

## Carbon dioxide fluxes in a semiarid environment with high carbonate soils

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Received 28 May 2002; received in revised form 21 October 2002; accepted 8 November 2002

### Abstract

Carbon dioxide is increasing in the atmosphere due to human activities. Over long time periods semiarid soils have sequestered inorganic carbon to accumulate the third largest global carbon pool. The hypothesis for this study was that these soils are maintaining this carbon pool under present climatic conditions and are a sink for some of the increasing atmospheric carbon. Bowen ratio systems were used to measure CO<sub>2</sub> fluxes from a brush and a grass community with different soil types over 4 years in southeastern Arizona. Aboveground biomass and soil samples taken in spring and fall were analyzed to determine seasonal changes in carbon content. Contrary to the hypothesis, both sites were found to be losing carbon annually. Absence and presence of rainfall were important carbon flux driving forces. The brush site, with higher inorganic carbon in the soil, had an average annual loss of 144 g C m<sup>-2</sup> and the grass site a loss of 128 g C m<sup>-2</sup> from organic and inorganic sources. Average annual daytime CO<sub>2</sub> flux from the brush site was a loss of 26 g C m<sup>-2</sup>, while the grass site had a gain of 86 g C m<sup>-2</sup>. Based on measured average annual aboveground biomass data and estimates of belowground biomass, the brush site sequestered 80 g C m<sup>-2</sup> and the grass site 135 g C m<sup>-2</sup> into biomass during the growing season. Analysis of combined inorganic soil carbon data from both sites showed a significant seasonal difference with more in the fall season than in spring. The average annual fall season soil inorganic carbon was 22.5 g kg<sup>-1</sup> and the spring season was 19.4 g kg<sup>-1</sup> to a depth of 30 cm. This significant seasonal difference indicated that some of the measured CO<sub>2</sub> fluxes were into and out of the inorganic carbon pool. The source of carbon for the measured annual losses from these sites was concluded to be from the large inorganic carbon pool with carbon cycling through both the organic and inorganic pools at the sites.

Published by Elsevier Science B.V.

**Keywords:** Rangeland; Bowen ratio; Inorganic and organic carbon pools

### 1. Introduction

Globally, arid and semiarid soils contain large amounts of inorganic carbon in the form of carbonates, which range from 750 to 950 Pg C (Schlesinger, 1985; Eswaran et al., 2000). Arid and semiarid regions represent 30% of the earth's land area (Lal and Kimble, 2000). Only the oceanic (38,000 Pg C)

and soil organic (1550 Pg C) carbon pools are larger (Schlesinger, 1997). Soil inorganic carbon can be classified as lithogenic inorganic carbon (LIC) and pedogenic inorganic carbon (PIC). LIC carbon is inherited carbonate from the parent material of the soil, such as limestone and alluvium. PIC can form through a dissolution and precipitation process of the carbonate parent material, with no change in the inorganic soil carbon content (Schlesinger et al., 1988). PIC can form with the weathering of Ca/Mg-bearing silicates and result in the sequestration of carbon.

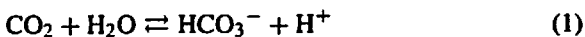
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The sequestration of carbon through the formation of PIC requires an arid environment for the precipitation of the carbonate and a source of Ca/Mg from a non-carbonate source. The increasing atmospheric concentration of CO<sub>2</sub> may aid in the formation of PIC and serve as a sink for some of the carbon.

PIC accumulations in arid zone soils take place in stages covering thousands of years (Gile, 1970). The inorganic carbon accumulations can exceed organic carbon by a factor of 10 or greater (Schlesinger, 1982). The turnover rate of inorganic carbon has been estimated from 120 years at a site in New Mexico (Monger and Gallegos, 2000) to 85,000 years on a global time scale (Schlesinger, 1985). Accumulation rates of inorganic carbon have been estimated from less than 0.1 to 12 g CaCO<sub>3</sub> m<sup>-2</sup> per year (Gile et al., 1981; Marion, 1989; Reheis et al., 1995) and are usually estimated by measurements of carbonate in the soil and soil profile age. These measurements can have large errors and they do not provide information on present day accumulation or potential losses.

Arid zone soil PIC and LIC accumulations and losses are controlled by the carbonate–bicarbonate equilibria (Eqs. (1) and (2)):



The increasing CO<sub>2</sub> content of the atmosphere coupled to the soil atmosphere or within the soil from decomposing additional organic matter would drive the equations to the right, dissolving the CaCO<sub>3</sub> and allowing translocation of the Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>. Precipitation increasing soil water content, and percolation, coupled with surface runoff removing Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, will also dissolve CaCO<sub>3</sub>. An input of hydrogen ions from acid precipitation or decomposing organic matter would dissolve CaCO<sub>3</sub> and release CO<sub>2</sub>. In contrast, CaCO<sub>3</sub> would precipitate in the soil by a drying of the soil, a decrease in the partial pressure of CO<sub>2</sub> in the soil, or a rise in pH. The weathering of Ca-rich minerals to release Ca<sup>2+</sup> or an external source providing Ca<sup>2+</sup> ions to the soil solution will result in the formation of CaCO<sub>3</sub>, thus sequestration of carbon.

Eqs. (1) and (2) are constantly shifting to the right and left on daily, annual and decadal cycles, controlling uptake and loss of inorganic carbon to the soil. Under the present climatic conditions, trends in

carbon sequestration, loss, or balance for this large carbon pool are mostly unknown. Intertwined with the inorganic carbon fluxes are the organic carbon fluxes from plant uptake and decomposition. Separation of inorganic and organic carbon fluxes is problematic, at best. In a tallgrass prairie, it has been estimated that several years of flux data are needed to begin an accurate quantification of grasslands as a sink/source for carbon (Suyker and Verma, 2001).

The study hypothesis is that semiarid rangeland soils containing large amounts of carbonates are maintaining the inorganic carbon pool and are sequestering inorganic and/or organic carbon on an annual basis under present climatic conditions. The objectives of this study were to: (1) characterize carbon fluxes in two different semiarid ecosystems over 4 years to evaluate them as a carbon sink or source; and (2) determine seasonal changes in soil carbon and aboveground biomass and relate these changes to organic and inorganic carbon fluxes.

