Sequestration of Atmospheric Carbon Dioxide as Inorganic Carbon under Semi-Arid Forests

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Introductions

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Greenhouse Gases

Atmosphere contains ~320 billion tons CO₂

Annual increase is ~20 billion tons CO₂

Excessive CO₂ greenhouse gas may cause global warming, climate change, rising sea levels, ocean acidification, melting icefields, more forest fires, reduced food supply, etc.
What can be done?

• Burn Less Fossil Fuels. (difficult to achieve)

• Nuclear power, develop safer reactors, deal more effectively with nuclear wastes. ("Greens" opposition)

• Climate engineering projects proposed for carbon dioxide removal (CDR) and solar radiation management (SRM). (large, expensive, controversial)

• Carbon reduction & storage via forestation. (low cost & low tech)
- Leaves inhale CO$_2$. Roots in semi-arid regions are deep. Exhale CO$_2$ into USZ at high partial pressure.

- CO$_2$ + H$_2$O $\rightarrow$ dissolved HCO$_3^-$ bicarbonate, combines with soil Ca$^{+2}$, precipitates CaCO$_3$ calcite.

- Trees in semi-arid regions sequester atmospheric CO$_2$ long term underground as stable calcite, low rainfall.

- These trees also sequester atmospheric CO$_2$ short term, as organic biomass.

- But burning, decomposition of biomass reinject CO$_2$ into the atmosphere.
Yatir forest, semi-arid, ~world’s driest. Beginning in 1966, Keren Kayemeth Lelsrael – Jewish National Fund foresters planted four million trees at Yatir. It is now the largest forest in Israel, covering 28 km² (6920 acres or 2,800 hectares). Extrapolation: Global semi-arid forestation may remove ~2.6 billion tons of atmospheric CO₂ per year.
Global distribution of semi-arid (Steppe, 17.7%) regions
Chemical Equations for Carbonate Precipitation

Soil gas dissolves into the soil moisture, forms carbonic acid.

(1) $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$

Carbonic acid dissolves pre-existing soil calcite and releases calcium ions.

(2) $\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{+2} + \text{HCO}_3^-$

Released Ca$^{+2}$ combines with the DIC, and precipitates calcite.

(3) $\text{Ca}^{+2} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}$

Eq. 3 (idealized) implies no net sequestration. Our isotopic data show net sequestration because: (a) most CO$_2$ from Eq. 3 does not return to atmosphere, (b) many other cation sources contribute to Eq. 3, from silicate weathering, desorption of Ca$^{+2}$ from clay, gypsum, sea spray, etc.
CO₂ from roots combines with soil water of unsaturated zone (USZ) to form DIC, comprised mainly of HCO₃⁻ bicarbonate. DIC concentration decreases with depth, as water flows down, due to CaCO₃ precipitation into USZ. Seen easily for plants with shallow roots, not tree roots.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>DIC (mmol C L⁻¹)</th>
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<tbody>
<tr>
<td>30-60</td>
<td>4.5</td>
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<tr>
<td>60-90</td>
<td>3.4</td>
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</tbody>
</table>
• Measure CO$_2$ precipitation rate (into CaCO$_3$) per cm per Liter of sediment (L$_s$) from decrease per cm of DIC (~1.6 mg cm$^{-1}$L$_s^{-1}$ at Yatir).

• Measure flow rate of water (11 cm yr$^{-1}$ at Yatir) using tritium in water (HTO) as tracer.

