Carbon Dioxide Emissions from Exhumed Petrocalcic Horizons
Alfonso Serna-Pérez, H. Curtis Monger, Jeffrey E. Herrick, and Leigh Murray

ABSTRACT
The second largest pool of terrestrial carbon is soil CaCO₃. In addition to being an important sink of atmospheric CO₂, soil carbonate is potentially an important source of atmospheric CO₂. The cemented form of soil carbonate—the petrocalcic horizon—develops in geographically stable soil in arid, semiarid, and some subhumid climates. In many of these dryland areas, such as the Chihuahuan Desert of North America, erosion has stripped away overlying soil and exhumed the petrocalcic horizon, thereby exposing it to a weathering zone above the calcification zone where it normally forms. This research tested the hypothesis that soil type 1 (eroded Aridisols with exhumed petrocalcic horizons) will emit more CO₂ than soil type 2 (noneroded Aridisols with petrocalcic horizons) or soil type 3 (Entisols formed in sandy, noncalcareous sediments). We tested this hypothesis by comparing the amount of CO₂ and the δ¹³C of CO₂ released from the three soil types. Using a randomized complete block design, CO₂ emissions were measured using NaOH and soda lime traps from June 2002 to October 2003. Neither the NaOH traps nor soda lime traps detected any statistical difference in cumulative CO₂ emissions from the three soil types at the α = 0.05 level. Moreover, the isotopic analysis of CO₂ did not match the isotopic values of pedogenic carbonate, nor were there any statistical differences (α = 0.05) in δ¹³C of CO₂ among the three soil types. We conclude, therefore, that exhumed petrocalcic horizons are not actively emitting CO₂ at a significant rate greater than adjacent soils, and thus carbon stored in petrocalcic horizons can be considered a recalcitrant reservoir within the decadal timeframe pertinent to carbon sequestration policies.

INCREASED CONCENTRATION of CO₂ in the atmosphere, largely the result of fossil fuel combustion and human land use, is a well-known issue of international concern (Houghton, 2004). This concern has stimulated much research of the global carbon cycle with a particular focus on carbon sequestration (Schlesinger, 1999; Post and Kwon, 2000; Lacker, 2003; Lal, 2004; White et al., 2004). For example, C sequestration potential in the U.S. is estimated to be 120 to 270 million Mg C yr⁻¹ for agricultural soils (Lal et al., 1998) and 17.5 to 90.5 million Mg C yr⁻¹ for grazing-land soils (Follett et al., 2001). However, in addition to being a sink for atmospheric CO₂, soils also have the potential for being a source of atmospheric CO₂, as was the case in the United States with the loss of soil organic matter from 1800 to 1950 (Houghton et al., 1999). Recent CO₂ flux measurements have also indicated that CaCO₃ in soil may be a source of atmospheric CO₂ (Emmerich, 2003). Soil carbonate-C is estimated to contain 940 Pg C (Eswaran et al., 2000), which is higher than the amount of carbon in the atmosphere (740 Pg C) or in global plant biomass (550 Pg C) (Schlesinger, 1997). In the western United States alone there is an estimated 50.2 to 65.7 Pg of carbonate-C (Monger and Martinez-Rios, 2001), which is more carbon than the 26.3 Pg of aboveground carbon estimated for the U.S. forests (Birdsey and Lewis, 2002).

Soil carbonate consists of two pools: geogenic (detrital limestone particles) and/or pedogenic (i.e., in situ precipitated CaCO₃). With time, pedogenic carbonates in the subsoil may progress through six developmental sequences, passing from Stage I carbonate filaments to Stage II nodules then to Stage III carbonate-plugged (calcic) horizons and, on stable Pleistocene land surfaces, to Stages IV, V, and VI (petrocalcic) horizons (Gile et al., 1966; Machette, 1985; Birkeland, 1999). In many areas of the arid and semiarid world, erosion, both natural and accelerated, has stripped away the upper soil profile and exposed the underlying petrocalcic horizon to the direct effects of rain, microbiotic crusts, and shallow roots. In theory, this could increase CO₂ emissions as the result of CaCO₃ dissolution via the reaction

\[ \text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \]

especially if dissociated protons from organic acids are available in micro-environments of the rhizosphere (Sposito, 1989). Therefore, when the petrocalcic horizon is brought into the shallow, more intense weathering zone of increased biologic activity above the depth where pedogenic carbonate normally forms, the possibility arises that such exhumed petrocalcic horizons are active sources of CO₂ emissions.