## 2. Materials and methods

### 2.1. Experimental site descriptions

The two sites for this study are located on the Walnut Gulch Experimental Watershed in southeastern Arizona. The climate is semiarid with cool winters and warm summers. Mean annual precipitation is 356 mm and mean annual temperature is 17°C. A present day brush community site was selected in mid-1996 on an area known as Lucky Hills (–110°3'5"W, 31°44'37"N; elevation: 1372 m). The dominant shrubs at this site are whitethorn Acacia (*Acacia constricta*), tarbush (*Flourensia Cernua*), creosotebush (*Larrea divaricata*), and desert zinnia (*Zinnia pumila*). The only grass species remaining at the site, which historically was a black grama (*Bouteloua eriopoda*) community, is bush muhly (*Muhlenbergia porteri*). The soil at this site is Lucky-hills series (coarse-loamy, mixed, thermic Ustochreptic Calciorthids) with 3–8% slopes. The eluvial parent material for this soil contains many rock fragments of limestone. Surface A horizon (0–6 cm) contained 650 g kg<sup>-1</sup> sand, 290 g kg<sup>-1</sup> silt, and 60 g kg<sup>-1</sup> clay with 290 g kg<sup>-1</sup> coarse fragments >2 mm, 8 g kg<sup>-1</sup> organic carbon, and 21 g kg<sup>-1</sup> inorganic carbon.

A grass site was selected in mid-1996 on an area identified as Kendall ( $-109^{\circ}56'28''\text{W}$ ,  $31^{\circ}44'10''\text{N}$ ; elevation: 1526 m). Vegetation at the site is predominantly sideoats grama (*Bouteloua curtipendula*), black grama (*Bouteloua eriopoda*), hairy grama (*Bouteloua hirsuta*), and lehmann lovegrass (*Eragrostis lehmanniana*), with a few existing shrubs of fairy duster (*Calliandra eriophylla*), and burroweed (*Haplopappus tenuisectus*). The soils at the site are a complex of Stronghold (coarse-loamy, mixed, thermic Ustollic Calciorthids), Elgin (fine, mixed, thermic, Ustollic Paleargids), and McAllister (fine-loamy, mixed, thermic, Ustollic Haplargids) soils, with Stronghold the dominant soil. The eluvial parent material for these soils contains some limestone rock fragments. Slopes range from 4 to 9%. The Stronghold surface A horizon (0–3 cm) contains  $670 \text{ g kg}^{-1}$  sand,  $160 \text{ g kg}^{-1}$  silt, and  $170 \text{ g kg}^{-1}$  clay with  $790 \text{ g kg}^{-1}$  coarse fragments  $>2 \text{ mm}$ ,  $11 \text{ g kg}^{-1}$  organic carbon, and  $7 \text{ g kg}^{-1}$  inorganic carbon.

## 2.2. Micrometeorological measurements

Continuous, 20 min average carbon and water vapor flux measurements were made at both sites using a Bowen ratio energy balance system (BREB) (Model 023/CO<sub>2</sub> Campbell Scientific Inc., Logan, UT, USA<sup>1</sup>). The systems were placed in locations with a fetch of  $>200 \text{ m}$  in all directions. The theory and procedures used to calculate the fluxes has been presented in detail by Dugas (1993) and Dugas et al. (1999). Briefly, atmospheric gradients of air temperature, moisture, and CO<sub>2</sub> were measured every 2 s and averaged every 20 min. The 20 min averages were stored in a datalogger (model 21X, Campbell Scientific Inc. (see footnote 1)). Kendall gradients were measured at 1 and 2.5 m, and Lucky Hills at 1.5 and 3.0 m above the soil surface. Vegetation canopy height at Kendall ranged from 0.4 to 0.7 m during the growing season and at Lucky Hills an almost constant 1 m height. Atmospheric carbon dioxide and moisture concentrations were measured with an infrared gas analyzer (IRGA) (LI-6262, LI-COR Inc., Lincoln, NE, USA (see foot-

note 1)). Meteorological data were obtained from a net radiation sensor model Q\*7 (REBS, Seattle, WA, USA (see footnote 1)), soil heat flux from five plates (model HFT3 REBS (see footnote 1)), average of soil temperature from thermocouples above each heat flux plate, wind speed and direction from model 03001 R.M. Young Wind Sentry Set (R.M. Young Company, Traverse City, MI, USA (see footnote 1)), and RH and air temperature from model HMP35C temperature and RH probe (Vaisala Inc., Woburn, MA, USA (see footnote 1)). Net radiometers were calibrated yearly over a grass canopy. Carbon dioxide, water vapor, and energy fluxes were calculated from the 20 min average data. Temperature and water vapor gradients were used to calculate Bowen ratios. Bowen ratio, net radiation, soil heat flux, and soil temperature were used to calculate sensible heat flux. Eddy diffusivity was calculated from sensible heat fluxes and temperature gradients and assumed to be equal for heat, water vapor, and CO<sub>2</sub>. Eddy diffusivity could not be calculated when sensible/latent heat flux was in the opposite direction of temperature/water vapor gradients, or when Bowen ratio approaches  $-1.0$  (Ohmura, 1982). Under these conditions, eddy diffusivity was calculated by using wind speed, atmospheric stability, and canopy height (Dugas et al., 1999). This alternative method for calculating eddy diffusivity was used about 12% of the time, primarily at night when gradients and fluxes were small, hence any errors from the alternative method would have minimal impact on the calculated annual flux values. For short periods of time, usually at sunset and sunrise and when Bowen ratio was near  $-1.0$ , fluxes were estimated by linear interpolation with less than 5% of the data interpreted in this way. For longer time periods (i.e. days, usually associated with equipment failure) when there was a clear trend in the flux data, linear interpolation was used to estimate fluxes, otherwise no estimate was made. Normally, fluxes were calculated as the product of the eddy diffusivity and CO<sub>2</sub> gradient corrected for vapor density gradients at the two heights (Webb et al., 1980). Temperature corrections for the two heights were not applied as Angell et al. (2001) have shown the temperature differences to be insignificant as the air enters the IRGA for analysis.

