

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 CaCO_3 . In addition to being an important sink of atmospheric CO_2 , soil carbonate is potentially an important source of atmospheric CO_2 . The cemented form of soil carbonate—the petrocalcic horizon—develops in geomorphically 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 CO_2 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 CO_2 and the $\delta^{13}\text{C}$ of CO_2 released from the three soil types. Using a randomized complete block design, CO_2 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 CO_2 emissions from the three soil types at the $\alpha = 0.05$ level. Moreover, the isotopic analysis of CO_2 did not match the isotopic values of pedogenic carbonate, nor were there any statistical differences ($\alpha = 0.05$) in $\delta^{13}\text{C}$ of CO_2 among the three soil types. We conclude, therefore, that exhumed petrocalcic horizons are not actively emitting CO_2 at a rate significantly 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 CO_2 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 CO_2 , soils also have the potential for being a source of atmospheric CO_2 , as was the case in the United States with the loss of soil organic matter from 1800 to 1950 (Houghton et al., 1999). Recent CO_2 flux measurements

have also indicated that CaCO_3 in soil may be a source of atmospheric CO_2 (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 above-ground 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 CaCO_3). 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 CO_2 emissions as the result of CaCO_3 dissolution via the reaction



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 CO_2 emissions.

To address this possibility, we tested the hypothesis that soils with exhumed petrocalcic horizons will emit more CO_2 than neighboring noneroded petrocalcic horizon soils or than sandy Entisols without petrocalcic horizons by (i) comparing the amount of CO_2 released from the three soil types and (ii) by measuring the isotopic composition ($\delta^{13}\text{C}$) of CO_2 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

A. Serna-Pérez, Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias, Calera, Zacatecas 98500, Mexico; H.C. Monger, Dep. of Plant and Environmental Science, New Mexico State Univ., Las Cruces, NM 88003; J.E. Herrick, USDA-ARS, Jornada Experimental Range, Las Cruces, NM 88003; L. Murray, Univ. Statistics Center, New Mexico State Univ., Las Cruces, NM 88003. Received 30 Mar. 2005. *Corresponding author (cmonger@nmsu.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

