Mesoscale effects. *Agricultural and Forest Meteorology*, 125, 187–205.

781 Webb, E.K., Pearman, G.I., Leuning, R., 1980. Correction of flux measurements for
782 density effects due to heat and water vapour transfer, *Quarterly Journal of Royal*
783 *Meteorological Society*, 106, 85–100.

784 Welles, J.M., Demetriades-Shah, T.H., McDermitt, D.K., 2000. Considerations for
785 measuring ground CO₂ effluxes with chambers. *Chemical Geology*, 177, 3-13.

786 Werner, C., Cardellini, C., 2006. Comparison of carbon dioxide emissions with fluid
787 upflow, chemistry, and geologic structures at the Rotorua geothermal system,
788 New Zealand. *Geothermics*, 35, 221–238.

789 Werner, C., Wyngaard, J.C., Brantley, S.L., 2000. Eddy-correlation measurement of
790 hydrothermal gases. *Geophysical Research Letters*, 27, 2925–2928.

791 Werner, C., Chiodini, G., Voigt, D., Caliro, S., Avino, R., Russo, M., Brombach, T.,
792 Wyngaard, J., Brantley, S., 2003. Monitoring volcanic hazard using eddy
793 covariance at Solfatara volcano, Naples, Italy. *Earth and Planetary Science*
794 *Letters*, 210, 561–577.

795 Werner, C., Chiodini, G., Granieri, D., Caliro, S., Avino, R., Russo, M., 2006. Eddy
796 covariance measurements of hydrothermal heat flux at Solfatara volcano, Italy.
797 *Earth and Planetary Science Letters*, 244, 72–82.

798 Wilczak, J.M., Oncley, S.P., Stage, S.A., 2001. Sonic anemometer tilt correction
799 algorithms. *Boundary Layer Meteorology*, 99, 127-150.

800 Wilson, K., Goldstein, A., Falge, E., Aubinet, M., Baldocchi, D., Berbigier, P.,
801 Bernhofer, C., Ceulemans, R., Dolman, H., Field, C., Grelle, A., Ibrom, A., Law,
802 B.E., Kowalski, A., Meyers, T., Moncrieff, J., Monson, R., Oechel, W.,
803 Tenhunen, J., Valentini, R., Verma, S., 2002. Energy balance closure at
804 FLUXNET sites. *Agricultural and Forest Meteorology*, 113, 223–243.

805

806 **Figure Captions**

807 Figure 1. View of the Horseshoe Lake tree kill located on the southeastern flank of
808 Mammoth Mountain, adjacent to Horseshoe Lake. Red square shows
809 approximate location of EC station.

810 Figure 2. Digital elevation model of the HLTK study area, outlined by white line
811 (modified from Lewicki et al., 2007). White dots show locations of the chamber
812 CO₂ flux measurement points. Red and yellow squares show approximate
813 locations of EC stations in the present and Anderson and Farrar (2001) studies,
814 respectively.

815 Figure 3. Plot of EC CO₂ flux versus friction velocity (u_*). Solid line is running average
816 of EC CO₂ flux over a $0.1 \text{ m s}^{-1} u_*$ window. Vertical dashed line shows $u_* = 0.25$
817 m s^{-1} .

818 Figure 4. Wind rose showing joint frequency distribution of mean horizontal wind speed
819 and direction (half-hour averages) from 09/08/2006 to 10/24/2006, constructed
820 using Frequency Works.

821 Figure 5. (a) Time series of average daily atmospheric pressure (stars) and wind speed
822 (dots). (b) Time series of average daily EC CO₂ flux corresponding to wind
823 directions from 250 to 290°. Symbols indicate number of measurements (n) used
824 to calculate average daily EC CO₂ fluxes. Error bars are standard error of mean.
825 Average daily EC CO₂ fluxes are missing on days where filtering has entirely
826 eliminated half-hour data. Diamonds are average of chamber CO₂ fluxes
827 measured repeatedly on daily basis over entire grid area grid from 09/12/2006 to

828 09/21/2006. Dark gray zones in indicate approximate timing of precipitation
829 events. See text for explanations of light grayed zones I and II.