To address this possibility, we tested the hypothesis that soils with exhumed petrocalcic horizons will emit more CO₂ than neighboring noneroded petrocalcic horizon soils or than sandy Entisols without petrocalcic horizons by (i) comparing the amount of CO₂ released from the three soil types and (ii) by measuring the isotopic composition (δ¹³C) of CO₂ from the three soil types.

MATERIALS AND METHODS
Geological and Climatic Setting

The research was performed in the Chihuahuan Desert of southern New Mexico at the Jornada Basin Long Term Ecological Research site on the USDA Jornada Experimental Range and the New Mexico State University Chihuahuan

Abbreviations: EPHS, exhumed petrocalcic horizon soils; IRGA, infrared gas analyzer; NEPHS, noneroded petrocalcic horizon soils; SWoPH, soils without petrocalcic horizons.
Desert Rangeland Research Center (Fig. 1A). The study area was located on basin floor and adjacent valley-border geomorphic surfaces produced by fluvial deposition of sediment by the ancestral Rio Grande in the middle Pleistocene and its entrenchment approximately 800,000 yr ago (Hawley and Kottlowski, 1969; Gile et al., 1981; Mack et al., 1996). Soil

Fig. 1. Location of study site and illustration of the three soil types. (A) Chihuahuan Desert and location of study site in New Mexico. (B) Locations of blocks and quadrats for the three soil types. The map units are of geomorphic units, including states of erosion (Monger et al., 2006). (C) Cross-section illustrating the three soil types evaluated for their CO$_2$ emissions. (D) Example of a noneroded petrocalcic horizon soil (NEPHS) in the study area.
parent materials are reworked arkosic sediments of the fluvial facies of the Camp Rice formation (Seager et al., 1987). The basin floor contains soils with well-developed petrocalcic horizons (Stages IV and V) that are exhumed by water erosion along the basin floor scarp and by wind erosion along streaks oriented in the prevailing north-northwest wind direction. Most of the erosion occurred prehistorically based on the degree of soil profile development in the resulting eolian sediments (Monger, 2006). However, overgrazing in the late 1800s exacerbated both wind and water erosion (Buffington and Herbel, 1965). The eroded areas on the basin floor contain the soil type (or “treatment” in the broad sense of the word) that we refer to as “exhumed petrocalcic horizon soils” (EPHS) (Fig. 1B and 1C). This unit consists of direct exposure of a petrocalcic horizon or petrocalcic fragments. The petrocalcic fragments, which range in size from about 3 to 15 cm, are typically disseminated throughout a zone of loamy sand material above the petrocalcic horizon when it is not completely exposed. The CO$_2$ traps were consistently placed over the forbs, and C. longiseta plants are common in the Chihuahuan absorption var. Torrey) with some creosotebush [ _Larrea tridentata_ (Sess. & Moc. ex DC.) Cov.]. Mesquite has trapped saltating sand and formed coppice dunes that are separated by bare interdune areas of about 100 m$^2$. Widely scattered _C. glandulosa_ shrubs, such as snakeweed [ _Gutierrezia sarothrae_ (Pursh) Britt. & Rusby], perennial and annual _C. forbs_, and _C. vernalis_ grasses occur in the interspaces. The perennial grasses are mainly black grama [ _Bouteloua eriopoda_ (Torrey) Torrey] with some mesquite dropseed [ _Sporobolus flexuosus_ (Thurb. ex Vasey) Rydb.] and red threeawn [ _Aristida purpurea_ var. _longiseta_ (Steud.) Vasey]. The grasses, especially black grama, were much more abundant a century ago (Buffington and Herbel, 1965; Gibbens et al., 2005). Plants with crassulacean acid metabolism (CAM plants), such as cacti, are rare. Two types of microbial crusts are common in the study area: cyanobacteria and lichens. Cyanobacteria occur mainly on the sheltered areas of coppice dunes while lichens are common on eroded soils, especially on exposed petrocalcic fragments. Cyanobacteria biomass is relatively low on these soils (Belnap and Gillette, 1998) and lichen cover is less than 1%.

