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CARBON BALANCE IN CALIFORNIA DESERTS: IMPACTS OF WIDESPREAD SOLAR POWER GENERATION

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PREFACE

The California Energy Commission Energy Research and Development Division supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

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Carbon Balance in California Deserts: Impacts of Widespread Solar Power Generation is the final report for the Multiple Campus Award project CIEE Subaward (500-11-033) conducted by the Center for Conservation Biology, University of California, Riverside. The information from this project contributes to the Energy Research and Development Division's Energy-Related Environmental Research Program.

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ABSTRACT

Large-scale solar development in desert ecosystems has the potential to generate electricity thereby reducing fossil carbon accumulation in the atmosphere. Large stores of carbon are buried as caliche, or calcium carbonate that is fragmented and exposed upon disturbance.

In this project, the researchers focused on developing techniques to measure baseline caliche carbon in areas proposed for development, developing models to assess organic and inorganic carbon sequestration, and to determine if stripping native vegetation can affect carbon exchange and create a loss of inorganic carbon.

To measure the amount of baseline caliche carbon, the researchers found that the complex soil layering makes ground penetrating radar of limited value to detecting caliche layers in southern California deserts.

The isotopic ratios of carbon and oxygen were measured to assess dynamics of inorganic carbon; these stable isotope ratios showed that in the surface layers of soil, caliche is dynamic as fractionation and exchange with modern ions are occurring. Finally, using sensors and flux towers, flux rates of carbon in soil and the atmosphere of an undisturbed desert vegetation setting were measured and then compared with those from a site with the vegetation removed. Using the actual concentration and flux values, caliche formation and weathering were modeled. It was determined that carbon is being cycled in complex ways including between organic and inorganic forms in desert shrublands, and that inorganic carbon may be lost from areas stripped of desert vegetation.

The authors concluded that protecting native riparian woodlands and vegetation types that have deep roots is important to guard buried inorganic soil carbon stocks and carbon sequestration capacity. Planting short-statured shrubs or sucullents in areas with solar panels to reduce erosion and protect soil carbon is also recommended. The researchers also recommend that solar developments be revegetated.

Keywords: Soil carbon, caliche, calcium carbonate, solar power, soil respiration, desert ecosystem, delta 13C, delta 18O, root dynamics, fungal dynamics, ground penetrating radar, soil isotopes, soil disturbance, soil ecology

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EXECUTIVE SUMMARY

Introduction

Large-scale solar development in desert ecosystems has the potential to generate electricity, reducing fossil carbon accumulation in the atmosphere, and in turn, lowering global warming rates. There remain, however, environmental concerns regarding this technology, including the associated disturbance of soil and vegetation covering square miles.

A concern not fully understood is the amount of carbon that a large-scale solar technology can mitigate versus release by disturbing the land. Underneath desert ecosystems in the California deserts, vast amounts of carbon are stored as inorganic caliche, or calcium carbonate ($CaCO_3$). Both caliche and organic matter losses from land disturbance can compromise the value of solar energy as an alternative to fossil carbon burning by destroying the ability of these deserts to sequester (capture) carbon and potentially release stored inorganic carbon into the atmosphere.

This research project compared carbon fluxes and natural sequestration of organic and inorganic carbon measurements in deserts that are proposed for solar electrical power development. The authors focused on developing techniques to measure baseline caliche carbon in areas proposed for development, developing newer assessment models which can be used to model organic and inorganic carbon sequestration, and determining if stripping native vegetation can affect carbon exchange and create a loss of inorganic carbon.

Measure Caliche Using Ground Penetrating Radar

One of the challenges is measuring the amount of caliche and how much carbon might be lost by removing vegetation and surface soil layers. Recent studies have used ground penetrating radar to distinguish depth and layering of caliche below the soil surface.

Test areas used a SIR-3000 system (Geophysical Survey Systems, Inc.), a DC-3000/1100 controller, and a 3101 (900 KHz) and a 5100 (1.2MHz) antenna that was manually moved across the soil surface. The researchers first tested the system to see if they could detect the shifting soil structure under desert ecosystems using a sand dune ecosystem. Then the unit was tested to detect caliche rocks buried in sand, and against road cuts with known caliche layers.

The researchers were able to detect shifting soil layers under sand, however, were unable to detect patches of caliche that were buried. The researchers were also unable to differentiate caliche from other soil/rock layering at field sites. This approach can provide a description of layering and differential moisture retention, but the complex layering of California desert soils make this approach problematic.

Isotopic Analysis of Organic and Inorganic Carbon

$CaCO_3$ formation has been modeled on a largely equilibrium geochemical basis using atmospheric carbon dioxide (CO_2) levels and precipitation as calcite saturation and the partial pressure of CO_2. But, several soil chemical and biological factors may affect caliche stability.

The goal in this project determined if the carbon and $\delta^{18}O$ in the near surface caliche layers and desert soils showed stable or if the ratios suggested that the exchange of carbon and oxygen is more dynamic than predicted by equilibrium models. To test this idea, the authors took caliche and soil and vegetation samples from multiple vegetation types, regions, and soil depths to determine the exchange rates of ^{13}C-^{12}C (from respired CO_2) and ^{18}O-^{16}O (from water) from the original deposition. These ratios are indicated as $\delta^{13}C$, and $\delta^{18}O$, respectively.

Soil carbon isotopic composition ($\delta^{13}C$, $\delta^{18}O$) was analyzed both as bulk fractions, and after fumigation with concentrated HCl to eliminate organic fractions.

Isotopic analyses are still being completed. But samples analyzed to date show distinct differences between $\delta^{13}C$ and $\delta^{18}O$ from patterns expected based on existing analyses (Table 1). Plant and soil organic matter tissue followed expected patterns, in that plants using a C3 photosynthetic pathway discriminated against ^{13}C and the soil reflected that discrimination. The individual plants with Crassulacean acid metabolism (CAM) photosynthesis showed less discrimination, as expected. The soil organic C under CAM plants was significantly less negative than under C3 plants, as expected.

The interesting result is that the caliche $\delta^{13}C$ varied between plants with different photosynthetic systems reflecting varied origins of C. The $\delta^{13}C$ also showed that fractionation beyond a physical fractionation had occurred. Both were still slightly negative, indicating that the ultimate source was plant-derived C. The different sites have different $\delta^{18}O$ signatures. The fragmented material shows modern signatures indicating that exchange has occurred, that fractionation has occurred, and that these layers are dynamic. If these are subject to exchange, then the CO_2 in $CaCO_3$ is potentially sensitive to loss.

Inorganic and Organic Carbon Fluxes in Desert Ecosystems

Data and models measuring estimating weathering and accumulation are inconclusive as to the impacts of vegetation disturbance on caliche stocks. Many models use atmospheric C (currently between 390 and 400ppm). But $\delta^{13}C$ data show that $CaCO_3$ is more dependent upon rhizosphere-respired CO_2 than atmospheric accumulation. In using rhizosphere-levels of CO_2, $CaCO_3$ precipitation should be significantly greater than atmospheric CO_2 levels. Thus, it is essential to get more accurate estimates of rhizosphere activity to accurately model soil C exchanges.

The goal was to provide a comparative measure of C fluxes and natural sequestration of organic and inorganic C in deserts that are proposed for solar electrical power development. Networked environmental observatories provide new approaches for understanding ecological dynamics through the dual capabilities of high temporal resolution and continuous observation. The researchers used CO_2 soil sensor networks and flux towers at Boyd Deep Canyon, part of the University of California Natural Reserve System (NRS), in a native desert shrubland, and a disturbed site where all vegetation was removed at the Coachella Valley Agricultural Experiment Station (CVARS). Coincident with continuous measurement of soil temperature, soil moisture, and soil CO_2, researchers modeled $CaCO_3$ concentrations. Finally, the researchers

looked for $CaCO_3$ or CaC_2O_4 crystal formation and dissolution using their soil observation systems with automated high-resolution minirhizotrons.

$CaCO_3$ is highly dynamic in response to root and mycorrhizosphere dynamics in the native ecosystem. $CaCO_3$ is also highly dynamic in the disturbed site, but the cycle is a largely inorganic one. Both are subject to CO_2 loss through respiration (Deep Canyon) or inorganic dissolution and diffusion. However, plants fix CO_2 in the vegetated desert, whereas any CO_2 lost in a flush with rainfall, is likely lost from the disturbed ecosystem. The researchers do not yet know the ultimate fate of the carbon in caliche, but these data show that the process is dynamic, and there is a potential for significant loss.