830 Figure 6 (a-i). Time series (09/12/2006 to 09/21/2006) of maps of log chamber CO₂ flux.
831 White squares denote approximate location of EC station.

832 Figure 7. Time series of EC CO₂ flux corresponding to mean wind direction between 190
833 and 360°, $u_* > 0.25 \text{ m s}^{-1}$, and stationary measurements. Gray zones indicate
834 approximate timing of precipitation events.

835 Figure 8. Source areas (area within which 90% of the measured EC flux was derived
836 from) for 73 modeled footprints. Square shows location of EC station.

837 Figure 9. Histogram of the relative difference between EC and footprint CO₂ fluxes,
838 expressed as percent of EC flux.

839 Figure 10. Plots of (a) EC CO₂ flux versus footprint CO₂ flux for half-hour EC
840 measurements and (b) average daily EC CO₂ flux versus average daily footprint
841 CO₂ flux. Error bars show standard error of mean. Gray area encompasses data
842 from diffusely degassing areas at Solfatara volcano, Italy (Location 1; Werner et
843 al., 2003).

844 Figure 11. Plot of sum of latent (LE) and sensible (H) heat flux measured by EC versus
845 difference between net radiation (Rn) and soil heat flux (G) measured by
846 radiometer and heat flux plates, respectively from 09/12/2006 to 09/21/2006. Red
847 dots are measurements made during the nighttime. Black dots and squares are
848 measurements made during neutral-and-stable-daytime ($\xi > -0.1$) and unstable-
849 daytime ($\xi \leq -0.1$) periods. 1:1 line is shown.

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852 Table 1. Daily averages of half-hour data used for EC-footprint CO₂ flux comparisons
 853 and mean vertical wind speed.

Date	<i>n</i>	EC CO ₂ flux (g m ⁻² d ⁻¹)	Footprint CO ₂ flux (g m ⁻² d ⁻¹)	<i>L</i> (m)	<i>u</i> _* (m s ⁻¹)	<i>σ</i> _v (m s ⁻¹)	Wind dir. (°)	\bar{w} (m s ⁻¹)
09/12/2006	3	1437.3	1327.9	-63.7	0.32	1.4	263	-0.05
09/13/2006	5	1252.2	1134.5	-62.5	0.32	1.4	225	0.03e ⁻¹
09/14/2006	23	856.8	1006.0	-1415.3	0.88	3.0	263	-0.26
09/18/2006	7	1032.4	1163.1	-76.9	0.37	1.5	236	-0.06
09/19/2006	14	1059.3	1061.4	-491.2	0.82	2.7	265	-0.25
09/20/2006	7	964.1	1060.5	-40.2	0.32	1.6	268	-0.09
09/21/2006	14	1436.4	1425.2	-60.4	0.51	1.9	262	-0.13

854
 855 Table 2. Relative differences for EC and chamber CO₂ flux comparisons in volcanic and
 856 hydrothermal systems.

Site	Mean ± standard deviation relative difference between EC and chamber CO ₂ fluxes	<i>n</i>	Reference
Yellowstone National Park, USA	-4.1 ± 68 %	6	Werner et al. (2000)
Solfatarata volcano, Italy	-0.4 ± 32%	66	Werner et al. (2003)
Mammoth Mountain, USA	-19 to -40 %	2	Anderson and Farrar (2001)
Mammoth Mountain, USA	-0.3 ± 23%	73	Present study