**Statistical Design**

The three soil types (i.e., EPHS, NEPHS, SWoPH) were organized into a randomized complete block design with subsampling (Fig. 1B). All blocks contained each soil type, making nine plots in total. Each plot was a square of 20 by 20 m and was selected based on uniformity of vegetation cover and type. Within the 20 by 20 m plots, there were five subsamples from 2 by 2 m quadrats. The CO$_2$ measurements were made over 51 sampling dates spanning the period from June 2002 to October 2003. There were 15 CO$_2$ measurements on every soil type, which is the amount needed to obtain a mean value of soil CO$_2$ emissions with a statistical confidence of 90% (Cropper et al., 1985; Raich et al., 1990). Therefore, for each of the 51 sampling dates, there were 45 NaOH samples and 45 soda lime samples, giving a total of 4590 samples for this study. Emission data were averaged over the five quadrats (subsamples) in each block by soil type combination, giving one value for each plot. These data were analyzed as a randomized complete block design by analysis of variance, and means and standard errors were calculated. Least significance difference (LSD) pairwise comparisons between soil types were performed. Analyses were done using SAS (SAS Institute, 1999).

Years were analyzed separately because summer weather conditions in 2002 and 2003 were very different, and the emphasis of the experiment was on overall differences in soil types, not in year-to-year differences.

**Carbon Dioxide Traps**

Carbon dioxide emissions were measured using inverted chambers with two types of absorbents: (i) a solution of 0.4 M NaOH and (ii) soda lime powder (Anderson, 1982; Edwards, 1982; Cropper et al., 1985; Raich et al., 1990). The composition of the oven-dried, dehydrated soda lime was calcium hydroxide (93%), potassium hydroxide (3.5%), NaOH (2.3%), and ethyl violet (1.2%). Blanks were used to account for CO$_2$ absorption when the alkali traps were not in the chambers. That is, blanks were identical in composition to the alkali traps and were treated identically to the traps except that they were not placed in the inverted chambers for the 24-h sampling period. The average amount of CO$_2$ absorbed by the blanks for the sampling date was subtracted from the alkali traps.

Accuracies of the NaOH and soda lime methods were determined by (i) a lab study that consisted of adding known amounts of CO$_2$ to the traps and by (ii) a field study that compared results of NaOH and soda lime with results of an infrared gas analyzer (IRGA). Results of the lab experiment showed that the NaOH traps had a high correlation ($r^2 = 0.9995$) between the known (which ranged from 10 to 70 mg CO$_2$) and measured amounts of CO$_2$. This method had an accuracy of 0.0013 g, where accuracy was quantified using the following equation:

$$
\text{Accuracy} = s = \sqrt{\frac{\sum_{i=1}^{n} (\text{estimated value} - \text{true value})^2}{n}}
$$

The soda lime traps also had a high correlation ($r^2 = 0.9929$) between the known (which also ranged from 10 to 70 mg CO$_2$) and measured amounts of CO$_2$, and had an accuracy of 0.0044 g (Serna-Pérez, 2004). Comparison between IRGA and the alkali traps revealed no significant difference between IRGA and...
NaOH at α = 0.05. However, the soda lime method gave higher CO₂ values than IRGA by about 20-fold (Serna-Pérez, 2004).

Soil CO₂ emissions were collected for 24-hour increments inside metal cans painted white to offset solar heating. These chambers were pushed into the soil to a depth of 3 cm to minimize CO₂ exchange with the atmosphere and were moved within quadrats on each sampling date to minimize soil disturbance effects and to minimize serial correlation. Sample collection was once every 2 wk from October 2002 to May 2003 and once a week during the summer rainy seasons. After determination of CO₂ and correction for CO₂ absorbed by the blanks, soil CO₂ fluxes were expressed in units of milligrams of CO₂ per square meter per hour (mg CO₂ m⁻² h⁻¹).