Conclusions

This research shows that caliche in the surface soil layers is not in equilibrium, but is dynamic. Caliche and organic matter losses compromise the value of solar energy as an alternative to fossil carbon burning by releasing stored inorganic carbon into the atmosphere and destroying the ability of the deserts to sequester carbon. The researchers recommend siting solar developments on previously disturbed lands. Desert riparian woodlands should especially be avoided for the protection of sequestered carbon, and their ability to increase that carbon sequestration. Their deep roots and microbial associations continue to sequester both organic and inorganic carbon. The researchers also recommend that solar developments be revegetated. Short-statured plants, such as cacti and shrubs continue to produce organic carbon, and also release CO_2 that increases the soil CO_2 concentrations, maintaining and increasing inorganic soil carbon sequestration.

CHAPTER 1: Introduction

Large-scale solar development in desert ecosystems has the potential to generate electricity, thereby reducing fossil carbon (C) accumulation in the atmosphere, and in turn, lessening the rates of global warming. But there remain environmental concerns around the technology applied and the siting evaluations remain. Careful decisions about the choice of technology used can make a solar installation an important tool in fighting climate change, or compromise the environmental goals for which these technologies are being supported (e.g., Hernandez et al. 2014).

One concern that is not understood is the carbon budget that a large-scale solar technology can mitigate versus release as a result of the altered land-use management. Underneath many desert ecosystems in California deserts, vast stores of carbon (C) are stored as inorganic caliche, or calcium carbonate ($CaCO_3$), of up to 8kg C/m^2 (Schlesinger 1985). Globally, there is nearly twice as much C in soils as the atmosphere, with a large fraction of that in inorganic forms, largely $CaCO_3$. Both caliche and organic matter losses can compromise the value of solar energy as an alternative to fossil C burning by destroying the ability of these deserts to sequester C and potentially releasing stored inorganic C into the atmosphere.

Most of the caliche in California deserts appears to have been formed in desert playas below weathering limestone or metamorphic limestone (marble, dolomite) mountains high in Ca. In deserts, during wet periods, likely mostly during the Pleistocene, there was more water, leaching the Ca and fixing $CaCO_3$ deep in the soil creating solid layers of caliche. Data and models measuring estimating weathering and accumulation are inconclusive as to the impacts of vegetation disturbance on existing caliche stocks. Many models use atmospheric C (currently approximately 400ppm). But $\delta^{13}C$ data show that $CaCO_3$ formation was more dependent upon rhizosphere-respired CO_2 than atmospheric accumulation (Schlesinger 1985) and in forest and agricultural ecosystems, rhizosphere CO_2 is far higher than atmospheric CO_2, making it essential to get more accurate estimates of rhizosphere activity to accurately model soil C exchanges (e.g., Allen et al., 2007). More recent data suggest that caliche is more dynamic than older modeling efforts reported. Caliche is known to degrade, especially on disturbed lands (Hirmas and Allen 2007) and $\delta^{13}C$ of caliche shows re-equilibration through time as vegetation changes (Knauth et al. 2003).

1.1 Electricity Generation Environmental Challenges: Carbon and Vegetation Removal

Deployment of solar installations in California deserts currently strips vegetation to eliminate shading and allow for building of either solar reflectors or solar photovoltaic cells. This results in a denuded site, the size of the deployment. Vegetation is removed and surface soils disturbed (Fig 1) In all California installations researchers observed “clean” sites with no vegetation is

maintained. The key question is: what are the impacts of removal of vegetation on the "stable" inorganic fraction, mostly CaCO3 in California deserts?

The research team proposes developing measurements and adapting models to measure stored inorganic C, organic C balances of differing vegetation types and changing soil temperature (T), moisture **(⚜),** and atmospheric CO_2 levels to determine of there are particular vegetation types that should be protected from disturbance, or others that, from a perspective of C balance, are less sensitive.

1.2 Background State of Knowledge

Desert soil carbon (C) is comprised of stored inorganic C (as caliche), vegetation and soil organic C (as buried organic matter). But, little is known of C sequestration and release, especially under conditions of global and regional temperature increase. Solar power has the potential to dramatically reduce C release to the atmosphere by reducing fossil fuel burning for electrical generation. Understanding how different vegetation types turn both organic and inorganic C over, in the context of regional C budgets and CO_2 savings from solar power is the largest unknown question facing solar development in California.

Soil is the largest global terrestrial pool of Carbon (C) at 1500Gt compared with the atmosphere at 800Gt and plants at 600Gt, but is extremely dynamic and variable spatially. In contrast to the 50g/m^2/y anthropogenic source of C and the sinks in desert soils range from 39 to 622g/m2/y. Even year-to-year variation is high, ranging from sequestration during wet periods to weathering and mineralization during dry. For all biomes there is little understanding of the longer-term allocation of net primary production (NPP) to and retention (sequestration) of soil C (e.g., Treseder et al. 2005, U.S. DOE 2010).

California's deserts have large amounts of CO_2, stored as caliche ($CaCO_3$). The amount of C in caliche, when accounted globally, may be equal to the entire C as CO_2 in the atmosphere and as much as 30 percent of global soil C. But the dynamics of inorganic C remains a huge gap in understanding stored C pools (e.g., Schlesinger 1985, Mielnick et al. 2005, Serrano-Ortiz et al. 2010). Most of the caliche in the state's deserts was formed during the ice ages, averaging 20,000 years ago, when vegetation was more productive. These deposits may have been stable since (Schlesinger 1985). Being stable, though, means that inputs equal exports. But $\delta^{13}C$ of caliche in Arizona can shift around indicating continuous exchange and equilibration through time (Knauth et al. 2003).

Figure 1: An example of a solar development showing the stripped vegetation to build and maintain the solar power unit.

1.3 Goals

This project provided a comparative measure of C fluxes and natural sequestration of organic and inorganic C in deserts that are proposed for solar electrical power development. Researchers focused on developing techniques to measure baseline caliche C as areas for development are proposed, developing newer assessment models which can be used to model organic C and inorganic C sequestration, and to determine if removal of native vegetation will alter the exchanges and lead to a loss of stored inorganic C.

Three goals were envisioned to explore developing carbon budgets for desert ecosystems likely to be impacted by placement of solar power generation systems.

1. Assess if caliche and root distribution can be determined using soil pits and ground-penetrating radar (GPR) to survey vegetation. This will provide a tool for an immediate assessment of the potential C lost to the atmosphere with perturbation.
2. Analyze $\delta^{13}C$ and $\delta^{18}O$ of inorganic C (caliche) and organic C (SOM) to determine the relationships between climate, vegetation, and soil C balance. These more accurate models can then be used to rapidly assess different vegetation types in different regions and their roles in C sequestration and weathering.
3. Measure C fixation, respiration and allocation for undisturbed native vegetation and a site where the vegetation has been removed, under variable climates. This will include determining the relationships between aboveground vegetation, climate, and rhizosphere CO_2 levels. From these relationships, model directionality and rates of caliche formation and weathering and C sequestration within soil organic matter can more accurately determined.

Together this information can be used to rapidly assess the impacts of solar electricity generation on different communities and ecosystems.

CHAPTER 2:
Measuring Caliche Using Ground Penetration Radar (GPR)

One of the difficult issues is measuring the amount of caliche and how much C might be lost with removal of vegetation and surface soil layers. However, recent studies have used GPR to distinguish depth and layering of caliche below the soil surface. Wilson et al. (2005) used GPR to characterize caliche depth and fractures as a means to study CO_2 leakage through soil. GPR was previously used in the Yucatan to describe fractures and soil layers within limestone $CaCO_3$ (Estrada-Medina et al. 2010). A number of locations in different vegetation types were tested to determine the distribution of caliche depths, roots, and soil of soil pits. It is believe that this approach provided a rapid means of assessing potential C balance.