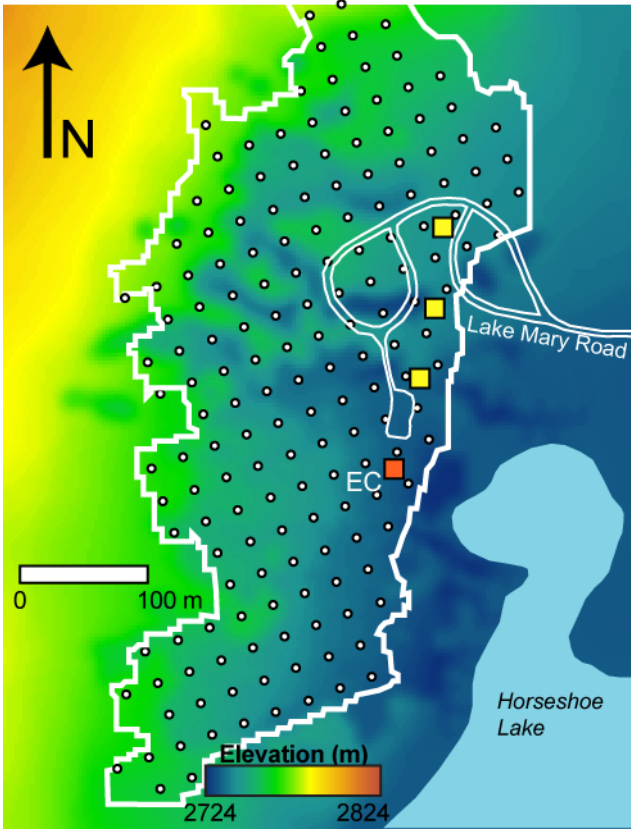
857 For Werner et al. (2000; 2003) and the present study, the relative difference is defined as
 858 the half-hour EC CO₂ flux minus footprint CO₂ flux, expressed as per-cent EC CO₂ flux.

859 The mean and standard deviation of these values are reported. For Anderson and Farrar
860 (2001), the relative difference is the mean EC CO₂ flux for study duration (two pilot
861 studies were considered) minus the mean chamber CO₂ flux measured in independent
862 studies, expressed as per-cent mean EC CO₂ flux. Only the range of these values is
863 reported.

864
865 Figures.
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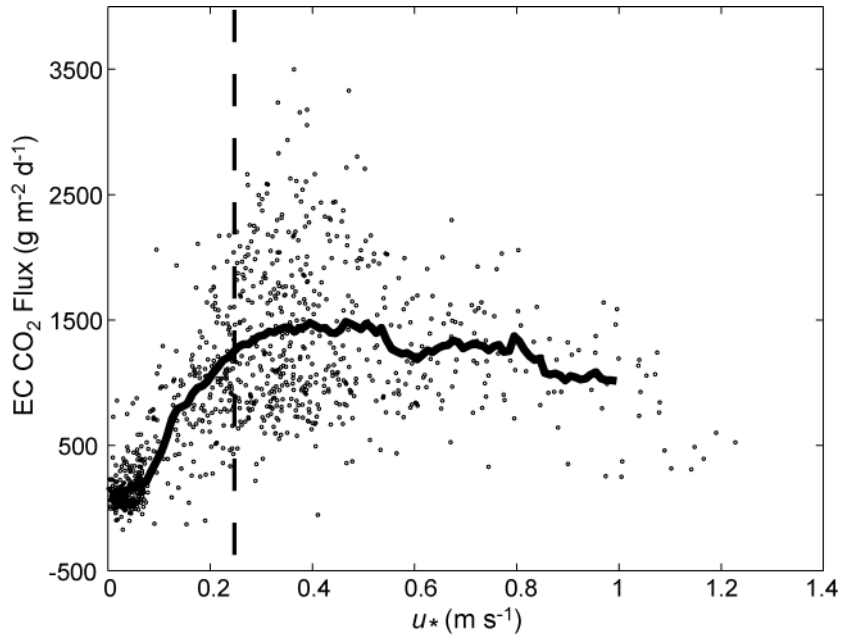


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868 Figure 1.