δ¹³C Analysis

The δ¹³C values of soil CO₂ emissions were determined by absorbing CO₂ with NaOH and soda lime, then correcting for isotopic fractionation based on lab experiments. Each month, 36 NaOH traps and 36 soda lime traps were used to capture CO₂ (i.e., four repetitions in each plot). Sealed traps were taken to the field, quickly uncovered and placed inside the white metal chambers for 6 d to collect enough CO₂ for analysis. At the end of the sixth day, samples were sealed and taken to the laboratory. The NaOH samples, because they were aqueous solutions, were evaporated by slightly loosening the lids and oven drying until the solutions were completely evaporated. The resulting crystals were Na₂CO₃ and NaOH based on X-ray diffraction analysis. All samples were sealed and stored in labeled plastic vials until measured using a Eurovector elemental analyzer interfaced with a continuous-flow isotope ratio mass spectrometer (Micromass Isoprime, Beverly, MA). δ¹³C values are reported relative to those of the Pee Dee belemnite (PDB) standard (Craig, 1957).

Isotopic fractionation of CO₂ trapped by NaOH and soda lime was determined by adding CO₂ from four standards (three calcite and one CO₂ gas cylinder) to NaOH and soda-lime traps. For the calcite standards, 0.1 g of standard was put into a clear 250-mL jar with 5 mL of 0.4 M HCl contained in a small ceramic cup that could be tipped over by tilting the jar. Also placed in the jar was 15 mL of 0.4 M NaOH in a 20-mL container that would not tip over. For the soda lime traps, the same procedure was used except 0.5 g of fresh soda lime was put into a test tube and inserted into the jar. The jars were sealed with parafilm and carefully tilted to spill the HCl onto the calcite standard to release the reference CO₂. The glass jar was then submerged in water to check for leaks. Every glass jar remained closed for 24 h. NaOH and soda lime samples were processed for isotopic analysis in the same manner as the field samples.

For the CO₂ standard from the gas cylinder, two variations of the above procedure were performed. In the first variation there was an application of 40 mL CO₂ gas (~0.065 g of CO₂ at lab pressure and temperature) with a hypodermic needle through the jar’s septa. The reaction time was 24 h. The 40 mL amount of CO₂ was chosen because it was roughly the maximum daily amount of CO₂ absorbed by the traps. In the second variation, 18 doses of CO₂ were applied over 6 d. The doses consisted of daily applications of 40 mL of CO₂ gas divided into three portions (13.3 mL). One portion was applied in the early morning, one was applied midday, and one was applied at night. The 6-d, three-injection method was devised to more closely replicate field conditions based on (i) the isotopic traps were left in the field for 6 d, which was the time needed to trap enough CO₂ for isotopic analysis, and (ii) the morning, noon, and night applications more evenly spread CO₂ absorption over the day than an all-at-once application would have.

The isotopic fractionation ratio αₐ₋ₐ was calculated using the following equation (Criss, 1999):

\[ \alpha_{A-B} = \frac{1000 + \delta^{13}C_A}{1000 + \delta^{13}C_B} \]  

where \( \delta^{13}C_A \) is the value of the standard sample and \( \delta^{13}C_B \) is the value of the CO₂ trapped by NaOH or soda lime. Because the αₐ₋ₐ value for the 6-d application of CO₂ (αCDG6d) was assumed to be the isotopic fractionation ratio that most closely represented field conditions, it was used to estimate the δ¹³C values of CO₂ emissions using the equation:

\[ \delta^{13}C_{BF} = \alpha_{CDG6d}(1000 + \delta^{13}C_{AF}) - 1000 \]

where \( \delta^{13}C_{BF} \) is the isotopic value of soil CO₂ emission before fractionation (i.e., before being trapped by NaOH or soda lime), αCDG6d is the 6-d fractionation factor for NaOH or soda lime, and \( \delta^{13}C_{AF} \) is the value of the soil CO₂ emission after fractionation.