The BREB system is an indirect method to measure fluxes compared to direct eddy covariance method. BREB calculations can become highly vari-

<sup>1</sup> Mention of a proprietary product does not constitute a guarantee or warranty of the product by USDA or the author and does not imply its approval to the exclusion of other products that may also be suitable.

able when the atmosphere is stable and heat and water vapor fluxes are very small, which usually occurs at night. Measurement errors and bias can occur and are propagated in estimating CO<sub>2</sub> fluxes (Sinclair et al., 1975). However, numerous studies have successfully used BREB systems to measure CO<sub>2</sub> fluxes over grasslands (Dugas et al., 1999; Frank et al., 2000; Frank and Dugas, 2001; Sims and Bradford, 2001). The BREB system has been validated in earlier studies using primarily closed chamber techniques (Dugas et al., 1991; Held et al., 1990; Malek and Bingham, 1993). Studies comparing BREB with chamber and eddy covariance methods on sagebrush and grassland sites including night time CO<sub>2</sub> fluxes found good agreement (Angell et al., 2001; Dugas et al., 2001). When BREB flux values became unusable, the described alternative methods were used to estimate fluxes. Angell et al. (2001) used the same Campbell Scientific Inc. BREB system on his sagebrush sites and these same alternative methods to make estimates in the comparison of BREB and close chambers to get the good agreement between the methods.

To look at how well the BREB systems performed at the sites in this study, the functional relationships between net radiation and CO<sub>2</sub> flux were evaluated. The BREB systems were able to measure the low CO<sub>2</sub> fluxes during the dry season (Figs. 1 and 2). The influence of the incoming radiation on the uptake of CO<sub>2</sub>

Table 1  
Yearly Lucky Hills and Kendall site Bowen ratio energy balance evapotranspiration and precipitation (mm)

Year	Lucky Hills		Kendall	
	BREB ET	Precipitation	BREB ET	Precipitation
1997	210	310	360	350
1998	340	340	400	370
1999	340	310	410	360
2000	370	450	370	480

was observed at the 20 min time step of the data during the growing season. A change in the net radiation produced an expected corresponding change in the CO<sub>2</sub> fluxes. Further evaluation of the data was done by comparing yearly BREB evapotranspiration (ET) and precipitation (Table 1). Reasonable agreement was found between the BREB ET and precipitation. The major areas that produced disagreement were missing BREB ET data, soil moisture storage changes, and surface runoff. All these studies and site data evaluations indicate BREB is an appropriate method to measure CO<sub>2</sub> fluxes on these brush and grassland sites.

2.3. Biomass and soil measurements

A compass rose was setup at each site with the BREB system in the center. Radials were laid out each

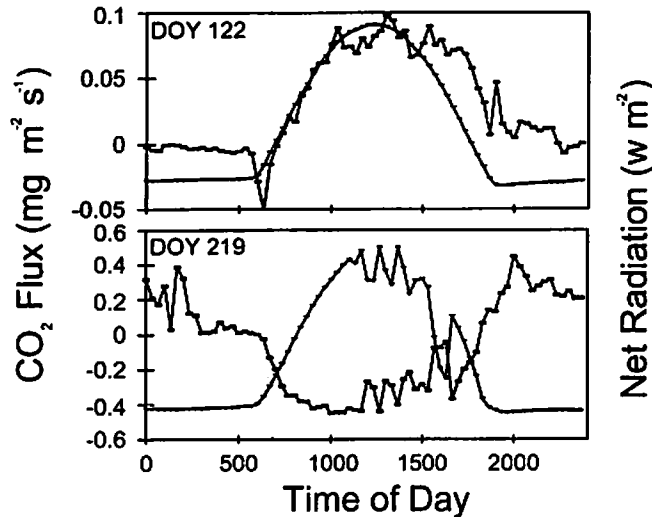


Fig. 1. Lucky Hills site, 122 and 219 DOY in 1999: carbon dioxide flux (■) and net radiation (▼) (negative values indicate carbon sequestration).

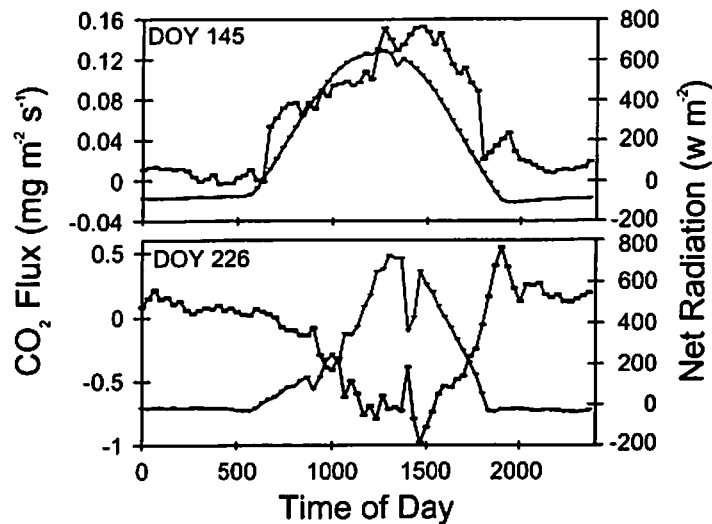


Fig. 2. Kendall site, 145 and 226 DOY in 1999: carbon dioxide flux (■) and net radiation (▼) (negative values indicate carbon sequestration).

30° with sample locations at 80, 90, 100, and 110 m. Biomass and soil samples were taken at sample locations on each radial in the spring and fall. Biomass was clipped at the soil surface from 2 m × 2 m plots at the Lucky Hills site and 1 m × 1 m plots at the Kendall site and the material separated into shrub, grass, forb, and litter. The biomass was dried at 65 °C, weighed, and amounts were calculated on a kg ha<sup>-1</sup> basis. Subsamples of each biomass type were ground and analyzed for total carbon by total combustion (CN-2000 Leco Corp. St. Joseph, MI, USA (see footnote 1)). Total aboveground carbon was calculated from the amount of biomass and carbon concentration data.