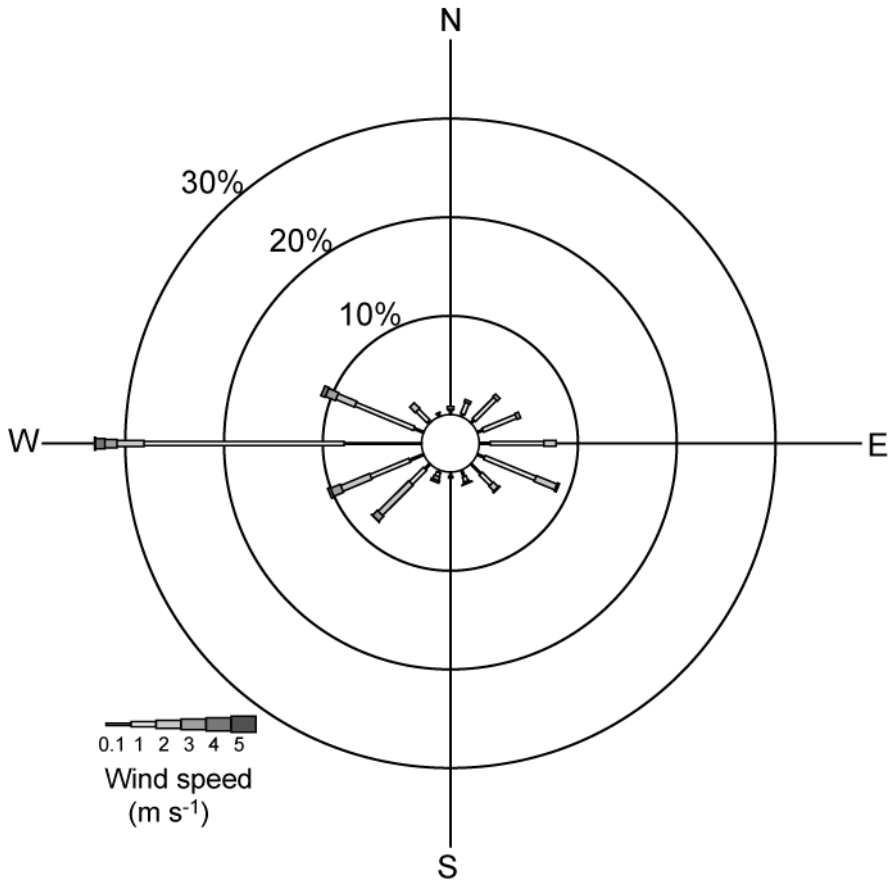
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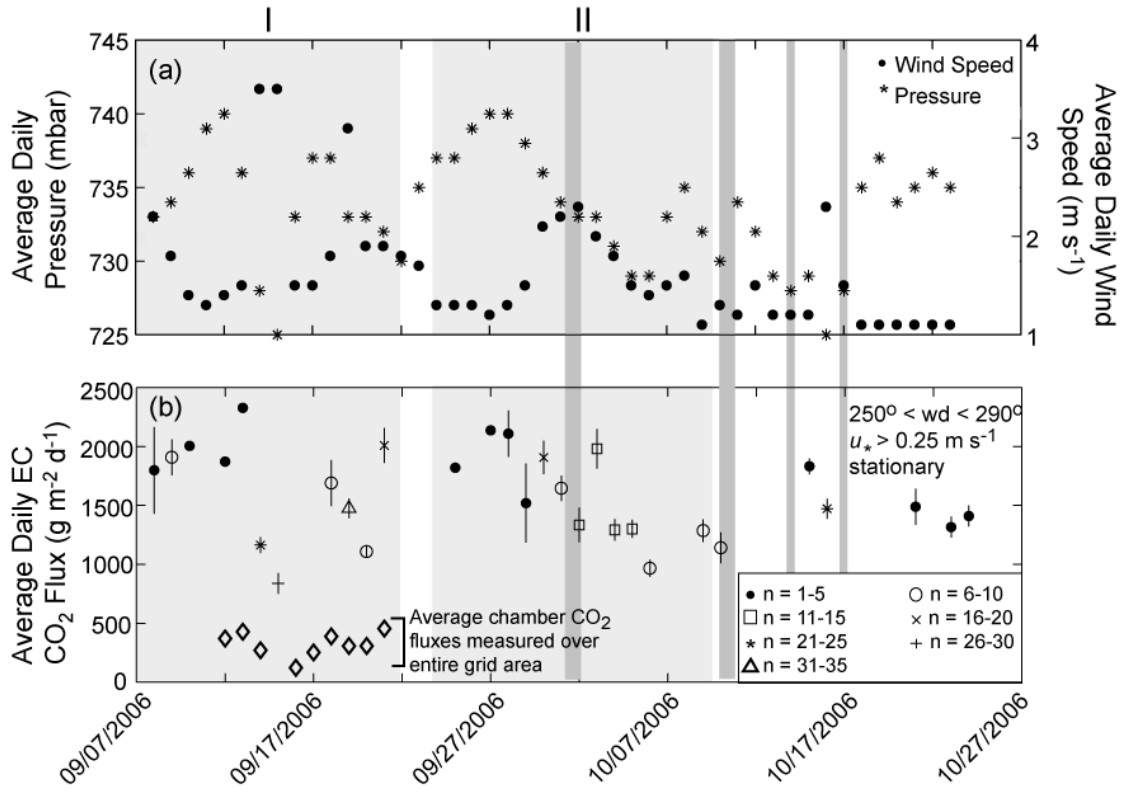