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

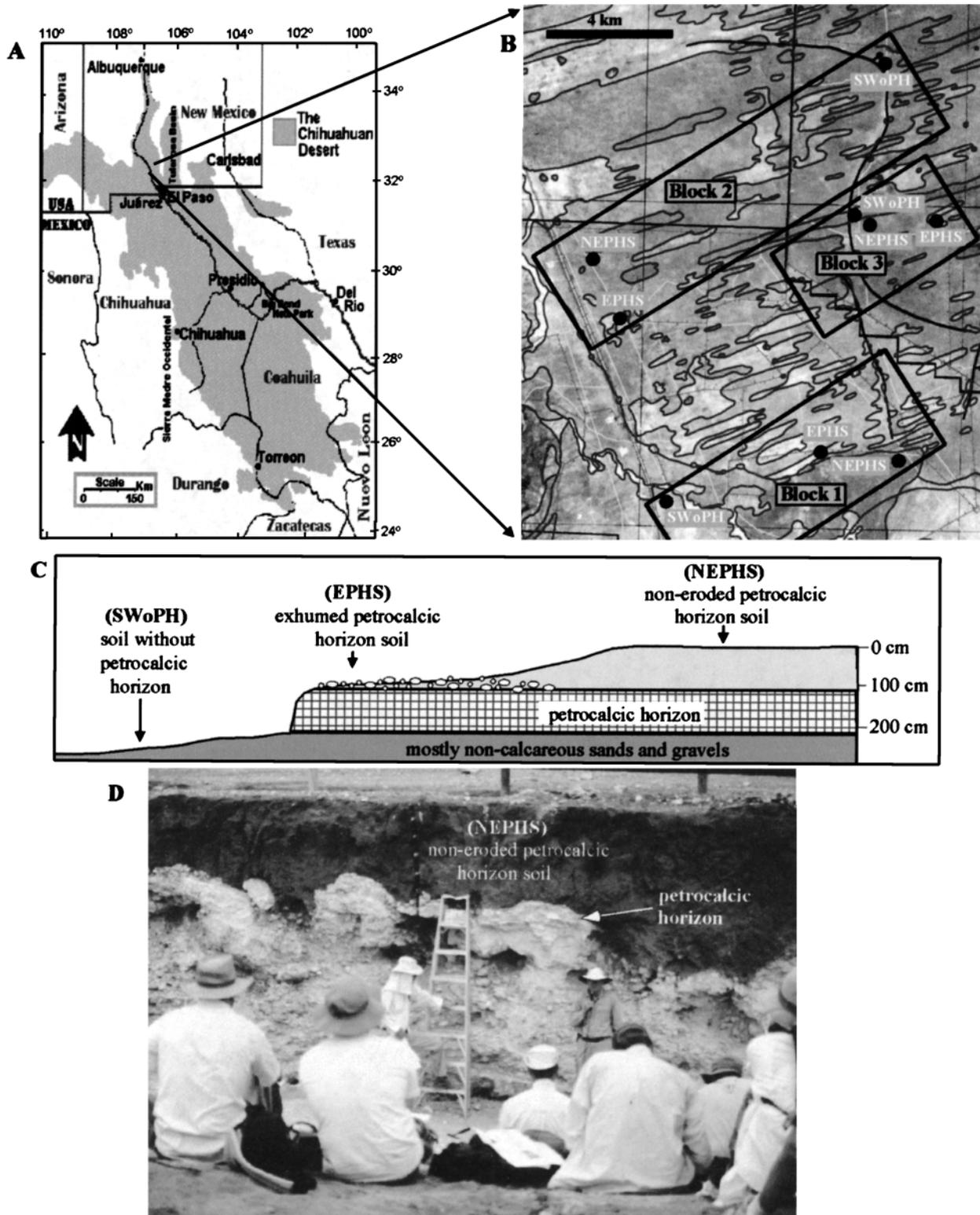


Fig. 1. Location of study site and illustration of the three soil types. (A) Chihuahuan Desert and location of study site in New Mexico. (B) Locations of blocks and quadrats for the three soil types. The map units are of geomorphic units, including states of erosion (Monger et al., 2006). (C) Cross-section illustrating the three soil types evaluated for their CO₂ 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 CO₂ traps were consistently placed over the smaller fragments of petrocalcic horizon at all EPHS sites. These soils classify as Typic Petrocalcids, unless the petrocalcic is highly ruptured, in which case they would be Haplocalcids (Soil Survey Staff, 1999).

Where erosion has not stripped away the upper profile and at least 100 cm remains above the petrocalcic horizon, the soils classify as Argic Petrocalcids if they have an argillic horizon, otherwise they are Typic Petroargids. These soils contain the second treatment: “noneroded petrocalcic horizon soils” (NEPHS) (Fig. 1C and 1D). The third treatment, “soils without petrocalcic horizons” (SWoPH), classify as Typic Torripsamments and occurs in two settings. The first is on actively eroding river sediment, mostly noncalcareous sands and gravels, downslope of the petrocalcic horizon (Fig. 1C). The second setting is along a fault scarp within the basin floor (Seager et al., 1987) where tectonic movement has offset the petrocalcic horizon and where noncalcareous eolian deposits have buried the petrocalcic-free fault scarp with sandy sediments. These sandy soils, because of their youthful age, contain at most faint Stage I filaments.

Annual rainfall in the study areas average 222 mm with more than 50% of this amount falling during July to September (usda-ars.nmsu.edu/general/generalinfo.htm; verified 5 Dec. 2005). Rainfall for this experiment was measured at each block. Rainwater was also collected for pH measurements for seven storm events from 16 Aug. to 11 Oct. 2003. Results of the pH measurements show a decreased in pH from 7.2 in mid-August to 6.1 in mid-October (Serna-Pérez, 2004).

Both C₃ and C₄ plants are common in the Chihuahuan Desert (Syvertsen et al., 1976). The vegetation in the study area is dominated by C₃ shrubs, mainly mesquite (*Prosopis glandulosa* 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 m². Widely scattered C₃ subshrubs, such as snakeweed [*Gutierrezia sarothrae* (Pursh) Britt. & Rusby], perennial and annual C₃ forbs, and C₄ perennial grasses occur in the interspaces. The perennial grasses are mainly black grama [*Bouteloua eriopoda* (Torrey) Torrey] with some mesa 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 microbiotic 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 plot, there were five subsamples from 2 by 2 m quadrats. The CO₂ measurements were made over 51 sampling dates spanning the period from June 2002 to October 2003. There were 15 CO₂ measurements on every soil type, which is the amount needed to obtain a mean value of soil CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂) and measured amounts of CO₂. 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 CO₂) and measured amounts of CO₂, 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 $\alpha = 0.05$. However, the soda lime method gave higher CO_2 values than IRGA by about 20-fold (Serna-Pérez, 2004).

Soil CO_2 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 CO_2 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 CO_2 and correction for CO_2 absorbed by the blanks, soil CO_2 fluxes were expressed in units of milligrams of CO_2 per square meter per hour ($\text{mg CO}_2 \text{ m}^{-2} \text{ h}^{-1}$).

$\delta^{13}\text{C}$ Analysis

The $\delta^{13}\text{C}$ values of soil CO_2 emissions were determined by absorbing CO_2 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 CO_2 (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 CO_2 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 Na_2CO_3 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). $\delta^{13}\text{C}$ values are reported relative to those of the Pee Dee belemnite (PDB) standard (Craig, 1957).