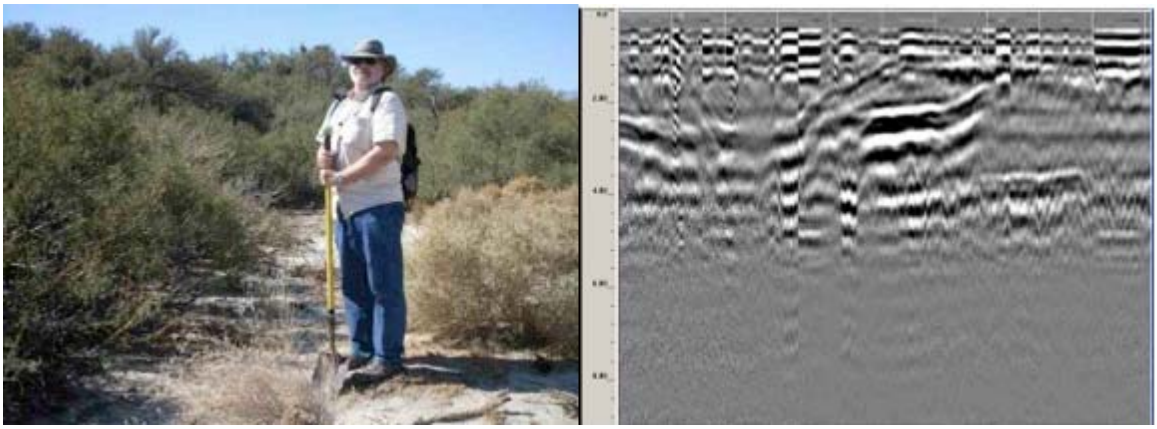
2.1 Methods

Evaluating test areas was undertaken using a SIR-3000 system (Geophysical Survey Systems, Inc.), a DC-3000/1100 controller, and a 3101 (900KHz) and a 5100 (1.2MHz) antenna that was manually moved across the soil surface. This approach is described in greater detail in Estrada-Medina et al. (2010). The system was tested first to see if the shifting soil structure under desert ecosystems using a sand dune ecosystem could be detected. The unit was then tested to detect caliche rocks within sand buried in sand, and against road cuts with known caliche layers.

2.2 Results

Researchers were able to detect shifting soil layers under sand (Figure 2), however, were unable to detect patches of caliche that they had buried. Researchers were also unable to differentiate caliche from other soil/rock layering at field sites.

Figure 2: A ground penetrating radar profile under a sand dune in the Coachella Valley.



2.3 Discussion

Ground Penetrating Radar is a useful tool for identifying coarse roots, pipes, and soil layers that are characterized by differential water content. The research team was able to differentiate

layers in the soil, but not buried caliche rocks. Nor could they differentiate caliche layers from other soil layering.

GPR has been used to identify gaps dissolving in limestone rock (Wilson et al. 2005, Estrada Medina et al. 2010). But those were in locations where the rock formations were limestone, and the silicaceous material and organic matter accumulated as the CaCO3 in the limestone dissolved. The caliche layers in California deserts studied were all embedded in a complex layered matrix of other consolidated and unconsolidated rock and soil layers. As such, while layers could be seen, the caliche from other layers, such as silicaceous or clay layers could not be differentiated. It might be that further work, especially under varying soil moisture conditions, might allow identification of these layers. Work will continue in this area.

CHAPTER 3:
Isotopic Analysis of Organic and Inorganic Carbon

$CaCO_3$ formation has been modeled on a largely equilibrium geochemical basis using atmospheric CO_2 levels (e.g., Hirmas et al 2010) and precipitation as a function of calcite saturation and the partial pressure of CO_2. But, organic matter can alter the calcite formation (e.g., LeBron and Suarez (1998), and $CaCO_3$ as well as other Ca-organic acids such as Ca-oxalate is also a biological process, forming along roots and hyphae (e.g., Jurinak et al. 1986). To add complexity, recent papers posit that CO_2 loss and gain from calcite soils can occur on a diurnal basis with wetting and drying of soil (Roland et al. 2013). These numbers are not trivial. Roland et al. (2013) reported peak ventilation of 0.5 to 6.4◎mol $CO_2 \cdot m^{-2} s^{-1}$ from karst vegetation during the dry summers, and Mielnick et al. (2005) reported losses of up to 145g $C/m^2/y$.

Contrary to many modeling efforts, soil CO_2 levels are not in equilibrium with atmospheric levels, but are a result of respiration, and may be far higher than atmospheric CO_2. The researchers postulated that carbon in caliche is therefore dynamic. High soil CO_2 from plant and microbial respiration may drive CaCO3 under moist soil conditions enhancing C sequestration. As soil dries, that added $CaCO_3$ crystalizes and is deposited. Additional research is necessary to understand and quantify these exchanges (Serrano-Ortiz et al. 2010), as there are C exchanges in desert ecosystems that are not understood.

^{14}C data show that the caliche below the desert playas was formed more than 20,000 years ago (e.g., Schlesinger 1985). An analysis of $\delta^{18}O$ of those same buried layers shows that the caliche came from water from Pleistocene climates. Further, analysis of $\delta^{13}C$ shows that the C came from root and microbial respiration from C_3 vegetation that dominated during that period. Just as importantly, $\delta^{13}C$ of caliche in Arizona can shift around indicating continuous exchange and equilibration through time (Knauth et al. 2003).

The goal in this experiment was to determine if the $\delta^{13}C$ and $\delta^{18}O$ in the near surface caliche layers and desert soils were stable, or if the ratios suggested that the exchange of C and O is dynamic. To test this idea, researchers took caliche and soil and vegetation samples from multiple vegetation types, regions, and soil depths to determine the exchange rates of ^{13}C-^{12}C (from respired CO_2) and ^{18}O-^{16}O (from water) from the original deposition.

3.1 Methods

Soil carbon isotopic composition ($\delta^{13}C$) was determined by drying soils at 65°C until constant mass, followed by sieving and grinding in a ball mill (8000D, Spex Sample Prep, Stanmore, UK). To distinguish soil organic carbon from pedogeneic carbonates (caliche), soils were analyzed both as bulk fractions, and after fumigation with concentrated HCl for six hours (Harris et al. 2001). All samples were measured for $\delta^{13}C$ and $\delta^{18}O$ with a continuous flow isotope ratio mass spectrometer (Delta *V* Advantage, Thermo Scientific, Bremen, Germany) equipped with a Gas Bench (Thermo Scientific) in the Department of Earth Sciences, University of California, Riverside.

Plant carbon isotopic composition ($\delta^{13}C$) was measured on leaf and root samples that had been dried at 65°C until constant mass, and ground to a fine powder in a ball mill (8000D, Spex Sample Prep, Stanmore, UK). Samples were analyzed with a an elemental analyzer (ECS 4010, Costech Inc., Valencia, CA) interfaced with an isotope ratio mass spectrometer (Delta *V* Advantage; Thermo Scientific) at the University of California Facility for Isotope Ratio Mass Spectrometry (FIRMS), Riverside, California.

Plant oxygen isotopic composition ($\delta^{18}O$) was measured on the cellulose fraction, extracted from bulk plant samples through micro digestion with a mixture of acetic and nitric acid, based on the original method of Brendel et al. (2000), as modified for small samples by Evans and Schrag (2004) and Gaudinski et al. (2005). Samples were analyzed with a temperature conversion elemental analyzer (TC/EA, Thermo Scientific) interfaced with an isotope ratio mass spectrometer (Delta *V* Advantage; Thermo Scientific) at the University of California Facility for Isotope Ratio Mass Spectrometry (FIRMS), Riverside, California.

3.2 Results

Isotopic analyses are still being completed. But samples analyzed to date show distinct differences between $\delta^{13}C$ and $\delta^{18}O$ from patterns expected based on existing analyses (Table 1). Plant and soil organic matter tissue followed expected patterns, in that plants using a C3 photosynthetic pathway discriminated against ^{13}C and the soil reflected that discrimination. The individual plants with CAM photosynthesis showed less discrimination, as expected. The soil organic C under CAM plants was significantly less negative than under C3 plants, as expected.

The interesting result is that the caliche $\delta^{13}C$ was significantly less negative under C3 than CAM plants. Both were still slightly negative, indicating that the ultimate source was plant-derived C.

Table 1: $\delta^{13}C$ from C3 versus CAM plant tissue, soil organic matter, and caliche fragments
(mean standard deviation (SD), sample number analyzed to date, and p-value for a t-test comparing C3 and CAM-associated material)

parameter	C3	CAM	P value
Plant	-23.9 ‰, SD=1.16, n=24	-15.2 ‰, SD=2.1, n=32	$1.2X10^{-13}$
Soil	-24.1 ‰, SD=1.51, n=14	-21.7 ‰, SD=2.1, n=25	0.0007
Inorganic (caliche)	-2.8 ‰, SD=1.6, n=12	-5.7 ‰, SD=1.5, n=12	0.00013

The $\delta^{18}O$ samples for the plant tissue and soil organic matter, as well as some of the caliche samples are still being analyzed. Initial results are very interesting. The preliminary analyses suggest that different sites have different $\delta^{18}O$ signatures. Imperial Valley samples show an average $\delta^{18}O$ signature of -6.4 ‰ (SD1.3) with the western Coachella Valley of -5.1 ‰ (SD1.6). The Chuckwalla Valley averaged (-7.1 ‰ (SD 1.7) and the San Raphael site -8.2 ‰ (SD=0.5). In pairing the samples, larger caliche fragments had a $\delta^{18}O$ value of -6.8 ‰ (SD 1.1) whereas the

smaller fragments were -5.9 ‰ (SD 2.2). While not significantly different overall, a paired t-test showed a trend toward the smaller fragments having a less negative value ($p=0.15$). Additional samples are being analyzed.