Soil samples were collected with a hand spade on the 12 radials adjacent to the biomass plots at depths of 0–15 and 15–30 cm. The samples were air dried, ground to a powder, and analyzed for total carbon by total combustion (CN-2000). Subsamples were analyzed for carbonate-carbon by the pressure-calcimeter method (Nelson, 1982). Organic carbon was calculated as the difference between total and carbonate-carbon. A SAS procedure for mixed models analysis of variance (Littell et al., 1996) was used to analyze the soils data for site, year, season, and depth effects and mean separation was determined by the Student's *t*-test ( $P < 0.05$ ).

### 3. Results and discussion

#### 3.1. Precipitation and wind effects on CO<sub>2</sub> flux

Precipitation was a major influence on CO<sub>2</sub> fluxes at both sites (Figs. 3 and 4). Measurement of fluxes during precipitation events is difficult due to moisture and energy flux reversals. However, for data sets that were obtained during precipitation events, there were numerous events associated with a sudden loss of CO<sub>2</sub>, down to the 20 min time step of the data collection. These releases of CO<sub>2</sub> were due, at least in part, to the dissolution of CaCO<sub>3</sub> by low pH (i.e. down to 3.5) rainfall events known to occur in the area (author's unpublished data) (Eqs. (1) and (2)). Acid precipitation would drive Eq. (2) to the right and Eq. (1) to the left, thus releasing CO<sub>2</sub> to the atmosphere. Precipitation events with substantial infiltration into the soil occur frequently (Figs. 3 and 4) displacing soil atmosphere enriched with CO<sub>2</sub> could have also contributed to these releases. Around day 200 at the start of the summer precipitation and growing season, precipitation events large enough to wet the soil profile caused increased CO<sub>2</sub> losses starting 6–24 h after the rainfall (see Lucky Hills, 1999, day 185, Figs. 3 and 5). These types of CO<sub>2</sub> losses have been attributed to increases in microbial activity (Kessavalou et al., 1998). The losses of

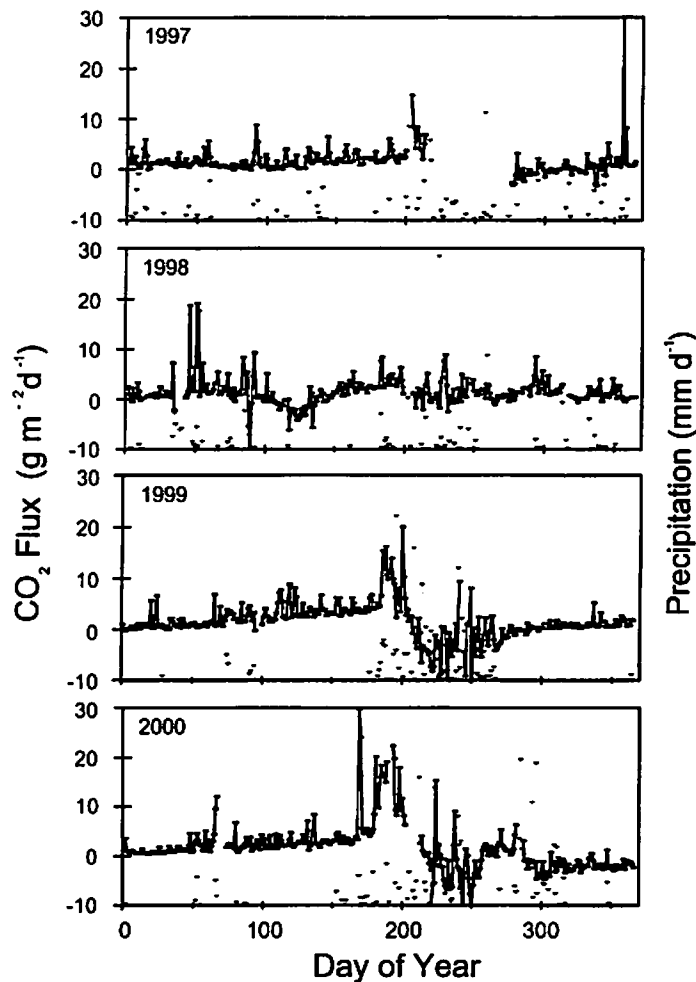


Fig. 3. Lucky Hills site yearly carbon dioxide flux (■) and precipitation (▼) (negative values indicate carbon sequestration).

CO<sub>2</sub> continued until the vegetation started its summer growth period, reversing the CO<sub>2</sub> loss with sequestration of carbon into plant biomass. Once the summer growing season started, the carbon sequestration flux rates were generally greater for the Kendall grassland site than for the Lucky Hills brush site (Figs. 3 and 4).

Precipitation timing throughout the year was another large influence on CO<sub>2</sub> flux. In 1999 and 2000, winter and spring at both sites were unusually dry (Figs. 3 and 4). As the soil profile dried and became warmer, the CO<sub>2</sub> loss rate gradually increased until the summer rainy season started. This corresponds to Eq. (1) shifting to the left by the removal of water from the soil solution causing the release of CO<sub>2</sub>, and

Eq. (2) shifting to the left with the precipitation of CaCO<sub>3</sub>. Soil microbiological activity as a source of CO<sub>2</sub> as the soil warmed up in the spring is unlikely, because soil moisture was exceedingly low at less than 20 g kg<sup>-1</sup>. In the absence of microbial activity, the CO<sub>2</sub> loss was likely from the inorganic carbon pool in the soil.

Precipitation timing and patterns were more typical at the sites in fall 1997 and winter/spring 1998 as contrasted with the dry winter/spring in 1999 (Figs. 3 and 4). Thus, the soil profiles in 1998 contained moisture that could be utilized by the vegetation as the temperatures warmed up for plant growth. Soil moisture utilization by the vegetation was evident by the