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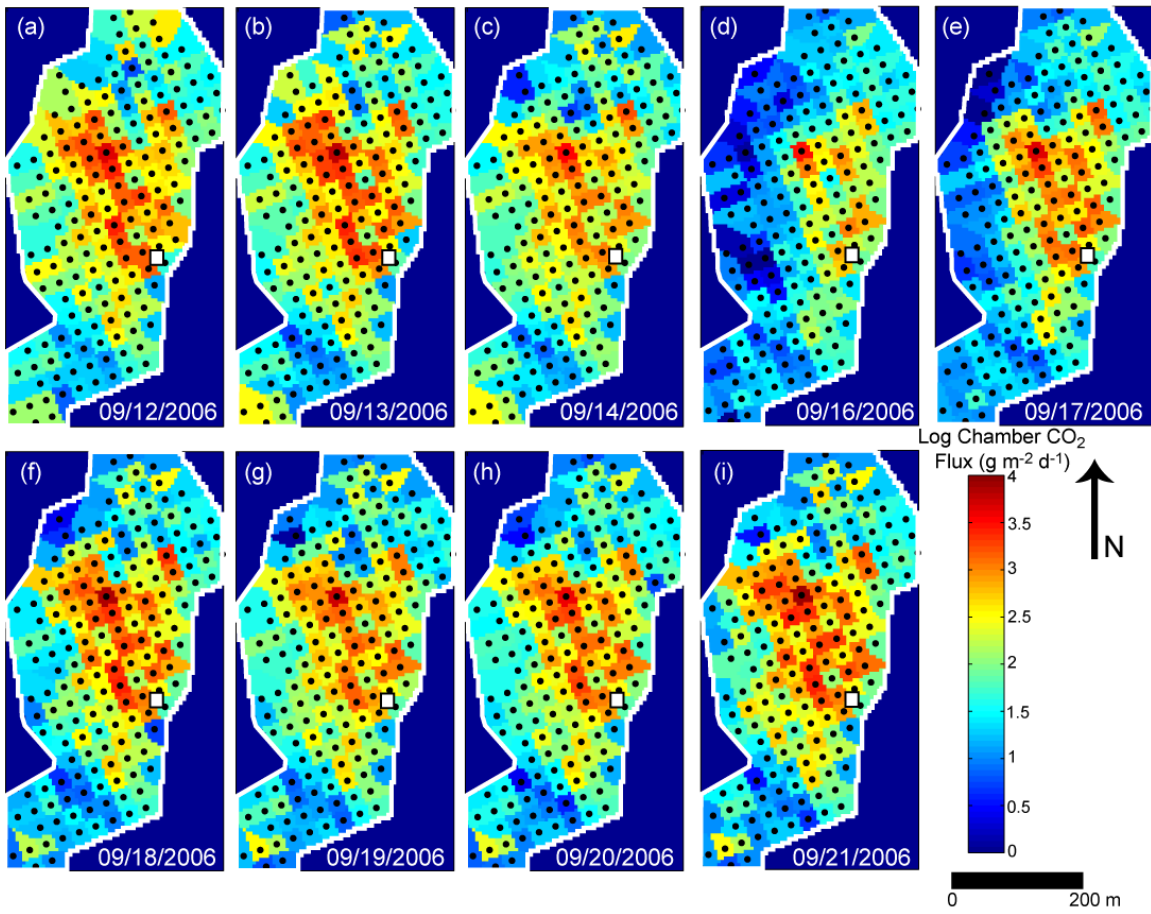