3.3 Discussion

Because deserts have low precipitation inputs, cations such as Ca are rarely leached out of the soils. High cation levels tend to bind nutrients, such as HPO_4^- and NO_3^-, creating $CaPO_4$ and $Ca(NO_3)_2$ making those nutrients unavailable to plants. But, roots and associated microorganisms respire CO_2, acidifying the soil in the presence of water (forming $HCO_3^-+H^+$) weathering $CaPO_4$, and increasing HPO_4^- availability. But, with time, that Ca would re-bind new anions, except that roots and mycorrhizal fungi produce organic acids (oxalic, citric) that bind the Ca allowing for plant uptake of HPO_4^-.

Rhizosphere-respired CO_2 is dependent upon the vegetation composition and activity. Further, a large, but relatively unknown amount of CO_2 is fixed and stored as organic C in deserts, with estimates ranging from 60 to 600g/m^2/y, but dependent upon the particular ecosystem. Desert plants have microbial associations including mycorrhizal fungi that respire CO_2, weathering $CaPO_4$ allowing uptake of P and increasing soil CO_2 as respiration (Jurinak et al. 1986, Knight et al. 1989). These organisms also produce organic acids that bind Ca sustaining P availability (Jurinak et al. 1986, Allen et al. 1996).

Atmospheric or respired CO_2 in the presence of water (H_2O) is converted to $HCO_3^- + H^+$ acidifying the soil. The HCO_3^- binds with Ca to form $CaCO_3 +H^+$. Under equilibrium conditions, the thermodynamics strongly favor $CaCO_3$ compared to CO_2 and Ca, but some CO_2 is continuously released under wetting and drying cycles. Moreover biological processes push ecosystems outside of equilibrium conditions. Some of the $CaCO_3$ is utilized by microorganisms making more CO_2. Some of this CO_2 can be re-fixed, but some is lost as soil respiration, potentially losing some of the C bound in $CaCO_3$. The amount lost is regulated by the amount of CO_2, Ca, and soil pH.

Researchers postulated that as caliche fragments in the upper layers are exposed to water and biological activity, the isotopic values ($\delta^{13}C$ and $\delta^{18}O$) will show exchange, indicating that the caliche itself is dynamic. If it is dynamic, CO_2 could be lost or gained depending upon the conditions of exposure. Thus, a first step is to look at the isotopic ratios of C and O.

A large number of samples were prepared and results still coming in. However, examination of the data completed show that the caliche in the exposed layers is dynamic. Several lines of evidence support this conclusion.

First, the difference between the soil organic matter and the caliche $\delta^{13}C$ is greater than that predicted simply by exposing caliche to water. If the atmosphere were the source of C, the $\delta^{13}C$ ratio should be highly positive. But all samples were negative, demonstrating a plant-derived source of C. The expected fractionation of ^{13}C in carbonate from CO_2 respired by plants or decomposers is +9.6 ‰ (Friedman and O'Neil 1977). If the caliche were derived from atmospheric C, a value greater than +9 ‰ would be expected. The caliche $\delta^{13}C$ was -2.8,

suggesting a source $\delta^{13}C$ of <-12.4 ‰ under C3 plants and -5.7 ‰ under CAM plants, or a $\delta^{13}C$ source of <-15.3 ‰. Some additional fractionation has occurred under C3 compared with under CAM plants, possibly more recycling, or the formation of different compounds in the source vegetation.

Second, the root systems of the C3 plants studied tend to be deep, supporting greater annual photosynthesis and more microbial biomass and activity per unit land surface than the CAM plants. The difference in $\delta^{13}C$ between C3 plant and caliche was 21.1 ‰ and 21.3 ‰ between the soils under C3 plants and caliche. The difference in ◎^{13}C between CAM plant and caliche was 9.5 ‰. The soil organic matter under the CAM plants was more negative than the plant tissue, but the difference between soil organic C and caliche C was 16 ‰, still less than that between C3 soil organic C and caliche C.

Finally, the $\delta^{18}O$ data suggest that as caliche fragments into smaller fractions, the $\delta^{18}O$ becomes less negative, showing either some loss of ^{16}O or exchange of H_2O with local inputs. The $\delta^{18}O$ data also show that the caliche in the upper layers is representative of the current water samples. The southern regions and Deep Canyon have signatures that represent warmer water input (more summer rains) whereas the areas bordering the Mojave have cooler precipitation input signature. The San Raphael site has water from the Laguana Mountains, also showing a somewhat more negative signal.

This is also supported by a lack of relationship between $\delta^{13}C$ and $\delta^{18}O$. Schlesinger (1985) noted that in his Chuckwalla Valley samples, there was a significant relationship between the $\delta^{13}C$ and $\delta^{18}O$ indicating a seasonal pattern regulating pCO_2 and soil water, and $CaCO_3$ precipitation. However, no relationship between $\delta^{13}C$ and $\delta^{18}O$ was found. In the samples, $\delta^{18}O=0.08\ (\delta^{13}C) + 4.35$, $r=0.07$, $r^2=0.005$. These data show either no seasonal pattern of precipitation, or that subsequent exchange has occurred.

Together, the $\delta^{13}C$ and $\delta^{18}O$ signatures indicate that the exposed and fragmented caliche is subject to exchange with modern C and O. If these are subject to exchange, then the CO_2 in $CaCO_3$ is potentially sensitive to loss. Understanding the larger exchanges is the subject of Chapter 4.

CHAPTER 4:
Inorganic and Organic Carbon Fluxes in Desert Ecosystems

California deserts have vast stores of carbon (C) stored as inorganic caliche, or $CaCO_3$, of up to 8kg C/m^2 in some locations (Schlesinger 1985). Data and models measuring estimated weathering and accumulation are inconclusive as to the impacts of vegetation disturbance on caliche stocks. Many models use atmospheric C (currently between 390 and 400ppm). But initial $\delta^{13}C$ data show that $CaCO_3$ is more dependent upon rhizosphere-respired CO_2 than atmospheric accumulation (Schlesinger 1985) and even desert rhizosphere CO_2 is far higher than atmospheric CO_2. In using rhizosphere-levels of CO_2, $CaCO_3$ precipitation is significantly greater than atmospheric CO2 levels (LeBron and Suarez 1998). Thus, it is essential to get more accurate estimates of rhizosphere activity to accurately model soil C exchanges. More recent data suggest that caliche may be more dynamic than older equilibrium-based modeling efforts reported. Caliche is known to degrade, especially on disturbed lands (Hirmas and Allen 2007) and $\delta^{13}C$ of caliche shows re-equilibration may occur through time as vegetation changes (Knauth et al. 2003).

$CaCO_3$ formation has been modeled largely on an equilibrium geochemical basis using atmospheric CO_2 levels (e.g., Hirmas et al 2010) and precipitation as a function of calcite saturation and the partial pressure of CO_2. In its simplest form, under aqueous conditions, $CaCO_3$ precipitation is formed as:

$2H_2O + 2CO_2 <-> 2H^+ + 2HCO_3^-$

$\mathbf{Ca_2^+ + 2HCO_3^- <-> CaCO_3 + H_2O + CO_2}$

As water evaporates, the $CaCO_3$ crystallizes, and at the depth to water penetration, these crystals accumulate forming caliche layers.

As the soil erodes, these layers become exposed. Isotopic ratios (Cpt 3) show that exchange occurs. But, as Ca weathers out, re-precipitation occurs in the presence of HCO_3^-, under equilibrium conditions. However, equilibrium conditions rarely exist in nature. CO_2 levels and organic matter can alter the calcite formation (e.g., LeBron and Suarez 1998), and $CaCO_3$ as well as other Ca-organic acids such as Ca-oxalate is also a biological process, forming along roots and hyphae (e.g., Jurinak et al. 1986). The researchers postulated that carbon in caliche is therefore dynamic. High soil CO_2 from plant and microbial respiration may drive $CaCO_3$ supersaturation under moist soil conditions enhancing C sequestration. But with vegetation loss, the soil CO_2 levels drop, H_2O is no longer transpired, and $CaCO_3$ weathered. To add complexity, recent papers posit that CO_2 loss and gain from calcite soils can occur on a diurnal basis with wetting and drying of soil (Roland et al. 2013). These numbers are not trivial. Roland et al. (2013) reported peak ventilation of 6.4δmol $CO_2 \cdot m^{-2}s^{-1}$ from karst vegetation during the dry summers, and Mielnick et al. (2005) reported losses of up to 145g C/m^2/y. Additional research is needed to understand and quantify these exchanges (Serrano-Ortiz et al. 2010), as there are C exchanges in desert ecosystems that are not fully understood.