RESULTS AND DISCUSSION

Plant Cover Percentage

To test the hypothesis that exhumed petrocalcic horizons are a greater source of atmospheric CO₂ than neighboring noneroded petrocalcic soils or soil without petrocalcic horizons, it was necessary to keep vegetation constant across all plots because root respiration and microbial decomposition of plant-derived soil organic matter are major sources of CO₂. Plant cover, therefore, affects both the amount and δ¹³C of CO₂. The study area was purposefully chosen because vegetation could be held constant while soil types varied. Although vegetation in the region at large commonly corresponds to changes in soil (Buffington and Herbel, 1965), this was

| Table 1. Mean plant cover (%) ± SE by vegetation type (Bonham, 1989)† and soil type in November 2002 and October 2003 and analyses of variance. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                | Soil without    | Exhumed         | Noneroded       | F value         | P > F           |
|                                | petrocalcic     | petrocalcic     | petrocalcic     |                 |                 |
|                                | horizon (SWoPH)| horizon soil    | horizon soil    |                 |                 |
|                                |                 | (EPHS)          | (NEPHS)         |                 |                 |
|                                | Year 2002       | Year 2003       |                 |                 |                 |
|                                | Shrubs          | Total           | Shrubs          |                 |                 |
| Perennial forbs                | 17.8 ± 0.5      | 21.7 ± 0.5      | 20.8 ± 0.6      | 0.1 ± 0.2       | 2.88 ± 0.0      |
| Annual forbs                   | 4.1 ± 0.4       | 4.2 ± 1.0       | 5.7 ± 0.5       | 0.1 ± 0.1       | 0.11 ± 0.0      |
| Grasses                        | 0.0 ± 0.0       | 0.1 ± 0.3       | 0.1 ± 0.5       | 0.0 ± 0.0       | 0.00 ± 0.0      |
| Total                          | 22.4 ± 0.7      | 21.4 ± 0.2      | 22.3 ± 0.7      | 1.8 ± 0.1       | 0.80 ± 0.0      |
| Perennial forbs                | 1.6 ± 0.5       | 3.5 ± 1.1       | 2.5 ± 0.8       | 0.2 ± 0.1       | 0.57 ± 0.0      |
| Annual forbs                   | 0.0 ± 0.0       | 0.2 ± 0.2       | 0.0 ± 0.0       | 0.0 ± 0.0       | 0.00 ± 0.0      |
| Grasses                        | 0.1 ± 0.1       | 0.1 ± 0.3       | 0.3 ± 0.1       | 0.1 ± 0.1       | 0.02 ± 0.0      |
| Total                          | 22.5 ± 1.8      | 17.9 ± 3.3      | 23.0 ± 3.6      | 2.88 ± 0.0      | 0.16 ± 0.0      |

† Plant cover was measured by the line intercept method. Canopy intercept was recorded wherever a canopy element (e.g., leaf or twig) occurred at least once every 5 cm.

‡ Means are based on five quadrats per plot times three plots.
§ There were 2 df for soil types and 4 df for the error. Data was transformed to arcsine square root (percentage of plant cover/100) for the analysis of variance (Steel and Torrie, 1980). Statistical results were similar between untransformed percentages and arcsine transformed values. Therefore, results for untransformed percentages are presented here.
not the case for the study area. The most likely reason for the uniform vegetation is because the soil types exist on the same or juxtaposed geomorphic surfaces (Fig. 1D) in which there are no major topographically controlled runoff-runon relationships.

Using the line intercept method to quantify vegetative cover (Bonham, 1989), two surveys of the vegetation were made: one in November 2002 and the other in October 2003 (Table 1). Based on this analysis, there was no difference at a significance level of $\alpha = 0.05$ in total plant cover or vegetation type among the three soil types (EPHS, NEPHS, and SWoPH) during the sample dates.

**Carbon Dioxide Emissions Measured with NaOH Traps**

Comparison of CO$_2$ emissions from exhumed petrocalcic horizon soils (EPHS) and neighboring soils based on NaOH traps is shown in Fig. 2. At a significance level of $\alpha = 0.05$, only two sampling dates (2 Oct. 2002 and 5 Aug. 2003) had CO$_2$ emissions from the exhumed petrocalcic horizon that were statistically higher than CO$_2$ emissions of at least one of the neighboring soils—NEPHS or SWoPH. However, on a third date (7 Oct. 2003) the mean CO$_2$ from the NEPHS soil was statistically higher than both EPHS and SWoPH. The rest of the sampling dates had no differences ($\alpha = 0.05$) among the three soil types. At this $\alpha$ level, almost all CO$_2$ emissions from the EPHS soil were similar to those observed in neighboring soils.