Isotopic fractionation of CO_2 trapped by NaOH and soda lime was determined by adding CO_2 from four standards (three calcite and one CO_2 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 CO_2 . 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 CO_2 standard from the gas cylinder, two variations of the above procedure were performed. In the first variation there was an application of 40 mL CO_2 gas (~ 0.065 g of CO_2 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 CO_2 was chosen because it was roughly the maximum daily amount of CO_2 absorbed by the traps. In the second variation, 18 doses of CO_2 were applied over 6 d. The doses consisted of daily applications of 40 mL of CO_2 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 replicated field conditions based on (i) the isotopic traps were left in the field for 6 d, which was the time needed to trap enough CO_2 for isotopic analysis, and (ii) the morning, noon, and night applications more evenly spread CO_2 absorption over the day than an all-at-once application would have.

The isotopic fractionation ratio α_{A-B} was calculated using the following equation (Criss, 1999):

$$\alpha_{A-B} = \left(\frac{1000 + \delta^{13}\text{C}_A}{1000 + \delta^{13}\text{C}_B} \right) \quad [1]$$

where $\delta^{13}\text{C}_A$ is the value of the standard sample and $\delta^{13}\text{C}_B$ is the value of the CO_2 trapped by NaOH or soda lime. Because the α_{A-B} value for the 6-d application of CO_2 (α_{CDG6d}) was assumed to be the isotopic fractionation ratio that most closely represented field conditions, it was used to estimate the $\delta^{13}\text{C}$ values of CO_2 emissions using the equation:

$$\delta^{13}\text{C}_{\text{BF}} = \alpha_{\text{CDG6d}}(1000 + \delta^{13}\text{C}_{\text{AF}}) - 1000 \quad [2]$$

where $\delta^{13}\text{C}_{\text{BF}}$ is the isotopic value of soil CO_2 emission before fractionation (i.e., before being trapped by NaOH or soda lime), α_{CDG6d} is the 6-d fractionation factor for NaOH or soda lime, and $\delta^{13}\text{C}_{\text{AF}}$ is the value of the soil CO_2 emission after fractionation.

RESULTS AND DISCUSSION

Plant Cover Percentage

To test the hypothesis that exhumed petrocalcic horizons are a greater source of atmospheric CO_2 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 CO_2 . Plant cover, therefore, affects both the amount and $\delta^{13}\text{C}$ of CO_2 . 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 (%) \pm SE by vegetation type (Bonham, 1989)† and soil type in November 2002 and October 2003 and analyses of variance.

| Vegetation type | Mean plant cover (%)‡ ANOVA summary§ | | | F value | P > F |
|-----------------|--|---|------------------------------------|---------|--------|
| | Soil without petrocalcic horizon (SWoPH) | Exhumed petrocalcic horizon soil (EPHS) | Noneroded petrocalcic soil (NEPHS) | | |
| | Year 2002 | | | | |
| Shrubs | 17.8 \pm 0.5 | 16.2 \pm 3.8 | 21.9 \pm 4.5 | 1.27 | 0.3747 |
| Perennial forbs | 4.1 \pm 0.4 | 4.2 \pm 1.0 | 3.2 \pm 2.1 | 0.42 | 0.6853 |
| Annual forbs | 0.0 \pm 0.0 | 0.1 \pm 0.1 | 0.1 \pm 0.1 | 0.55 | 0.6143 |
| Grasses | 0.5 \pm 0.4 | 0.9 \pm 0.6 | 2.0 \pm 2.0 | 0.11 | 0.8967 |
| Total | 22.4 \pm 0.7 | 21.4 \pm 2.4 | 27.2 \pm 0.5 | 6.32 | 0.0578 |
| | Year 2003 | | | | |
| Shrubs | 20.8 \pm 1.3 | 14.0 \pm 4.4 | 20.2 \pm 5.2 | 2.19 | 0.2273 |
| Perennial forbs | 1.6 \pm 0.5 | 3.5 \pm 1.1 | 2.5 \pm 1.8 | 0.57 | 0.6065 |
| Annual forbs | 0.0 \pm 0.0 | 0.2 \pm 0.2 | 0.0 \pm 0.0 | 1.00 | 0.4444 |
| Grasses | 0.1 \pm 0.1 | 0.2 \pm 0.2 | 0.3 \pm 0.3 | 0.12 | 0.8935 |
| Total | 22.5 \pm 1.8 | 17.9 \pm 3.3 | 23.0 \pm 3.6 | 2.88 | 0.1682 |

† Plant cover was measured by the line intercept method. Canopy intercept was recorded where 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 CO₂ 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 CO₂ emissions from the exhumed petrocalcic horizon that were statistically higher than CO₂ emissions of at least one of the neighboring soils—NEPHS or SWoPH. However, on a third date (7 Oct. 2003) the mean CO₂ 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 α level, almost all CO₂ 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 CO₂ 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 CO₂. Like the $\alpha = 0.05$ level, at this α level almost all CO₂ 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 CO₂ 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 CO₂ flux of the SWoPH soil was higher ($\alpha = 0.05$) than EPHS and similar to NEPHS. There were no differences in soil CO₂ flux at the level $\alpha = 0.05$ among the soil types for the rest of the sampling dates. At this α level, almost all the CO₂ 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 CO₂ emissions from EPHS were higher than at least one of

the neighboring soils (Fig. 3). However, there were also seven additional sampling dates when CO₂ emissions from either SWoPH or NEPHS were significantly higher.