Rhizosphere-respired CO_2 is dependent upon the vegetation composition and activity. A large, but relatively unknown amount of CO_2 is fixed and stored as organic C in deserts, with estimates ranging from 60 to 600g/m^2/y, but dependent upon the particular ecosystem perturbed. Woody legumes, in particular, have roots and associated microbes more than 3m deep (Virginia et al. 1986), sequestering organic C where it is only slowly respired back to the atmosphere. Respired CO_2 in the presence of water (H_2O) and calcium (Ca) produces $CaCO_3$.

The goal was to provide a comparative measure of C fluxes and natural sequestration of organic and inorganic C in deserts that are proposed for solar electrical power development. Researchers focused on developing techniques to measure caliche C dynamics, and as areas for development are proposed, develop newer assessment models which can be used to model organic C and inorganic C sequestration, and determine if sites with vegetation removed have different exchanges and potential loss rates of inorganic C compared with undisturbed wildland desert ecosystems.

4.1 Methods: A Networked Environmental Observatory – Continuous Sensors, Manual Measurements, Experiments, and Soil Surveys

Networked environmental observatories provide new approaches for understanding ecological dynamics through the dual capabilities of high temporal resolution and continuous observations (Allen et al. 2007). The research team are currently running CO_2 sensor networks at Boyd Deep Canyon, part of the University of California Natural Reserve System (NRS), in a native desert shrubland, and the Coachella Valley Agricultural Experiment Station (CVARS). The goal was to compare the dynamics at Deep Canyon with a site where the vegetation was removed for the developing solar PV projects in the Salton Sea, led by Dr. Alfredo Martinez-Morales. The unique combination of natural resources and challenging environmental conditions at the Salton Sea require that a feasibility study be conducted to truly determine the potential of developing utility scale energy projects in the area. The Martinez-Morales project was not funded, and the disturbed lands have not yet been deployed. But, the environmental conditions of the PV deployment are mimicked nearby at the CVARS. The undisturbed vegetation is the same as Boyd Deep Canyon, and the soils of all three sites are Entisols consisting of alluvium derived from granite. The CVARS site has been cleared of vegetation for more than four years and is the same soil type as exists at Deep Canyon, the Martinez-Morales location, and across most of the Coachella and Imperial Valleys and provides comparable data to that of Salton Sea projects.

Each location is instrumented with replicated solid-state CO_2, soil temperature, and soil moisture sensors at 2, 8 and 16 cm soil depths. The CO_2 sensors are calibrated every six months after deployment to ensure the quality of the measurements. Soil CO_2 was measured using Vaisala soil CO_2 sensors (Vargas and Allen 2008, Kitajima et al. 2010). These provided accurate CO_2 inputs to caliche modeling in comparison with simply using atmospheric CO_2 values (Hirmas et al. 2010). From these data, soil respiration from the soil using a CO_2 gradient flux method based on concentrations of CO_2 in the soil profile (Vargas and Allen 2008) was calculated. Eddy Covariance (EC) was used for monitoring the fluxes of CO_2, H_2O, and energy

of whole ecosystems (Baldocchi 2003). A closed path eddy covariance model CPEC200 (Campbell Scientific, Logan Utah) was used to analyze CO_2 and H_2O vapor fluxes from the CVARS site. The eddy covariance data from Deep Canyon NRS are available from M. Goulden, UC Irvine.

Coincident with continuous measurement of soil temperature (T), soil moisture, and soil CO_2, we modeled $CaCO_3$ concentrations using the model of Hirmas et al. (2010).

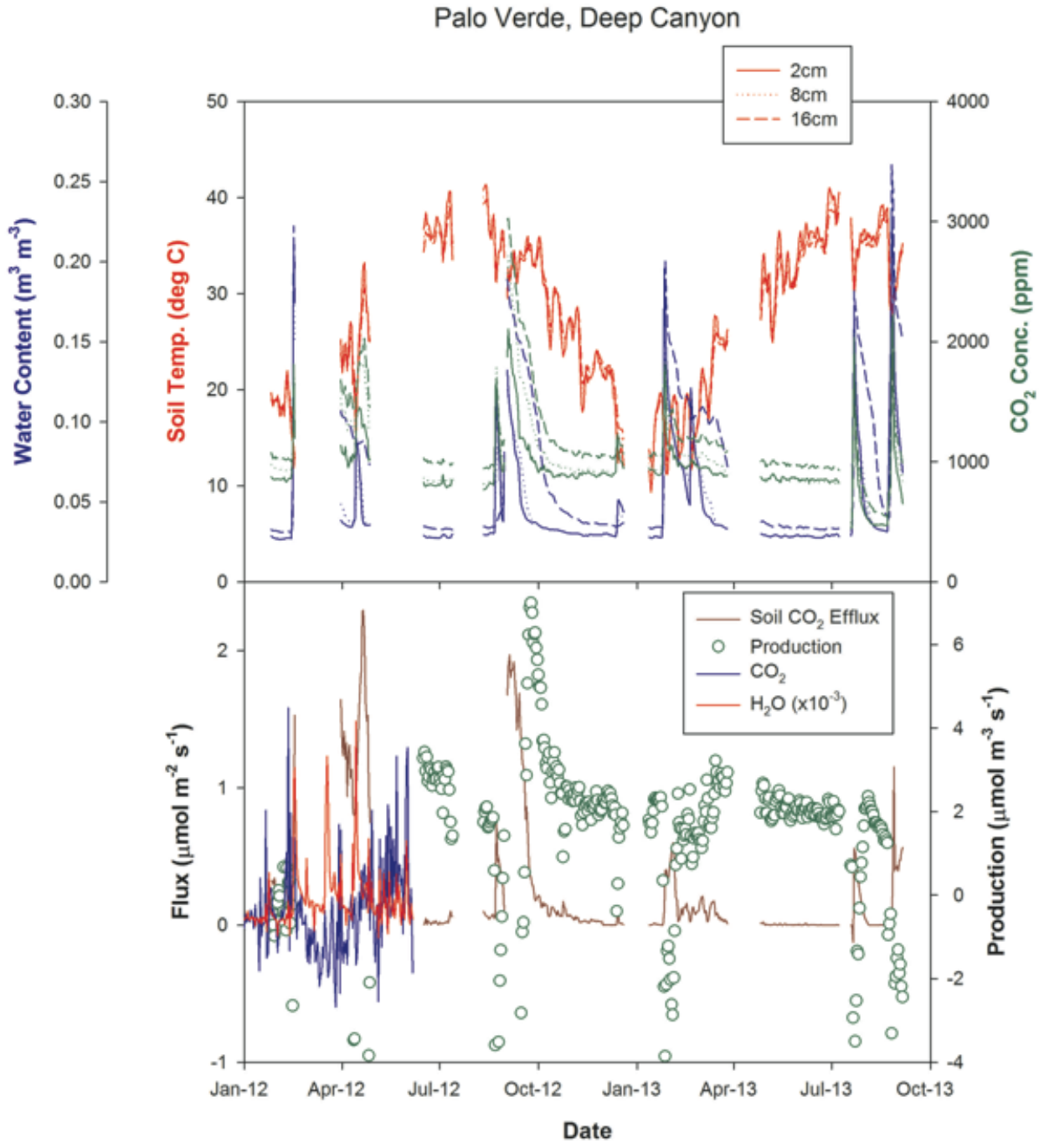
Finally, the researchers looked for $CaCO_3$ or CaC_2O_4 crystal formation and dissolution using the soil observation systems using an automated high-resolution minirhizotrons (Allen et al. 2007, Hernandez and Allen 2013, Allen and Kitajima 2013). These *in situ* microscopy systems allow us to track the fates of roots and fungal hyphae, and identify $CaCO_3$ crystals forming or disappearing in soil on hyphae or on soil particles.

4.2 Results

Soil ecosystems in undisturbed deserts are highly dynamic. With each precipitation event, there is rapid new root growth and fungal hyphal production. Hyphal growth of up to 2mm per day was observed, during spring warming following a precipitation event. Just as importantly, hyphal mortality can equal growth as the soil dries out.

Shortly following those precipitation events, soil CO_2 production can be very high and distributed well into the soil profile (Fig 3). The resulting soil CO_2 concentrations can be more than an order of magnitude higher than atmospheric CO_2 and the soil CO_2 concentrations measured during the dry period.