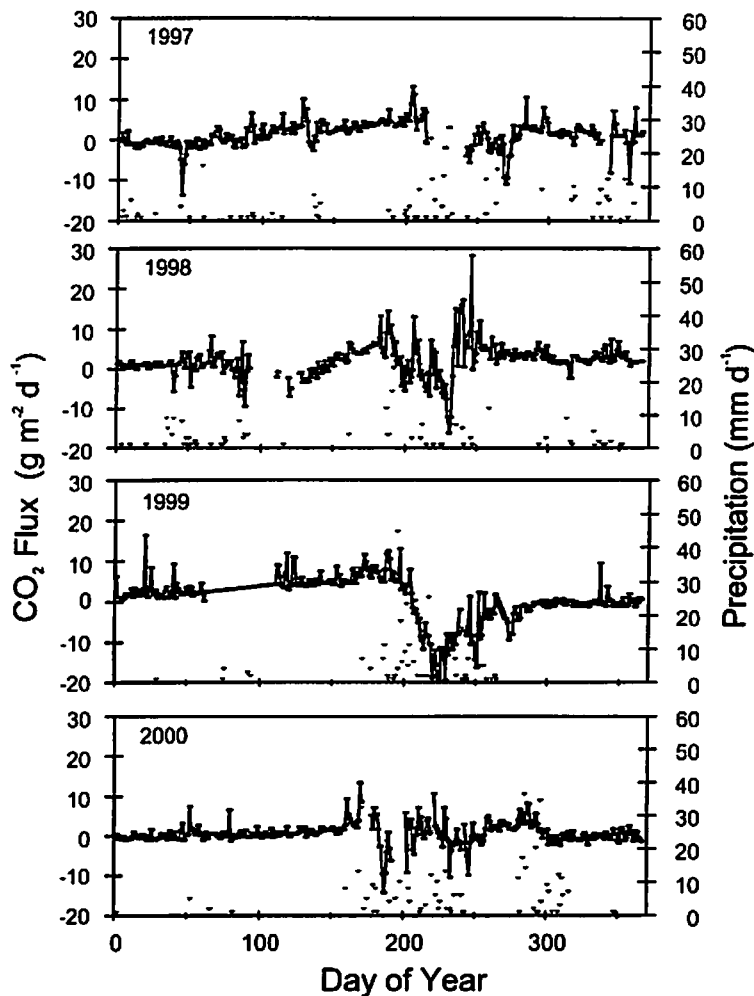


Fig. 4. Kendall site yearly carbon dioxide flux (■) and precipitation (▼) (negative values indicate carbon sequestration; values estimated, 1999, days 62–115 and 266–271).

sequestration of carbon starting around day 100 and continuing until soil moisture was depleted. At the Kendall site, sporadic equipment failure prevented continuous measurement of carbon fluxes, but it is clear from the data collected that carbon was sequestered in plant biomass during this time (Fig. 4). The summer rains again provided moisture for plant growth, but the rate of carbon uptake tended to be less as the vegetation had already completed part of its summer growth cycle.

Precipitation was the major influence on CO<sub>2</sub> fluxes at the sites, but there were other losses of carbon

suggested by the data that were not related to precipitation events. For example, on day 21 in 1999 at the Kendall site, there was a large loss of CO<sub>2</sub> (Fig. 4). The wind speed on day 21 started at near 0 at midnight and increasing dramatically, reaching 16 m s<sup>-1</sup> late in the afternoon and returning to about 2.5 m s<sup>-1</sup> just after midnight on day 22 (Fig. 6). Once the wind speed increased above 5 m s<sup>-1</sup>, observations showed increases in the loss of CO<sub>2</sub> from the sites. The source of this CO<sub>2</sub> was presumed to be from the CO<sub>2</sub> enriched soil atmosphere. As the wind velocity increased over the soil surface, there would be increased

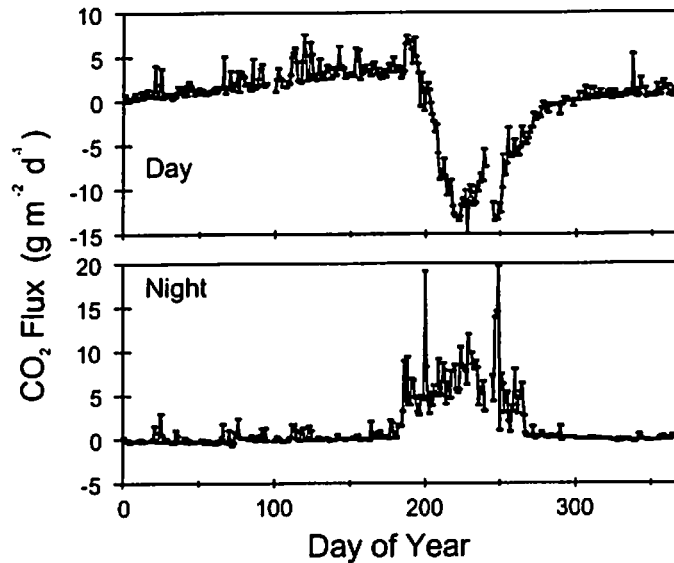


Fig. 5. Lucky Hills site, 1999 year, day and night carbon dioxide fluxes (negative values indicate carbon sequestration).

exchange of  $\text{CO}_2$  from the  $\text{CO}_2$ -rich soil atmosphere to the earth's atmosphere. The  $\text{CO}_2$  in the soil atmosphere would be from the soil organic and inorganic carbon pools, with more expected from the inorganic pool as it is larger and  $\text{CO}_2$  originating from plant root and microbial respiration would tend to be very low at this time of the year because plants are dormant and soils are cool. This 1-day carbon loss was greater than the carbon sequestration that took place on almost any day during the growing season at both sites (Figs. 3 and 4).

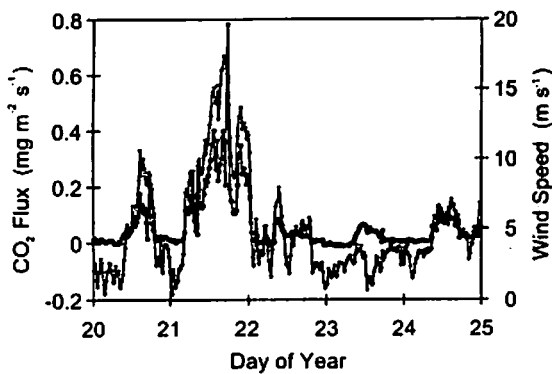


Fig. 6. Kendall site 1999 carbon dioxide flux (■) and wind speed (▼).