Cumulative Carbon Dioxide Emissions

Cumulative amounts of CO₂ are shown in Table 2. In all cases, there were no significant statistical differences ($\alpha = 0.05$) among the mean quantities of soil CO₂ 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 CO₂ data measured with an IRGA (Serna-Pérez, 2004). Further research is needed to understand why soda lime overestimated CO₂ in this arid system. Perhaps the soda lime powder, which has a high surface area, created a strong diffusion gradient by vigorously absorbing CO₂, thereby causing more CO₂ 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 CO₂ than neighboring soils were correct, and if the source of the CO₂ emissions was CaCO₃ in the petrocalcic horizon, then $\delta^{13}\text{C}$ values of CO₂ emissions from EPHS should have $\delta^{13}\text{C}$ values similar to the petrocalcic horizons. Moreover, if the hypothesis were true, $\delta^{13}\text{C}$ values of CO₂ 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 CO₂. While using alkali traps has the advantage of providing many samples, this method has the disadvantage of involving an isotopic fractionation that occurs when CO₂ is absorbed by alkali solutions, and, therefore, requires a correction factor to obtain $\delta^{13}\text{C}$ values representative of CO₂ emission in the field. Fractionation of CO₂ 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 $\delta^{13}\text{C}$ values was added to NaOH and soda lime traps. The results revealed that fractionation depended on the initial $\delta^{13}\text{C}$ value, reaction time, and amount applied (Fig. 4). With time held constant at 24 h, the heavier $\delta^{13}\text{C}$ values had slightly greater fractionation factors (α_{A-B}) for both the