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 875 Figure 4.
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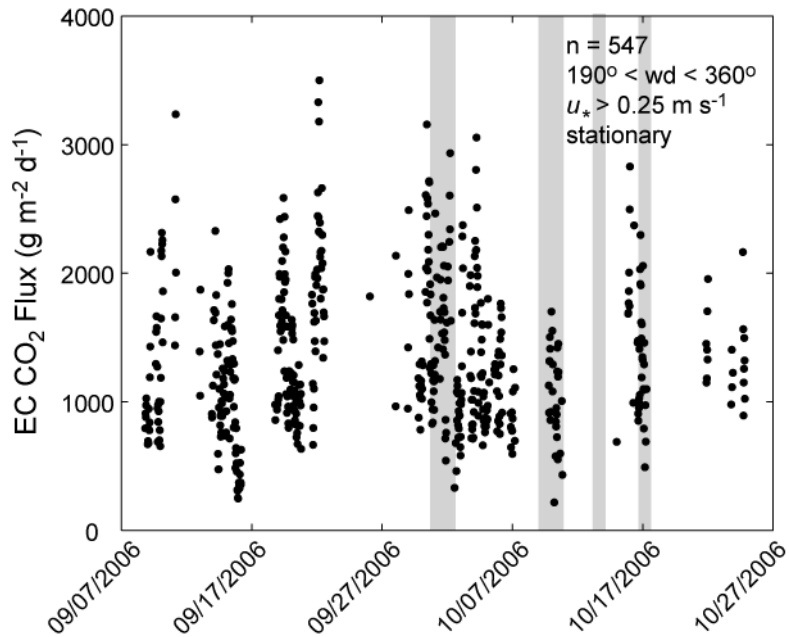
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Figure 5.