### 3.2. Potential $\text{CO}_2$ flux sources

Carbon dioxide fluxes in and out of the two sites were from the organic and inorganic pools. Though exact separation of the carbon fluxes from the two pools is difficult without the use of carbon isotopes and not possible within the scope of this study, the data did provide important insights into the origin of the measured fluxes. The dry winter and spring in 1999 and 2000 provided an opportunity to look further at  $\text{CO}_2$  fluxes that likely would originate from the inorganic source because  $\text{CO}_2$  from microbial activity and plant growth would be minimal. The 1999 daily fluxes were separated into day and night time fluxes (Figs. 5 and 7). The night time fluxes are respiration fluxes that remained relatively constant and small until the advent of summer rains, when night fluxes greatly increased. The constant night time fluxes during the dormant period were a further indication that there was no increase in soil microbial activity as the soil and air temperatures increased. The increase in night time fluxes corresponding to the beginning of the summer rains represented soil microbial activity and plant respiration, hence an organic origin of the  $\text{CO}_2$  fluxes (Linn and Doran, 1984). The increasing daytime fluxes from winter to spring (i.e. dormant



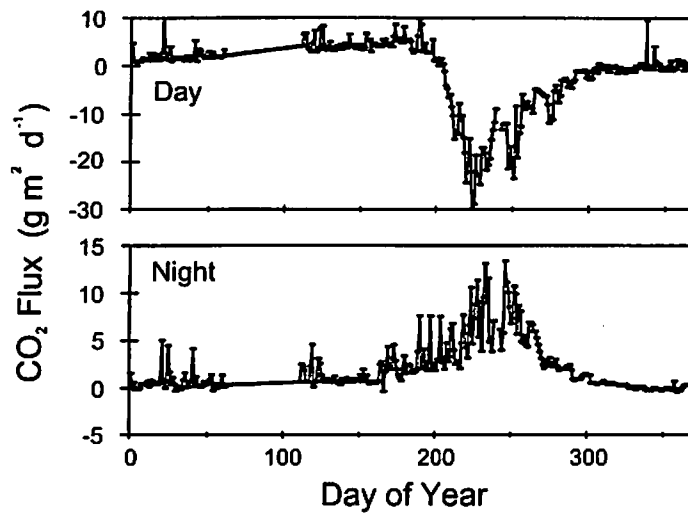


Fig. 7. Kendall site 1999 year, day and night carbon dioxide fluxes (negative values indicate carbon sequestration, values estimated, days 62–115 and 266–271).

period) would then be predominately from the inorganic pool of carbon controlled by evaporation shifting Eqs. (1) and (2) to release  $\text{CO}_2$  from the inorganic pool.

The growth and decomposition of the plant biomass at the two sites would be sources of organic carbon fluxes. Measured spring and fall aboveground biomass showed there was more carbon in the fall (Table 2). Averaged over 4 years, the annual increase in aboveground biomass carbon in the fall was  $28 \text{ g C m}^{-2}$  at the Lucky Hills site and  $19 \text{ g C m}^{-2}$  at Kendall. This represented part of the organic carbon sequestered during the summer growing season (Figs. 3 and 4).

Table 2  
Yearly spring and fall aboveground biomass for Lucky Hills and Kendall site ( $\text{g C m}^{-2}$ )

Year	Spring	Fall
Lucky Hills		
1997	190	170
1998	150	240
1999	210	230
2000	210	230
Kendall		
1997	90	120
1998	60	80
1999	100	150
2000	90	60

The total organic carbon sequestered was likely greater because some would have gone into belowground biomass. Cox et al. (1986) measured biomass distributions in these same plant communities and determined 65% of the biomass was belowground at the Lucky Hills site and 86% at Kendall. If these same percentages hold for carbon sequestered in the aboveground and belowground biomass, the average annual total organic carbon sequestration for the Lucky Hills site would be 80 and  $135 \text{ g C m}^{-2}$  for Kendall.

The results of the soil analysis gave additional information on the potential sources of the  $\text{CO}_2$  fluxes at the sites. SAS (Littell et al., 1996) analysis of variance results indicated there were significant site, depth and seasonal differences in the inorganic carbon at the two sites. The Lucky Hills site had higher inorganic carbon and the carbon increased with depth at both sites (Table 3). The site and depth results were expected from soil profile observations and descriptions (SCS, 1974). The significant seasonal effect had a mean  $22.5 \text{ g kg}^{-1}$  inorganic carbon in the top 30 cm of soil in the fall season and  $19.4 \text{ g kg}^{-1}$  in the spring season averaged between both sites with a SAS calculated standard error of  $0.22 \text{ g kg}^{-1}$ . The seasonal differences imply that some of the measured carbon flux loss from fall through spring at the sites was from the inorganic pool and that some of the carbon sequestered during the summer growing season went into the

Table 3  
Percent soil inorganic and organic carbon by site, year, season, and depth

Year	Spring		Fall	
	Depth 0–15 cm	Depth 15–30 cm	Depth 0–15 cm	Depth 15–30 cm
<b>Inorganic carbon<sup>a</sup></b>				
Lucky Hills				
1997	2.4	3.4	2.8	3.7
1998	2.2	2.9	3.1	4.1
1999	2.5	3.4	2.9	4.1
2000	2.9	3.8	2.9	3.8
Kendall				
1997	0.7	1.5	0.8	1.4
1998	0.6	1.1	0.9	1.3
1999	0.8	1.7	0.7	1.5
2000	0.5	0.9	0.6	1.4
<b>Organic carbon<sup>b</sup></b>				
Lucky Hills				
1997	0.6	0.7	0.8	0.5
1998	0.9	0.8	0.8	0.5
1999	1.0	1.0	0.8	0.7
2000	0.7	0.6	0.8	0.6
Kendall				
1997	1.2	1.0	1.0	1.0
1998	1.1	1.1	0.7	0.8
1999	1.5	1.0	0.9	0.9
2000	1.6	1.4	0.9	1.0

<sup>a</sup> Inorganic carbon standard error Lucky Hills = 0.50, Kendall = 0.29

<sup>b</sup> Organic carbon standard error Lucky Hills = 0.12, Kendall = 0.14.

inorganic carbon pool (Figs. 3 and 4). The absence of a statistical year effect indicated that the sites were not sequestering or losing inorganic carbon annually in measurable quantities for the study duration. The sites still could be sequestering or losing inorganic carbon on a yearly basis at a rate smaller than detectable by the sampling method used. Schlesinger (1985) estimated the long-term accumulation of inorganic carbon to be  $2 \text{ g m}^{-2}$  per year in the Mojave Desert. This small rate would be within the changes observed between seasons and years.