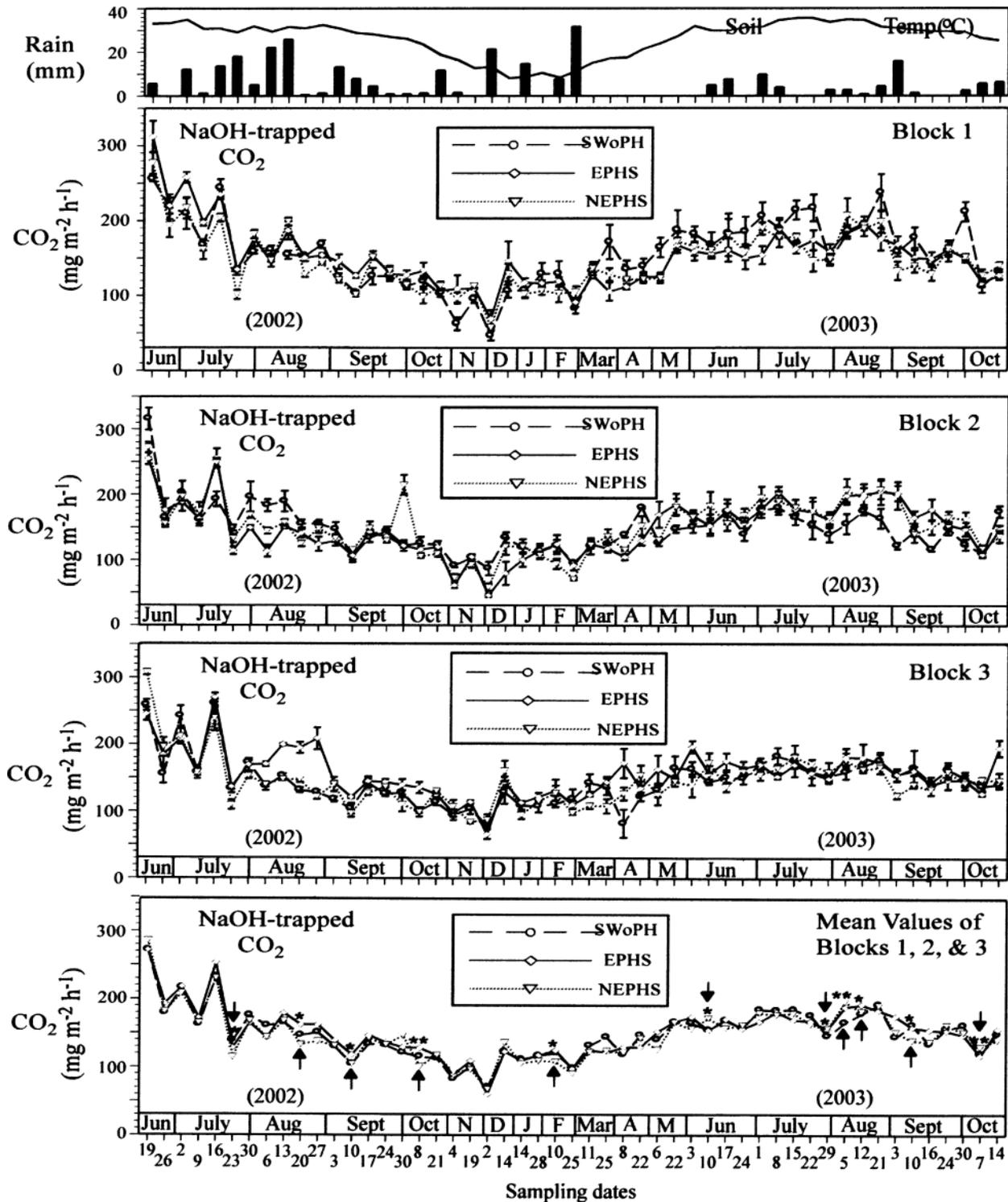


Fig. 2. Soil CO₂ emissions based on NaOH traps for the three sampling blocks. Soil temperature was taken at 10 cm at Jornada Long Term Ecological Research (LTER) weather station. Rainfall is the accumulated amounts between sampling dates (weekly from July to September and biweekly October to May). Soil temperature and rainfall share the same scale on the graph. 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 other two soil types. Arrows pointing down signify times when EPHS is lower than at least one of the other two soil types.

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 CO₂ with a reaction time of 24 h had a higher fractionation factor