When the significance level was increased to $\alpha = 0.2$, there were five additional sampling dates when CO$_2$ flux from the EPHS soil was higher than at least one of the neighboring soils (Fig. 2). However, there were also three additional times when either SWoPH or NEPHS emitted the highest amount of CO$_2$. Like the $\alpha = 0.05$ level, at this $\alpha$ level almost all CO$_2$ emissions from the EPHS soil were similar to those observed in neighboring soils. In addition, this suggests that the conclusion that there is no soil effect is not simply due to a lack of statistical power associated with the small sample size ($n = 3$ sites).

**Carbon Dioxide Emissions Measured with Soda Lime Traps**

Comparison of CO$_2$ emissions from EPHS and neighboring soils based on soda lime traps is shown in Fig. 3. At a significance level of $\alpha = 0.05$ there were three sampling dates (9 July 2002 and 22 May and 22 July 2003) when EPHS was significantly higher than at least one of the neighboring soils. On a fourth date (7 Oct. 2003) the mean soil CO$_2$ flux of the SWoPH soil was higher ($\alpha = 0.05$) than EPHS and similar to NEPHS.

There were no differences in soil CO$_2$ flux at the level $\alpha = 0.05$ among the soil types for the rest of the sampling dates. At this $\alpha$ level, almost all the CO$_2$ emissions measured with soda lime traps were similar for each soil type, which is in agreement with the NaOH results.

When the level of uncertainty was increased to $\alpha = 0.2$, there were five additional sampling dates when CO$_2$ emissions from EPHS were higher than at least one of the neighboring soils (Fig. 3). However, there were also seven additional sampling dates when CO$_2$ emissions from either SWoPH or NEPHS were significantly higher.

**Cumulative Carbon Dioxide Emissions**

Cumulative amounts of CO$_2$ are shown in Table 2. In all cases, there were no significant statistical differences ($\alpha = 0.05$) among the mean quantities of soil CO$_2$ emitted from the three soil types. This was true for a period of 1 yr (July 2002 to June 2003) as well as for the entire study period (June 2002 to October 2003).

The data in Table 2 also make it apparent that soda lime values are greater than the NaOH values (by about fourfold). The NaOH data are thought to be closer to the true values because the NaOH data were not significantly different at $\alpha = 0.05$ than CO$_2$ data measured with an IRGA (Serna-Pérez, 2004). Further research is needed to understand why soda lime overestimated CO$_2$ in this arid system. Perhaps the soda lime powder, which has a high surface area, created a strong diffusion gradient by vigorously absorbing CO$_2$, thereby causing more CO$_2$ to be removed from the soil. Nevertheless, the soda lime values, although higher, still lead to the same conclusion.

**Isotopic Analysis**

If the hypothesis that EPHS emits more CO$_2$ than neighboring soils were correct, and if the source of the CO$_2$ emissions was CaCO$_3$ in the petrocalcic horizon, then $\delta^{13}$C values of CO$_2$ emissions from EPHS should have $\delta^{13}$C values similar to the petrocalcic horizons. Moreover, if the hypothesis were true, $\delta^{13}$C values of CO$_2$ from EPHS should also be different than the other soil types, especially the Torripsamment that contains only trace amounts of pedogenic carbonate. To compare a large number of isotopic values from the field, NaOH and soda lime traps were used instead of direct measurements of CO$_2$. While using alkali traps has the advantage of providing many samples, this method has the disadvantage of involving an isotopic fractionation that occurs when CO$_2$ is absorbed by alkali solutions, and, therefore, requires a correction factor to obtain $\delta^{13}$C values representative of CO$_2$ emission in the field. Fractionation of CO$_2$ during alkali absorption is dependent on the alkali solution used as well as reaction time, temperature, and concentration (Usdowski and Hoefs, 1986; Fritz et al., 1985; Davidson, 1995). Therefore, a lab study was undertaken to derive a fractionation factor that could be applied to the NaOH and soda lime traps.