The soil organic carbon analysis of variance indicated a significant site by season by depth interaction, therefore the analysis was performed for each site separately. The Lucky Hills site had significant depth and year effects. The organic carbon was greater in the top 15 cm of soil than the next 15 cm and was greater in

the 0–30 cm soil profile in 1999 than in 1997 and 2000 (Table 3). Higher organic carbon in the surface was expected as soil profile organic carbon almost universally decreases with depth and soil profile reports indicated a decrease with depth (SCS, 1974). Precipitation in 1999 winter and spring was very low, producing a dry soil profile which would slow microbial decomposition of soil organic carbon (Fig. 3). The higher organic carbon in 1999 and the lack of a seasonal effect gives further evidence that the carbon lost during this dry time was from the inorganic pool. The Kendall site had a season by depth interaction. The interaction resulted from spring season organic carbon being significantly greater in the top 15 cm of soil compared to the fall and in the next 15 cm depth almost significant at  $P = 0.06$ . In the spring, organic carbon was greater in the top 15 cm soil depth compared the next 15 cm depth and in the fall the organic carbon in the top 15 cm was less than the next 15 cm depth (Table 3).

### 3.3. Annual $\text{CO}_2$ fluxes

Annual  $\text{CO}_2$  fluxes calculated from daily flux values showed both sites were losing carbon (Table 4). The 4-year average annual loss was  $144 \text{ g C m}^{-2}$  for the Lucky Hills site and  $126 \text{ g C m}^{-2}$  for Kendall. Even daytime  $\text{CO}_2$  fluxes from Lucky Hills showed that the site was losing carbon annually. During the daytime Kendall sequestered three times the carbon lost from the Lucky Hills brush site on an annual basis. This was due primarily to the higher carbon uptake at Kendall compared to Lucky Hills (Figs. 5 and 7).

Table 4  
Total annual, and annual day and night time carbon fluxes at Lucky Hills and Kendall sites for years 1997 through 2000 ( $\text{g C m}^{-2}$ )

Year	Total	Day	Night
Lucky Hills			
1997	130	70	60
1998	140	10	130
1999	155	5	150
2000	150	10	140
Kendall			
1997	130	–30	160
1998	210	–140	350
1999	110	–80	190
2000	60	–100	160

Positive values: source; negative values: sink.

The higher fluxes agree with the estimated higher total biomass accumulations during the growing season at the Kendall site. The average annual night time CO<sub>2</sub> flux losses at Kendall were twice those of Lucky Hills. The higher estimated biomass accumulation and higher night time CO<sub>2</sub> fluxes suggest there was more carbon cycling through Kendall than through Lucky Hills annually. The source of the additional carbon cycled at Kendall was likely organic due to the higher carbon uptake rates at Kendall. Higher night time CO<sub>2</sub> fluxes would be respiration/decomposition of this organic carbon.

The 126–144 g C m<sup>-2</sup> average annual loss of carbon from these sites indicate they are a source of carbon to the atmosphere under the present climatic conditions (Table 4). For each of the 4 years, there was a carbon loss, even for 2000, a year with 30% above annual precipitation. The additional precipitation did not indicate the potential for organic carbon sequestration annually. Recent studies indicate that some prairie sites are near equilibrium for organic carbon annually (Frank and Dugas, 2001; Suyker and Verma, 2001). If the Arizona sites are near annual equilibrium for organic carbon, much of the carbon loss could be from the inorganic carbon pool, which is substantial due to the limestone parent material in the soil. An estimation of the inorganic carbon soil profile pool was not made, but soil pits at the sites indicate increasing carbonate with depth (SCS, 1974). This large inorganic carbon pool could easily supply the observed annual carbon flux losses.

#### 4. Summary and conclusions

The hypothesis was that semiarid rangeland soils already containing carbonates are still sequestering carbon on an annual basis under the present climatic conditions. Actually, the Lucky Hills and Kendall rangeland sites with different vegetation and soil types were found to be a source of CO<sub>2</sub> to the atmosphere annually. The source of this carbon appears to be from the large inorganic carbon pool in these soils. The Lucky Hills brush site with more inorganic carbon in the soil had daytime CO<sub>2</sub> fluxes that showed an average annual loss of 26 g C m<sup>-2</sup>. The Kendall grass site, with less inorganic carbon in the soil, had an average annual daytime carbon sequestration of 86 g C m<sup>-2</sup>.

Night time CO<sub>2</sub> fluxes (i.e. respiration) at both sites represented a carbon loss. Inorganic soil carbon in the surface 30 cm was significantly greater in the fall than in the spring. This result implied that some of the observed CO<sub>2</sub> fluxes during the winter dormant season cycled through the inorganic carbon pool. Carbon dioxide flux losses during very dry periods suggest that the source was primarily from the inorganic carbon pool. More organic carbon cycled through the Kendall grass site than the Lucky Hills brush site.

#### Acknowledgements

The author would like to thank Drs. William Dugas, Resident Director and Pat Mielnick, Scientist, at the Blackland Research Center, Temple, TX, and Charmaine Verdugo physical sciences technician at the Southwest Watershed Research Center, Tucson, AZ for their invaluable assistance in Bowen ratio system setup, maintenance, and data processing and interpretation.