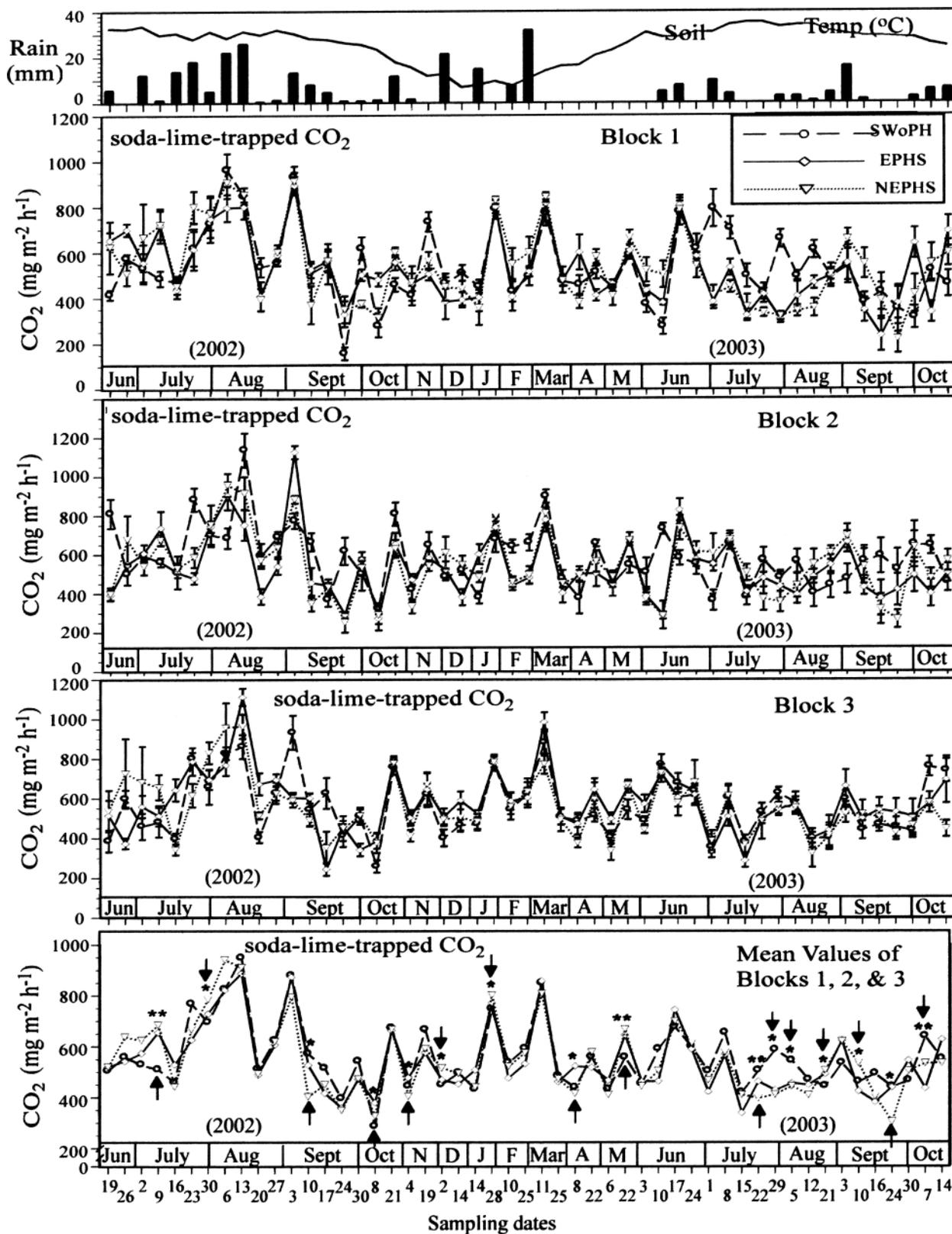


Fig. 3. Soil CO₂ emissions using soda lime traps for the three sampling blocks. Soil temperature and rainfall are the same as described in Fig. 2. Means with ** are different at $\alpha = 0.05$. Means with * are different at $\alpha = 0.20$. Arrows pointing up signify times when exhumed petrocalcic horizon 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.

Table 2. Cumulative soil CO₂ trapped by NaOH and soda lime for 1 yr and for the length of sampling period.†

| Soil type | Cumulative soil CO ₂ emissions | | | |
|---|---|------------------------------|------------------------------------|------------------------------|
| | One year July 2002–June 2003 | | Sampling period June 2002–Oct 2003 | |
| | Mean | SD | Mean | SD |
| g cm ⁻² | | | | |
| NaOH-trapped CO₂ | | | | |
| Noneroded petrocalcic soil | 0.1120 | 0.0026 | 0.1615 | 0.0042 |
| Exhumed petrocalcic horizon soil | 0.1165 | 0.0076 | 0.1665 | 0.0071 |
| Soil without petrocalcic horizon | 0.1149 | 0.0036 | 0.1630 | 0.0058 |
| | <i>F</i> = 0.41 | <i>P</i> > <i>F</i> = 0.6903 | <i>F</i> = 0.52 | <i>P</i> > <i>F</i> = 0.6301 |
| Soda lime-trapped CO₂ | | | | |
| Noneroded petrocalcic soil | 0.4886 | 0.0180 | 0.6310 | 0.0216 |
| Exhumed petrocalcic horizon soil | 0.4910 | 0.0318 | 0.6319 | 0.0365 |
| Soil without petrocalcic horizon | 0.4913 | 0.0238 | 0.6401 | 0.0319 |
| | <i>F</i> = 0.02 | <i>P</i> > <i>F</i> = 0.9814 | <i>F</i> = 0.17 | <i>P</i> > <i>F</i> = 0.8471 |

† Data are the sum of the 24-h trapping periods for the 51 sampling dates. CO₂ values are not significantly different at $\alpha = 0.05$ for the three soil types regardless of whether the NaOH or soda lime traps were used.

(α_{A-B}) 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 α_{A-B} value of 1.0012 was used as a correction factor for field samples collected with NaOH traps, and the CDG6d α_{A-B} value

of 1.0021 was used as a correction factor for field samples collected with soda lime traps (Fig. 4).