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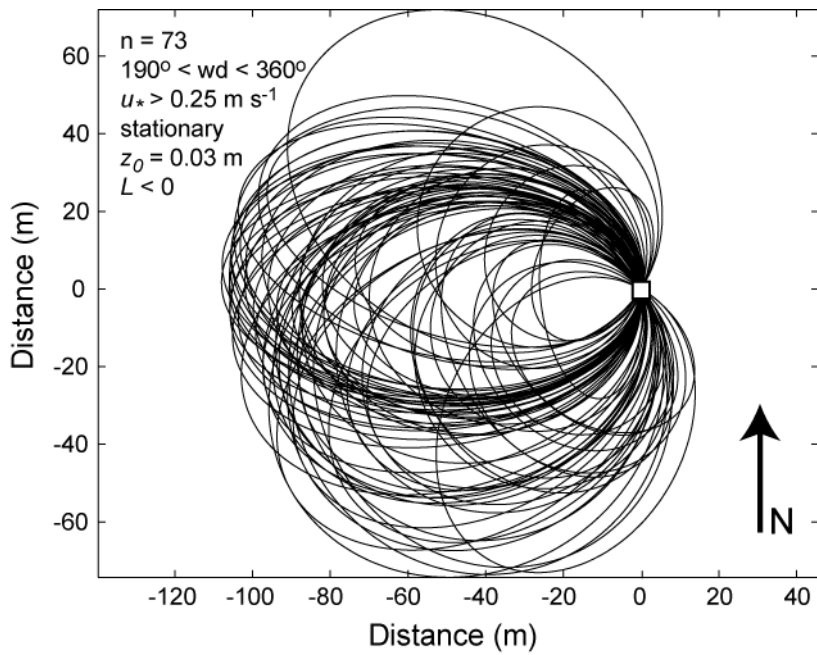
Figure 6.



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Figure 7.

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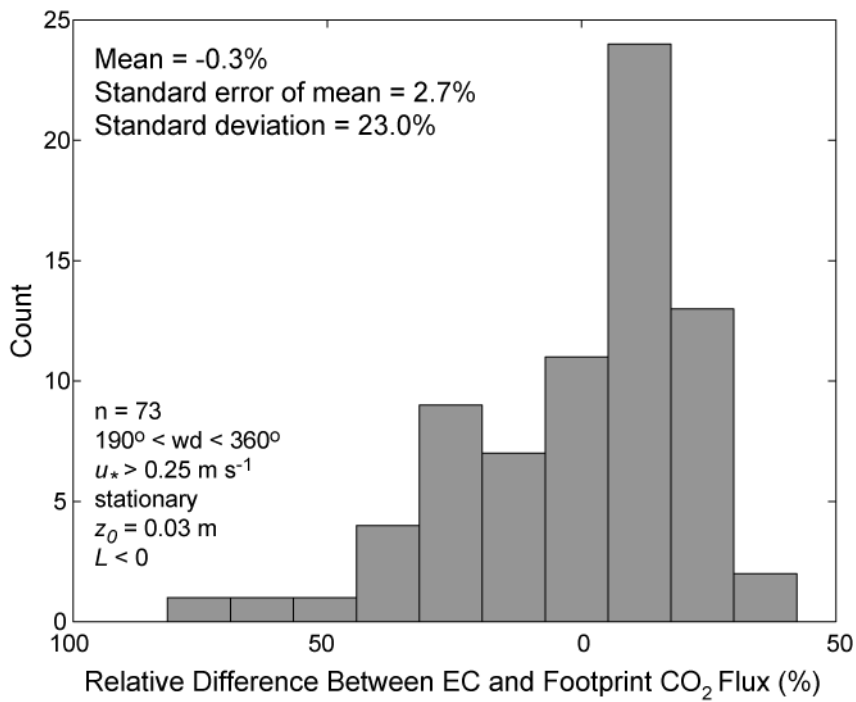


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Figure 8.