Figure 3: Soil CO2 dynamics in response to changing soil temperature and moisture under a Palo Verde (Cercidium microphyllum) tree at the Deep Canyon NRS

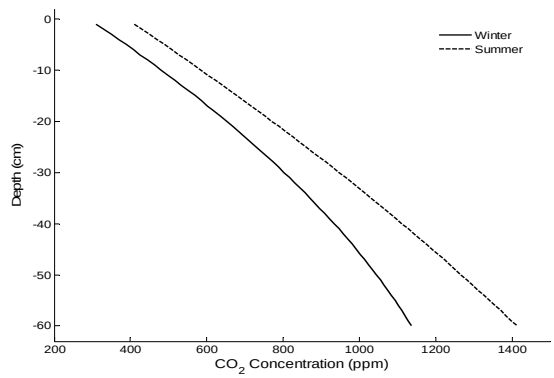


Similar patterns were observed under other vegetation units, including creosote bush (Larrea tridentata), fishhook barrel cactus (Ferocactus cylindraceus), and brittlebush (Encelia farinosa).

The modeled values (from Hirmas et al. 2010) for estimating soil CO_2 directly from atmosphere showed that the values ranged from 400ppm CO_2 to 600 ppm CO_2 at 16cm, and 1,100ppm CO_2

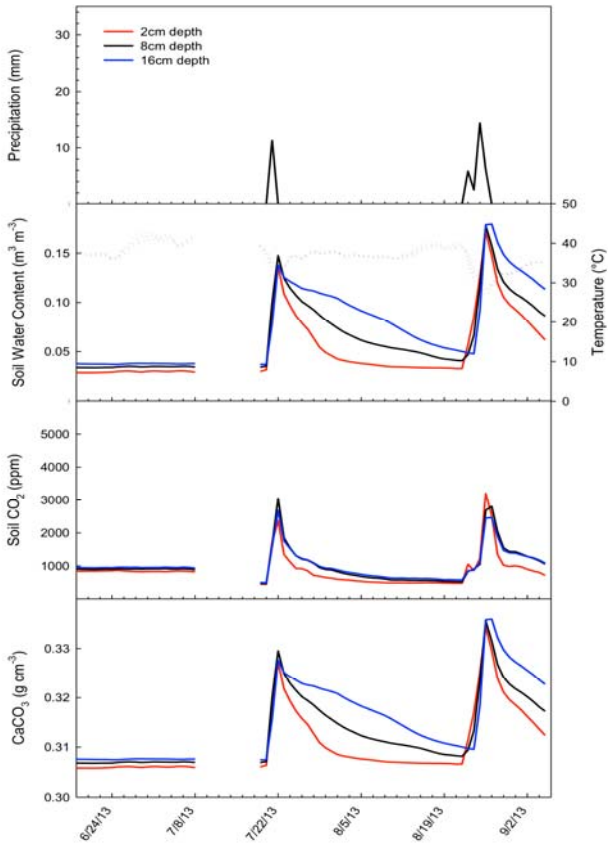
at 60cm during the winter, and 500ppm CO_2 (2cm) to 1,400ppm CO_2 at 60cm (Figure 4). These values are below the values that were measured at the undisturbed site (Figure 3). Current model projects the equilibrium $CaCO_3$ levels for measured CO_2, based on the measured Ca concentrations and other relevant parameters.

Figure 4: Modeled soil CO2 Using the model of Hirmas et al. (2010).



Additional soil analyses are underway for Deep Canyon, but the Ca concentrations in soil exceed 10 meq/l and organic C from to 30g/kg in shrub islands. This means that there is Ca available such that when soil moisture is high; respiration is also high, forming HCO_3^- and precipitating $CaCO_3$ from some of the high CO_2 concentrations. Indeed, with the high levels of CO_2, researchers saw the concentration of solution $CaCO_3$ dramatically increase (Figures 3, 5).

Figure 5: Solution $CaCO_3$ in response to precipitation events at the Boyd Deep Canyon NRS, under a Palo Verde tree. The high levels of Ca in soil coupled with the high soil moisture and high rate or respiration results in a high $CaCO_3$ formation. Subsequently, as the soil moisture declines, and respiration due to reduced fungal and root activity declines the $CaCO_3$ in solution declines.

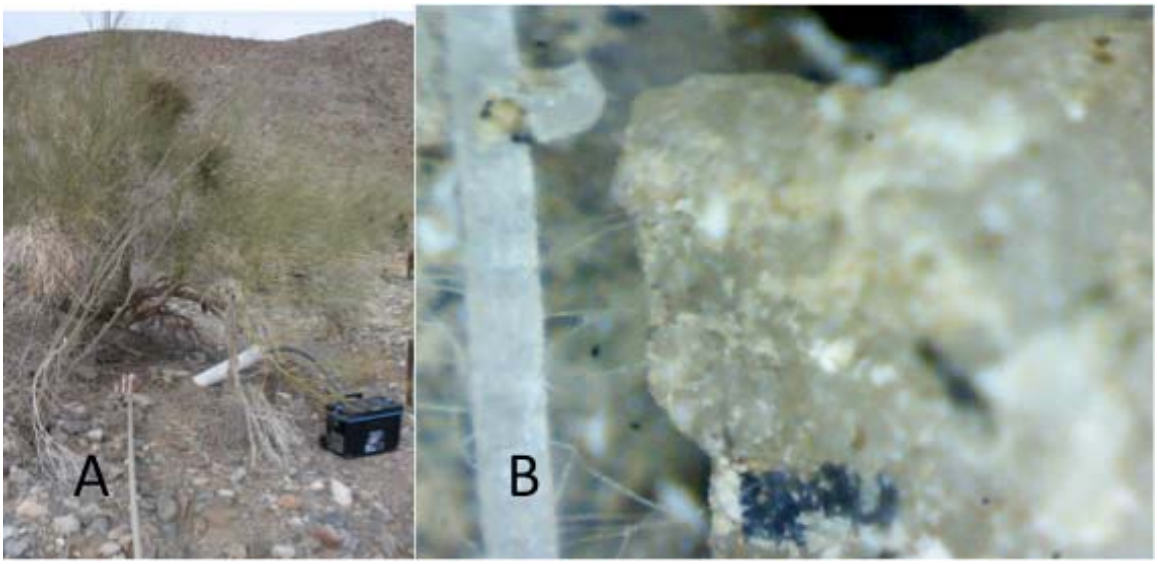


As arbuscular mycorrhizal fungal hyphae grow in response to soil water inputs, they respire CO_2 and provide nucleation centers, which attracts the Ca and resulting in $CaCO_3$ crystals along the hyphae (Fig 6) on the soil particles (Fig 7).

The soils from CVARS, devoid of vegetation, showed much different patterns. Importantly, organic carbon had largely decomposed, with only a small amount of recalcitrant C remaining. The total soil C was 3.2g/kg. The organic C was only 1.5g/kg where as the C as $CaCO_3$ was 2.4g/kg. (The 0.9g/kg difference is due to the different methods for determining organic and inorganic C). Thus, the percent of total C as $CaCO_3$ averaged 73 percent. This contrasts with the percent of Ca bound with CO_3 of less than one percent (0.78+/-0.08 SEM).

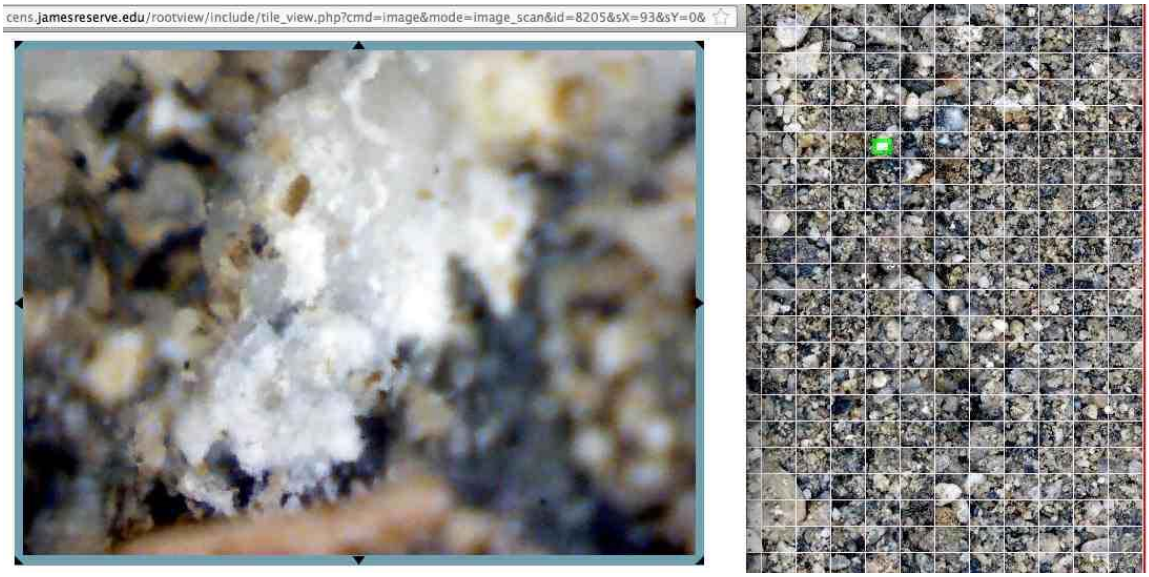
The dynamics of the CVARS-solar deployment simulation site soils is also different. Importantly, higher than atmospheric levels of soil CO_2 still occurred, even without organic C or plant root/microbial respiration following precipitation events (Figure 8).