$\delta^{13}\text{C}$ of Carbon Dioxide Field Samples

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

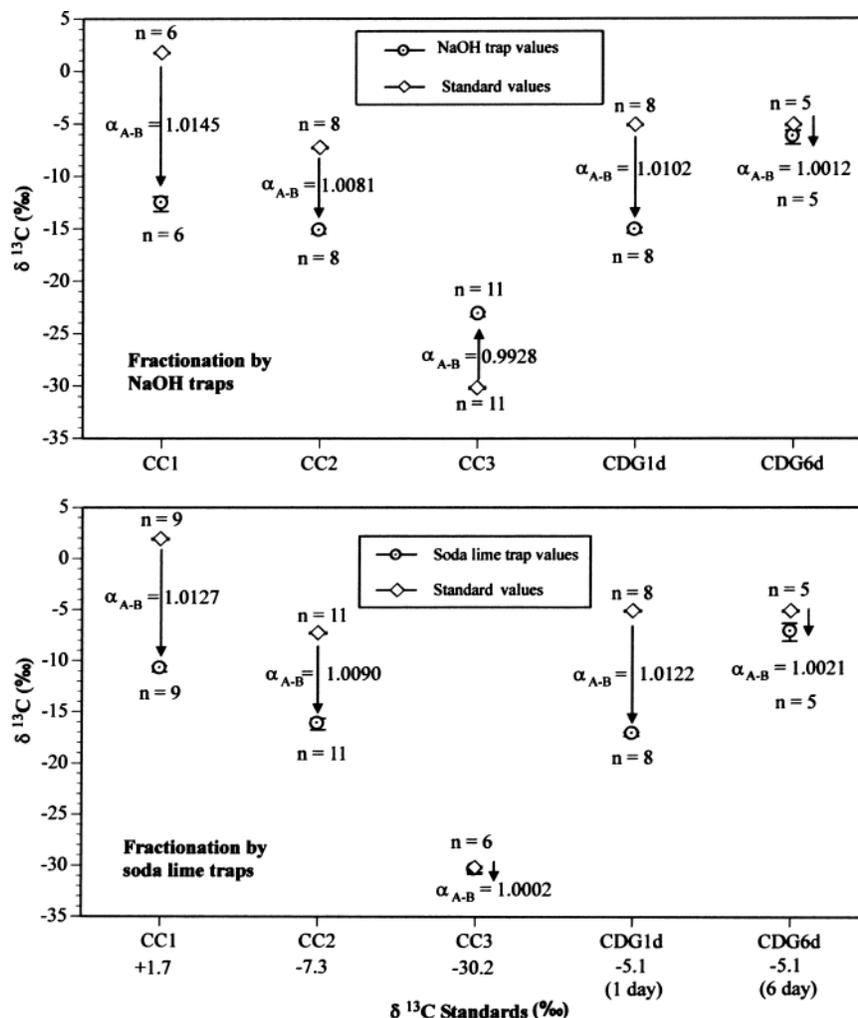


Fig. 4. Fractionation values between $\delta^{13}\text{C}$ values of standards and $\delta^{13}\text{C}$ values of alkali traps. Reaction time for all alkali traps was 24 h except CDG6d which was 6 d.