**Lab Experiment to Determine Fractionation Factors**

Carbon dioxide gas with known $\delta^{13}$C values was added to NaOH and soda lime traps. The results revealed that fractionation depended on the initial $\delta^{13}$C value, reaction time, and amount applied (Fig. 4). With time held constant at 24 h, the heavier $\delta^{13}$C values had slightly greater fractionation factors ($\alpha_{A,B}$) for both the
NaOH and soda lime traps. All fractionations caused depletion with respect to the standards except for the NaOH absorption of the most depleted standard (CC3) (Fig. 4).

An increase in absorption time decreased fractionation as shown by standards CDG1d and CDG6d (Fig. 4). The one-dose application of 40 mL of CO$_2$ with a reaction time of 24 h had a higher fractionation factor.
Fig. 3. Soil CO$_2$ emissions using soda lime traps for the three sampling blocks. Soil temperature and rainfall are the same as described in Fig. 2. Means with ** are different at $\alpha = 0.05$. Means with * are different at $\alpha = 0.20$. Arrows pointing up signify times when exhumed petrocalcic horizon soils (EPHS) is higher than at least one of the neighboring soils. Arrows pointing down signify times when EPHS is lower than at least one neighboring soil.
than the 18-dose, 6-d application wherein 40 mL of CO₂ was divided into three applications per day for 6 d (Fig. 4). Because the 6-d application is thought to more closely represent field conditions, which also consisted of a 6-d trapping period, the CDG₆d A-B value of 1.0012 was used as a correction factor for field samples collected with NaOH traps, and the CDG₆d A-B value of 1.0021 was used as a correction factor for field samples collected with soda lime traps (Fig. 4).

**δ¹³C of Carbon Dioxide Field Samples**

Isotopic values of CO₂ trapped by NaOH and soda lime were corrected for fractionation using Eq. [2] and are

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<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
</tr>
<tr>
<td>NaOH-trapped CO₂</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Noneroded petrocalcic soil</td>
<td>0.1120</td>
<td>0.0026</td>
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<td>0.1149</td>
<td>0.0036</td>
<td>0.1630</td>
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<tr>
<td></td>
<td>F = 0.41</td>
<td>P &gt; F = 0.6903</td>
<td>F = 0.52</td>
</tr>
<tr>
<td>Soda lime-trapped CO₂</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>0.0180</td>
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</tr>
<tr>
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<tr>
<td>Soil without petrocalcic horizon</td>
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<td>0.0238</td>
<td>0.6401</td>
</tr>
<tr>
<td></td>
<td>F = 0.02</td>
<td>P &gt; F = 0.9814</td>
<td>F = 0.17</td>
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† Data are the sum of the 24-h trapping periods for the 51 sampling dates. CO₂ values are not significantly different at α = 0.05 for the three soil types regardless of whether the NaOH or soda lime traps were used.

Fig. 4. Fractionation values between δ¹³C values of standards and δ¹³C values of alkali traps. Reaction time for all alkali traps was 24 h except CDG₆d which was 6 d.
To increase the possibility of detecting a δ\textsuperscript{13}C signature from EPHS, sampling dates were chosen for times when CO\textsubscript{2} emissions from EPHS were higher than at least one of the neighboring soils (Fig. 2 and 3). Figure 5 reveals that δ\textsuperscript{13}C values of both NaOH- and soda lime–trapped CO\textsubscript{2} were always more negative than values of pedogenic carbonates in the Jornada Basin floor. They are also more negative than any pedogenic carbonate reported for surrounding areas (Gardner, 1984; Monger et al., 1998; Buck and Monger, 1999). For the NaOH traps, δ\textsuperscript{13}C values were intermediate between the C\textsubscript{4} and C\textsubscript{3} plants. For soda lime traps, δ\textsuperscript{13}C values were within the C\textsubscript{3} range. Moreover, for both NaOH and soda lime, the δ\textsuperscript{13}C values from EPHS were similar to those from SWoPH and NEPHS (Fig. 5). That is, there were no statistical difference among the soil types at the α = 0.05 level (Table 3).