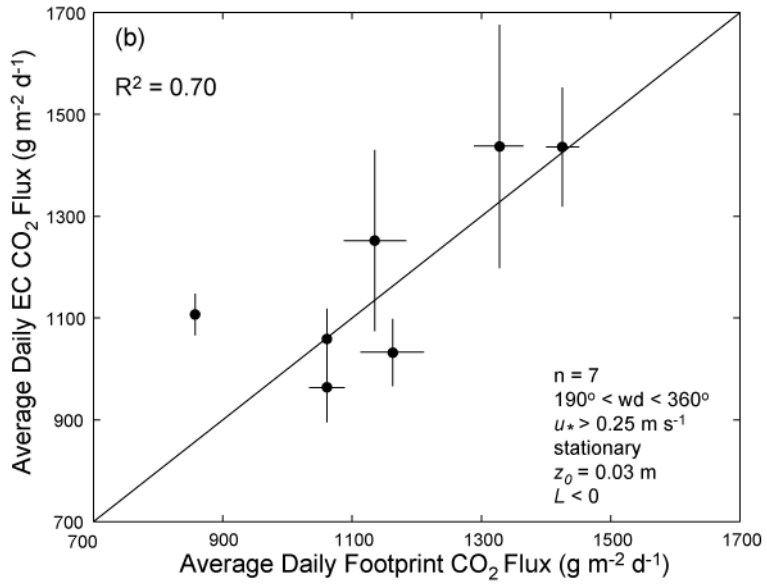
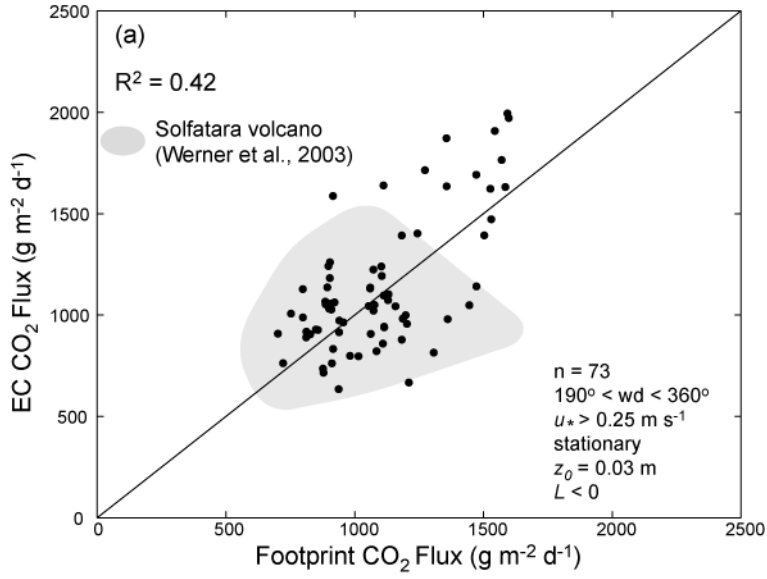


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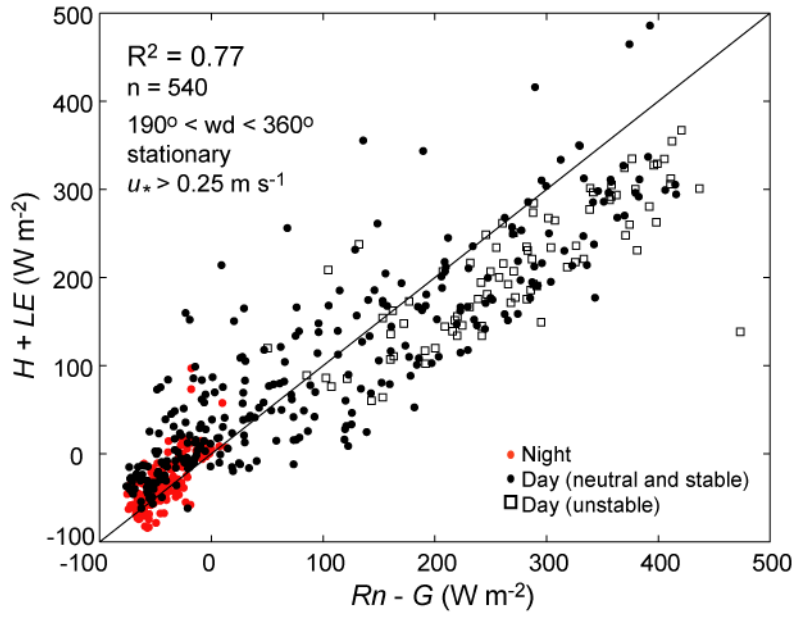
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Figure 9.



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Figure 10.



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898 Figure 11.