Figure 6: Palo Verde tree with AMR unit (A) and *In situ* arbuscular mycorrhizal fungal hyphae with $CaCO_3$ crystals forming at the hyphal-soil particle interface (B).



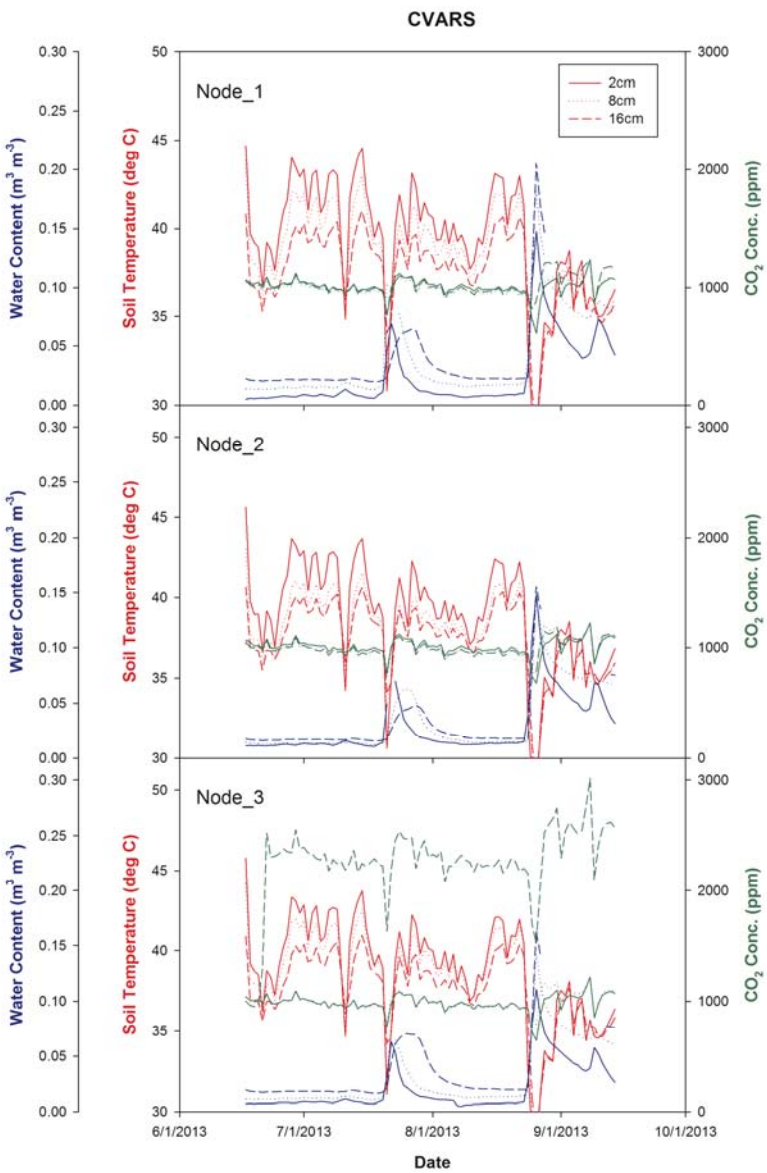
(From Deep Canyon NRS. The image is 3.01mm X 2.26mm, 100x)

Figure 7: *In situ* $CaCO_3$ crystals formed along hyphae and on the surfaces of soil particles under Palo Verde trees at the Deep Canyon NRS



(These crystals were formed as soils dried out and persisted until the next rainfall event wherein most dissolved into solution. The image is 3.01mm X 2.26mm, 100x)

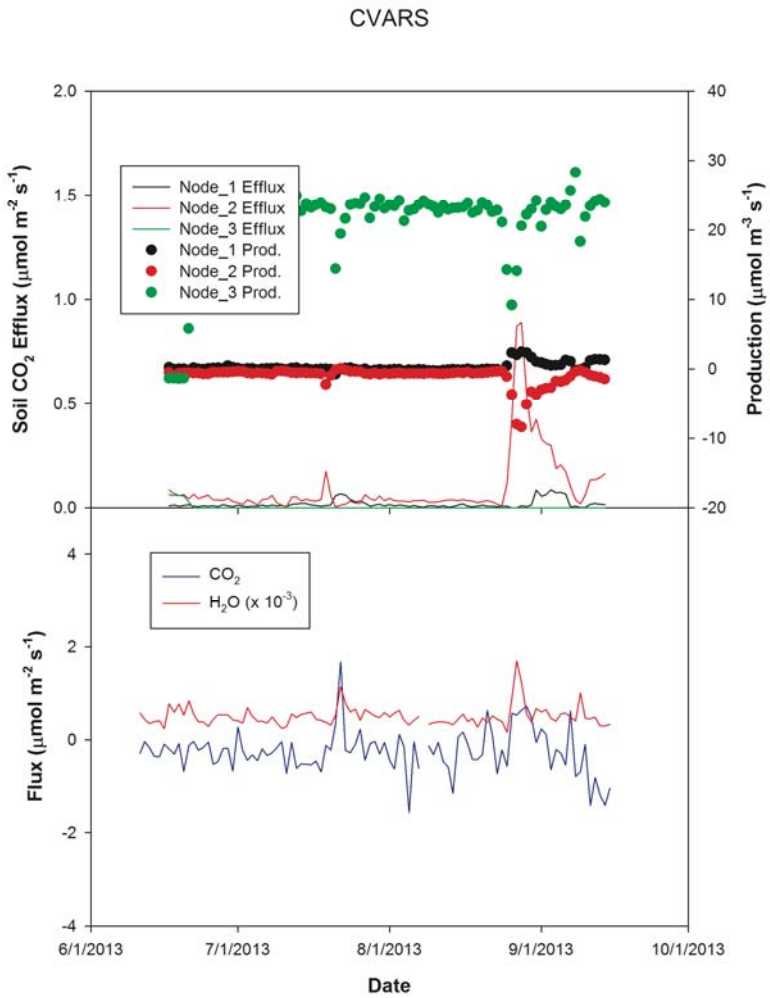
Figure 8: Concentration of CO2 in response to temperature and moisture inputs at the CVARS/Solar Installation simulation site.



Note that as soil moisture jumps in response to a rainfall event, CO_2 concentration initially drops then increases above the dry baseline.

The fluxes of CO_2 also vary with rainfall events (Fig 9). Generally the fluxes oscillate around 0, to a generally slight uptake of CO_2 (negative flux) by these soils. As there are no plants, most of this uptake is likely a chemical reaction of soil moisture taking up atmospheric CO_2, forming HCO_3^- and potentially, even $CaCO_3$. However, with the rainfall events, there is a net drop in the CO_2 production rates, as CO_2 diffuses and is lost to the atmosphere (positive flux).

Figure 9: Fluxes of CO_2 and water vapor in response to rainfall events and production of CO_2 by soils with no vegetation (simulated solar installation).



Soil CO_2 production and efflux are calculated from changes across concentration boundaries in soil (production) and soil-atmosphere (efflux). Flux is derived from the eddy covariance measurements for water and CO_2. Note, the sign is gain or loss from the atmosphere, where positive number represents from soil to atmosphere, and negative from atmosphere to soil.