![Figure 5](image)

**Table 3.** Cumulative mean carbon isotopic signatures (δ\textsuperscript{13}C) shown in Fig. 5. Values are mean ± SD for the three soil types and two methods of trapping CO\textsubscript{2}\textsuperscript{†}.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>NaOH</th>
<th>Soda lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noneroded petrocalcic horizon soil</td>
<td>16.7 ± 1.4</td>
<td>21.5 ± 4.4</td>
</tr>
<tr>
<td>Exhumed petrocalcic horizon soil</td>
<td>16.8 ± 1.5</td>
<td>20.5 ± 3.6</td>
</tr>
<tr>
<td>Soil without petrocalcic horizon</td>
<td>17.0 ± 1.3</td>
<td>20.3 ± 4.6</td>
</tr>
</tbody>
</table>

\textsuperscript{†}Means in the same column followed by the same letter (a or b) are not significantly different at the α = 0.05 level.
Based on these data, the predominant source of CO$_2$ from EPHS was soil respiration, not the dissolution of CaCO$_3$ in the exhumed petrocalcic horizon. The dominant plant species in the study area is mesquite. This C$_3$ plant has $\delta^{13}$C values ranging from $-25.0$ to $-25.8$% (Connin et al., 1997a; Monger, 2003). Mesquite roots have been shown to be widely distributed, even in the relatively large interspaces where measurements were taken (Gibbens and Lenz, 2001).

Because the $\delta^{13}$C data shown in Fig. 5 are isotopically less negative than C$_3$ vegetation, it is probable that the measured CO$_2$ was a mixture of two or more CO$_2$ sources instead of C$_3$ respiration alone. One possibility is the mixing of CO$_2$ from the current C$_3$ plant community with CO$_2$ from C$_4$ organic matter remaining from former black grama grasslands (Connin et al., 1997b). Another possibility is the mixing of soil respiration with atmospheric CO$_2$ that has entered the soil as a result of low respiration rates (Quade et al., 1989; Cerling and Quade, 1993). A further possibility that cannot be disproven at this stage is the mixing of soil respiration with CO$_2$ from pedogenic carbonate. Although the isotopic composition of CO$_2$ indicates that CaCO$_3$ is not the main source, we cannot rule out the possibility that CaCO$_3$ might be contributing some CO$_2$. This is because there are no soils in the study area that are totally devoid of CaCO$_3$, although the SWoPH (Torripsamments) typically contain less than 3 wt.% (mostly less than 1 wt.%) in any horizon. An additional possibility is a preferential release of $^{12}$CO$_2$ by the partial dissolution of CaCO$_3$.

**CONCLUSIONS**

Arid and semiarid landscapes, like the Chihuahuan Desert in southern New Mexico, contain large areas where erosion has exposed petrocalcic horizons at or near the land surface making it a potential source of atmospheric CO$_2$. However, CO$_2$ emissions measured with both NaOH and soda lime traps showed similar trends: although there were times when EPHS emitted more CO$_2$ than neighboring soil types, there were other times when neighboring soil types emitted more CO$_2$ than EPHS. Cumulatively for the period analyzed between June 2002 and October 2003, there was no significant difference between EPHS, SWoPH, or NEPHS at the $\alpha = 0.05$ level.

Isotopic signatures of CO$_2$ corroborated the CO$_2$ trap evidence. After applying correction factors for isotopic fractionation resulting from absorption of CO$_2$ by the NaOH and soda lime traps, the $\delta^{13}$C values of CO$_2$ did not match the $\delta^{13}$C values of petrocalcic horizons. Furthermore, the $\delta^{13}$C values of CO$_2$ from EPHS were not significantly different than the other soil types at the $\alpha = 0.05$ level, which would be expected if exhumed petrocalcic horizons were active CO$_2$ sources.

Globally, petrocalcic horizons store huge amounts of C (Eswaran et al., 2000) and have the potential to be an important source of atmospheric CO$_2$ by means of CaCO$_3$ dissolution. However, at the timeframe of a couple of years and within the detection capabilities of the methods employed, we conclude that exhumed petrocalcic horizons are not a significantly greater source of atmospheric CO$_2$ than neighboring soils without petrocalcic horizons or noneroded petrocalcic soils.

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