#### References

- Angell, R., Svejcar, T., Bates, J., Saliendra, N.Z., Johnson, D.A., 2001. Bowen ratio and closed chamber carbon dioxide flux measurements over sagebrush steppe vegetation. *Agric. Forest Meteorol.* 108, 153–161.
- Cox, J.R., Frasier, G.W., Renard, K.G., 1986. Biomass distributions at grassland and shrubland sites. *Rangelands* 8, 67–69.
- Dugas, W.A., 1993. Micrometeorological and chamber measurements of CO<sub>2</sub> flux from bare soil. *Agric. Forest Meteorol.* 67, 115–128.
- Dugas, E.A., Fritschen, L.J., Gay, L.W., Held, A.A., Matthias, A.D., Reicosky, D.C., Steduto, P., Steiner, J.L., 1991. Bowen ratio, eddy correlation, and portable chamber measurements of sensible and latent heat flux over irrigated spring wheat. *Agric. Forest Meteorol.* 56, 1–20.
- Dugas, W.A., Heuer, M.L., Mayeux, H.S., 1999. Carbon dioxide fluxes over bermudagrass, native prairie, and sorghum. *Agric. Forest Meteorol.* 93, 121–139.
- Dugas, W.A., Evans, R., Hollinger, D., 2001. Eddy correlation and Bowen ratio/energy balance measurements of sensible heat, latent heat, and CO<sub>2</sub> flux over a tallgrass prairie. BRC Report No. 01-31. Blackland Research Center, Temple, TX, p. 16.
- Eswaran, H., Reich, P.F., Kimble, J.M., Beinroth, F.H., Padmanabhan, E., Moncharoen, P., 2000. Global carbon sinks. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, FL, pp. 15–26.

- Frank, A.B., Dugas, W.A., 2001. Carbon dioxide fluxes over a northern, semiarid mixed-grass prairie. *Agric. Forest Meteorol.* 108, 317–326.
- Frank, A.B., Sims, P.L., Bradford, J.A., Mielnick, P.C., Dugas, W.A., Mayeux, H.S., 2000. Carbon dioxide fluxes on three native grasslands. In: Follett, R.F., Kimble, J.M., Lal, R. (Eds.), *The Potential of US Grazing Lands to Sequester Carbon and Mitigate the Greenhouse Effect*. CRC Press, Boca Raton, FL, Chapter 7, pp. 167–188.
- Gile, L.H., 1970. Soils of the Rio Grande Valley Border in southern New Mexico. *Soil Sci. Soc. Am. Proc.* 34, 465–472.
- Gile, L.H., Hawley, J.W., Grossman, R.B., 1981. Soils and geomorphology in the basin and range area of southern New Mexico—guidebook to the desert project. In: *New Mexico Bureau of Mines and Mineral Resources, Memoir 39*. Socorro, New Mexico, p. 222.
- Held, A.A., Steduto, F.O., Matista, A., Hsiao, T.C., 1990. Bowen ratio/energy balance technique for estimating crop net CO<sub>2</sub> assimilation, and comparison with a canopy chamber. *Theor. Appl. Climatol.* 42, 203–213.
- Kessavalou, A., Doran, J.W., Mosier, A.R., Drijber, R.A., 1998. Greenhouse gas fluxes following tillage and wetting in a wheat-fallow cropping system. *J. Environ. Qual.* 27, 1105–1116.
- Lal, R., Kimble, J.M., 2000. Pedogenic carbonates and the global carbon cycle. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, FL, pp. 1–14.
- Linn, D.M., Doran, J.W., 1984. Effects of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Sci. Soc. Am. J.* 48, 1267–1272.
- Littell, R.C., Stroup, G.A., Stroup, W.W., Wolfinger, R.D., 1996. SAS<sup>®</sup> System for Mixed Models. SAS Institute Inc., Cary, NC, p. 633.
- Malek, E., Bingham, G.E., 1993. Comparison of the Bowen ratio energy balance and water balance methods for the measurement of evapotranspiration. *J. Hydrol.* 146, 209–220.
- Marion, G.M., 1989. Correlation between long-term pedogenic CaCO<sub>3</sub> formation rate and modern precipitation in deserts of the American southwest. *Quaternary Res.* 32, 291–295.
- Monger, H.C., Gallegos, R.A., 2000. Biotic and abiotic processes and rates of pedogenic carbonate accumulation in the southwester United States—relationship to atmospheric CO<sub>2</sub> sequestration. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, FL, pp. 273–289.
- Nelson, R.E., 1982. Carbonate and gypsum. In: Page, A.L. (Ed.), *Methods of Soil Analysis. Part 2*, second ed. Agronomy Monographs 9. ASA, Madison, WI, pp. 181–197.
- Ohmura, A., 1982. Objective criteria for rejecting data for Bowen ratio flux calculations. *Appl. Meteorol.* 21, 595–598.
- Reheis, M.C., Goodmacher, J.C., Harden, J.W., McFadden, L.D., Rockwell, T.K., Shroba, R.R., Sowers, J.M., Taylor, E.M., 1995. Quaternary soils and dust deposition in southern Nevada and California. *Geol. Soc. Am. Bull.* 107, 1003–1022.
- Schlesinger, W.H., 1982. Carbon storage in the caliche of arid soils: a case study from Arizona. *Soil Sci.* 133, 247–255.
- Schlesinger, W.H., 1985. The formation of caliche in soils of the Mojave Desert, California. *Geochim. Cosmochim. Acta* 49, 57–66.
- Schlesinger, W.H., 1997. *Biochemistry: An Analysis of Global Change*, second ed. Academic Press, New York, p. 588.
- Schlesinger, W.H., Marion, G.M., Fonteyn, P.J., 1988. Stable isotope ratios and dynamics of caliche in desert soils. In: Rundel, P.W., Ehleringer, J.R., Nagy, K. (Eds.), *Stable Isotopes in Ecological Research*. Springer, Berlin, pp. 309–317.
- Sims, P.L., Bradford, J.A., 2001. Carbon dioxide fluxes in a southern plains prairie. *Agric. Forest Meteorol.* 109, 117–134.
- Sinclair, T.R., Allen Jr., L.H., Lemon, E.R., 1975. An analysis of errors in the calculation of energy flux densities above vegetation by a Bowen ratio profile method. *Boundary-Layer Meteorol.* 8, 129–139.
- Soil Conservation Service (SCS) USDA, 1974. *Soil Survey Laboratory Data and Descriptions for Some Soils of Arizona*. Soil Survey Investigations Report No. 28.
- Suyker, A.E., Verma, S.B., 2001. Year-round observations of the net ecosystem exchange of carbon dioxide in a native tallgrass prairie. *Global Change Biol.* 7, 279–289.
- Webb, E.K., Pearman, G.I., Leuning, R., 1980. Correction of flux measurements for density effect due to heat and water vapour transfer. *Quart. J. R. Meteorol. Soc.* 106, 85–100.