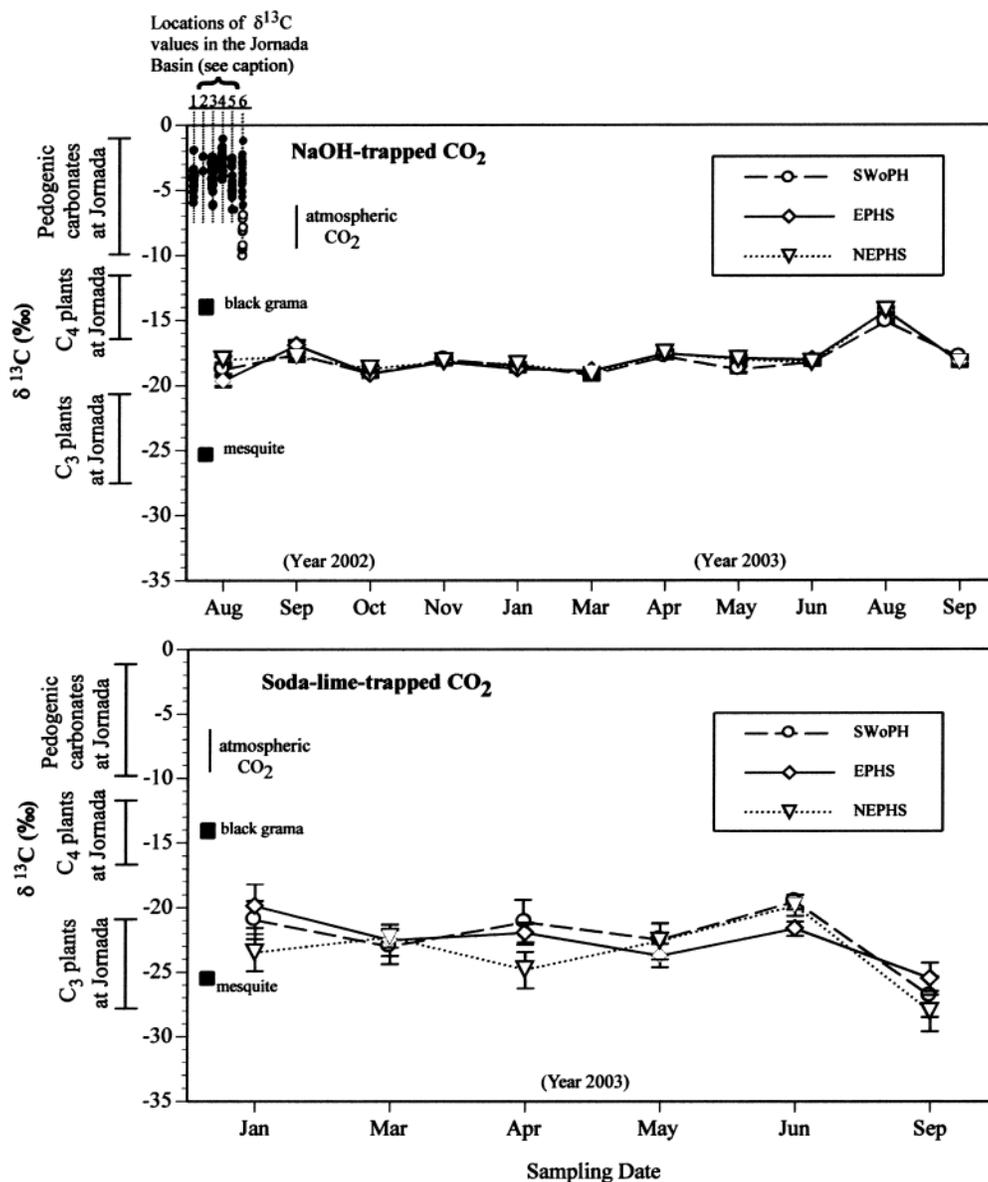


Fig. 5. Carbon isotopic values ($\delta^{13}\text{C}$) of CO_2 emissions after correction using fractionation factors. Each point is the mean of $n = 12$ (i.e., four replications in each plot times three plots per soil type). Range of atmospheric CO_2 from Clark and Fritz (1997). Range of C_4 black grama and C_3 mesquite, shown with black boxes, are from Connin et al. (1997a) and Monger (2003). Values for pedogenic carbonates shown in upper left of top figure are from the following areas in the Jornada Basin: (1) Stressor site; (2) Mayfield well; (3), (4), and (5) Liu (2002); (6) Connin et al. (1997a, 1997b). Open circles are Stage I pedogenic carbonates formed in coppice dunes.

shown in Fig. 5. To increase the possibility of detecting a $\delta^{13}\text{C}$ signature from EPHS, sampling dates were chosen for times when CO_2 emissions from EPHS were higher than at least one of the neighboring soils (Fig. 2 and 3).

Figure 5 reveals that $\delta^{13}\text{C}$ values of both NaOH- and soda lime-trapped CO_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, $\delta^{13}\text{C}$ values were intermediate between the C_4 and C_3 plants. For soda lime traps, $\delta^{13}\text{C}$ values were within the C_3 range. Moreover, for both NaOH and soda lime, the $\delta^{13}\text{C}$ 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 $\alpha = 0.05$ level (Table 3).

Table 3. Cumulative mean carbon isotopic signatures ($\delta^{13}\text{C}$) shown in Fig. 5. Values are mean \pm SD for the three soil types and two methods of trapping CO_2 .[†]

| Soil type | Mean carbon isotopic value ($\delta^{13}\text{C}$ ‰) CO_2 trap | |
|------------------------------------|--|-------------------|
| | NaOH | Soda lime |
| Noneroded petrocalcic horizon soil | -16.7 a \pm 1.4 | -21.5 b \pm 4.4 |
| Exhumed petrocalcic horizon soil | -16.8 a \pm 1.5 | -20.5 b \pm 3.6 |
| Soil without petrocalcic horizon | -17.0 a \pm 1.3 | -20.3 b \pm 4.6 |

[†] Means in the same column followed by the same letter (a or b) are not significantly different at the $\alpha = 0.05$ level.

Based on these data, the predominant source of CO₂ from EPHS was soil respiration, not the dissolution of CaCO₃ in the exhumed petrocalcic horizon. The dominant plant species in the study area is mesquite. This C₃ plant has δ¹³C 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 δ¹³C data shown in Fig. 5 are isotopically less negative than C₃ vegetation, it is probable that the measured CO₂ was a mixture of two or more CO₂ sources instead of C₃ respiration alone. One possibility is the mixing of CO₂ from the current C₃ plant community with CO₂ from C₄ organic matter remaining from former black grama grasslands (Connin et al., 1997b). Another possibility is the mixing of soil respiration with atmospheric CO₂ 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 CO₂ from pedogenic carbonate. Although the isotopic composition of CO₂ indicates that CaCO₃ is not the main source, we cannot rule out the possibility that CaCO₃ might be contributing some CO₂. This is because there are no soils in the study area that are totally devoid of CaCO₃, 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 ¹²CO₂ by the partial dissolution of CaCO₃.

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 CO₂. However, CO₂ emissions measured with both NaOH and soda lime traps showed similar trends: although there were times when EPHS emitted more CO₂ than neighboring soil types, there were other times when neighboring soil types emitted more CO₂ 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 α = 0.05 level.

Isotopic signatures of CO₂ corroborated the CO₂ trap evidence. After applying correction factors for isotopic fractionation resulting from absorption of CO₂ by the NaOH and soda lime traps, the δ¹³C values of CO₂ did not match the δ¹³C values of petrocalcic horizons. Furthermore, the δ¹³C values of CO₂ from EPHS were not significantly different than the other soil types at the α = 0.05 level, which would be expected if exhumed petrocalcic horizons were active CO₂ sources.

Globally, petrocalcic horizons store huge amounts of C (Eswaran et al., 2000) and have the potential to be an important source of atmospheric CO₂ by means of CaCO₃ dissolution. However, at the timeframe of a couple of years and within the detection capabilities of the methods employed, we conclude that exhumed petro-

calcic horizons are not a significantly greater source of atmospheric CO₂ than neighboring soils without petrocalcic horizons or noneroded petrocalcic soils.

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