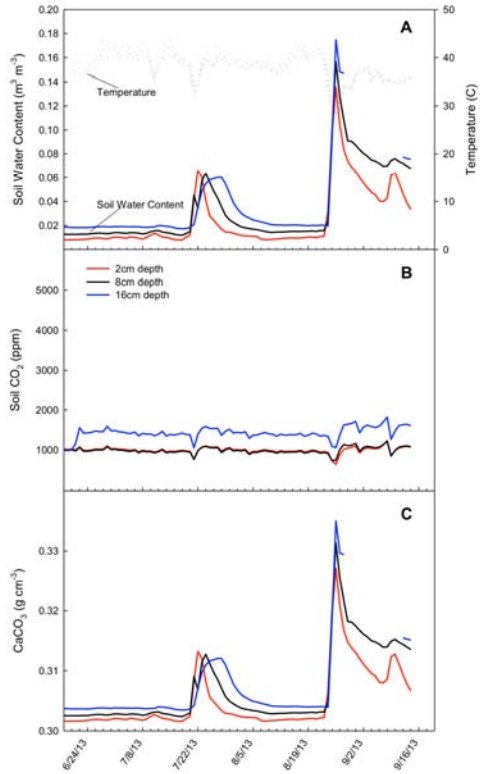
When the soils were examined using the Soil Observatory Network, automated minirhizotron observations showed a nearly sterile soil without particles of soil organic matter, or roots or fungal hyphae (Figure 10).

Figure 10: The CVARS solar-simulation site (A) and a hi-resolution in situ AMR image of the soil (3.01mm X 2.26mm, 100x image) showing soil particles.

Few pieces of organic matter, or fungi or roots were observed in the CVARS soil. No CaCO3 crystals were observed.

Based on the soil CO_2 and soil moisture data, $CaCO_3$ was formed with the rainfall event (Figure 11), but nearly equal to those from the Deep Canyon native vegetation site (Figure 5). However, no crystals were observed.

Figure 11: CaCO3 concentrations in response to rainfall events from the CVARS solar installation simulation site with no vegetation present.



Soil CO2 remained low in response to rainfall in contrast with Boyd Deep Canyon (Figure 5) but CaCO3 responses resemble those found at Boyd Deep Canyon.

4.3 Discussion

The data from the soil respiration, flux, soils, and $CaCO_3$ modeling all point to a suite of dynamic processes and one that, because of the large fluxes, is rarely if ever in equilibrium. At the natural area site (Boyd Deep Canyon NRS), Ca that is weathered from the dolomite outcroppings is abundant in the soil. It is cycled as $CaPO_4$ or $CaNO_3$, weathered by the respiration of plant roots and associated rhizosphere microorganisms. These organisms also produce organic acids that bind the Ca, such as CaC_2O_4, facilitating nutrient uptake. Other microorganisms then utilize the CaC_2O_4 (Morris and Allen 1994), thereby additionally increasing HCO_3^- and freeing Ca_2^+. During dry periods, found little root or microbial growth or respiration was found. With little H_2O, there is little respiration, or $CaCO_3$ in solution. However, crystals of $CaCO_3$ that precipitated on the surface of hyphae or other nucleation centers are seen.

With a large rainfall event, the $CaCO_3$ crystals dissolved and were solubilized. Organic C is mineralized and inorganic CO_2 released. There is a spike in aqueous $CaCO_3$, some of which is

leached deeper into the profile, and some of which forms a supersaturated solution, re-precipitating as the soil dries out.

The CVARS site chosen as a model for a solar installation site, as there has been no vegetation for greater than four years shows a different, albeit also dynamic pattern. Presumably, the processes reflect soil geochemistry with little or no input by biological processes. There, CO_2 is produced and lost to the atmosphere or fixed by Ca into $CaCO_3$ in small amounts based on day-night vapor pressure change. With a large event, $CaCO_3$ rapidly increases. But CO_2 is also released spiking soil respiration and loss of CO_2 to the atmosphere was measured. Some $CaCO_3$ was likely leached to deeper soil layers, but researchers observed no crystal formation, such as we found at Deep Canyon. However, $CaCO_3$ remains relatively high in the soils at CVARS, binding the majority of soil C.

The key point here is that $CaCO_3$ is highly dynamic in response to root and mycorrhizosphere dynamics in the native ecosystem. $CaCO_3$ is also highly dynamic in the disturbed site, but the cycle is a largely inorganic one. Both are subject to CO_2 loss through respiration (Deep Canyon) or inorganic dissolution and diffusion. However, plants fix CO_2 in the desert, whereas any CO_2 lost in a flush with rainfall, is likely lost from the system.

It is not yet known the ultimate fate of the C in caliche, but these data show that the process is dynamic, and there is a potential for significant loss.

CHAPTER 5: Conclusions

The research shows that caliche in the surface soil layers is not in equilibrium, but is dynamic. The isotopic ratios indicate that fractionation of $^{13C}/^{12}C$ has occurred, especially as the caliche in the upper soils weathers, and that $\delta^{18}O$ reflects local water sources. Carbon flux measurements show that high levels of CO_2 are generated within soil where native vegetation remains following rainfall during periods of maximum root and rhizosphere peaks. Arbuscular mycorrhizal fungi are particularly active, providing crystal seeds for $CaCO_3$ as soil dries out. Organic matter from plant and microbial residues is decomposed, mineralizing CO_2 along with Ca and nutrients from the plant tissue. With the next rainfall, the $CaCO_3$ dissolves. By repeated wetting, drying, root and microbial growth, caliche forms dissolves, and reforms.

However, in disturbed soils, there is little or no CO_2 from plant or microbial respiration. This is reflected in the lack of soil CO_2 response to a rainfall event. Nevertheless, CO_2 is generated and lost from the soil to the atmosphere, especially following a rainfall. With little organic matter, from aeolian deposition or recalcitrant C, much of the CO_2 likely comes from inorganic C, predominantly $CaCO_3$. With a rainfall, the modeling suggests that $CaCO_3$ is solubilized and CO_2 released to the atmosphere.

Researchers are not yet successful in distinguishing caliche layers in soil with ground penetrating radar (GPR). Researchers can distinguish layering, however in the California deserts, there are many depositional layers that, at this point, can only be distinguished by direct observation coupled with understanding the underlying and surrounding geology of a site.

5.1 Carbon in Desert Ecosystems and Vegetation Removal

Large-scale solar development in desert ecosystems has the potential to generate electricity, thereby reducing fossil carbon (C) accumulation in the atmosphere, and in turn, lessening the rates of global warming (e.g., Hernandez et al. 2014). However, both caliche and organic matter losses compromise the value of solar energy as an alternative to fossil C burning by releasing stored inorganic C into the atmosphere and destroying the ability of the deserts to sequester C. A number of concerns, including loss of inorganic C cycling have been raised with solar development, but the majority of concerns can be addressed with careful attention to siting the facilities and roads (e.g., Hernandez et al. 2014).

5.2 Research Needs

Three key study areas have been identified from this one-year study to better understand the dynamics of inorganic C in our desert ecosystems.

First, the pathways were characterized, however a longer-term study is required on multiple sites across the entire range of solar deployment area, to characterize the rates and time scales of C dynamics. The preliminary results indicate that caliche can weather at 5 percent per year. During a 20-year lifetime of a plant, that caliche exposed might well degrade, however, the

actual field rates would be expected to be highly variable based on the specific weather of each individual year and the fragmentation of the caliche material. Averages mean little in the desert.

Second, the vertical redistribution of Ca in the field is needed. Modeling studies suggest that caliche is formed and weathered rapidly. Is the Ca released eroded or leached reforming deeper caliche, or does it remain in the soil, subject to repeated cycles and a net loss of CO_2?

Third, the impacts of multiple interacting changes on caliche weathering and formation are needed. Sites with little nitrogen (N) deposition were specifically chosen. N deposition as nitrate, and especially ammonium, will acidify the soils. N deposition is a product of transportation corridors, development, and industrial activity. These are all collateral impacts of desert development, whether for solar power or other human activity.

All of these areas need additional research. These should be undertaken by continued monitoring of sites that were established, continued modeling work, and incorporate newer field-based isotope measurement capacity.

5.3 Siting of Solar Power Plants and Power Corridors

Data shows that caliche is dynamic, and the processes of formation and weathering can occur within the time scales of solar unit deployments. Undisturbed vegetation produces $CaCO_3$ as long as Ca is present or coming in by wind or water erosion. But, CO_2 appears to be lost from $CaCO_3$ where the vegetation has been removed.

Siting solar developments on previously disturbed lands are recommended. Desert riparian woodlands should especially be avoided for the protection of sequestered, and their ability to increase that C sequestration. Their deep roots and microbial associations continue to sequester both organic and inorganic carbon.

It is also recommended that solar developments be revegetated. Short-statured plants, such as cacti and shrubs such as *Encelia farinosa* also respire CO_2, but continue to produce organic C and build up both organic and inorganic soil C. The modeling work under these shrubs is continuing, but these steps alone should provide the critical information to allow solar developments to produce needed, “green” energy and simultaneously reduce C loss and sustain buried inorganic and organic C.

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