• CO$_2$ precipitation rate (within calcite CaCO$_3$) at Yatir is ~18 mg yr$^{-1}$ L$_s^{-1}$ of CO$_2$ (11 cm yr$^{-1}$ x 1.6 mg cm$^{-1}$L$_s^{-1}$ ).
Isotope exchange in Yatir (and Nizzanim) forests

- $^{13}$C and $^{14}$C are tracers for precipitation reaction
- Soil contains up to 20% relict marine calcite.
- DIC concentration decreases with depth.
- Relict calcite: $\Delta^{14}$C = -1000 (zero $^{14}$C).
- Relict calcite: $\delta^{13}$C=0 (same $^{13}$C as standard)
- Continuous exchange between DIC and marine calcite in USZ as rainwater flows down.
- $\delta^{13}$C and $\Delta^{14}$C values in solid (nodules) vary due to exchange between DIC and relict calcite; & precipitation onto nodule surface.
Isotopic evidence for CO₂ incorporation and sequestration into pedogenic carbonate

• δ¹³C and Δ¹⁴C trace the incorporation of atmospheric CO₂ from DIC into pedogenic carbonate, as DIC descends down profile interacting with relict marine limestone
• Depleted δ¹³C values in DIC from atmospheric CO₂ - exchanges (continuous dissolution and precipitation) with δ¹³C- enriched relict marine limestone to form pedogenic calcite (solid) of intermediate δ¹³C values
• Atmosphere is the sole source of ¹⁴C, introduced into the USZ as ¹⁴CO₂ via roots and decay
• Pedogenic solid in the USZ incorporates ¹⁴C, as DIC exchanges with relict limestone
• Therefore: atmospheric CO₂ tagged by radiocarbon is incorporated into pedogenic carbonate
Yatir forest research implications

• Until now, atmospheric CO\textsubscript{2} sequestration by forestation was considered only for short-term organic carbon storage (tree biomass, tree liter, soil organics).

• We prove that semi-arid forestation abstracts more atmospheric CO\textsubscript{2} in a manner not previously considered. More importantly, forestation provides for long-term inorganic carbon storage into the USZ.

• Our research quantifies inorganic carbon sequestration by forestation in semi-arid regions.
Consider sediment volume 1 km$^2$ & 6 m depth (6x10$^9$ L), trees above, roots below. Precipitation ~105 tons of CO$_2$ per year (18. x10$^{-3}$ x 6x10$^9$ gm).

More accurate estimates require global data on calcite precipitation rates in semi-arid forests.

A particular global land management policy is tentatively suggested - widespread tree planting in semi-arid regions.

Extrapolating semi-arid sequestration rate **globally** yields rate of ~2.6 billion tons CO$_2$/yr (~105 tons km$^{-2}$ x 25 x 10$^6$ km$^2$ ~ 2.6 Pg), ~13% of the rate by which atmospheric CO$_2$ is currently increasing.
Summary

• Atmospheric derived CO$_2$ is sequestered long term as calcite in USZ.

• Yatir forest receives only ~28 cm/yr rainfall. Low rainfall precludes re-solution of calcite. Calcite sequestration much longer term than biomass carbon. Helped by deep roots compared to temperate regions.

• Semi-arid forestation does not decrease productive temperate-region agricultural land. Provide steady employment instead of marginal herding & agriculture, & useful products (lumber, charcoal, off-sets, etc.).

• Global extrapolation yields CO$_2$ annual semi-arid forest sequestration rate of ~2.6 billion tons CO$_2$/yr, ~13% of rate of atmospheric CO$_2$ increase.
THANK YOU!
Sequestration of Atmospheric Carbon Dioxide as Inorganic Carbon under Semi-Arid Forests
• The Paris Agreement deals with GHG emissions mitigation, adaptation and finance starting in the year 2020, to help stop the gradual warming of the Earth.

• Main aim is to limit the increase in the global average temperature to well below 2°C above pre-industrial levels, by reducing GHG emissions.

• Many researchers now claim that such targets require "negative emissions", i.e., extraction of CO$_2$ from the atmosphere.

• Paris Agreement opened for signature on 22 April 2016. On 5 Oct. 2016, it reached the required 55 countries representing 55 percent of global emissions for the accord to enter into effect. But these agreements need to be followed by actions.
• Large & expensive climate engineering projects have been proposed for carbon dioxide removal (CDR) and solar radiation management (SRM). CDR captures CO₂ produced by large industrial plants, compresses it for transportation, and then injects it deep into a rock formation for permanent storage. SRM projects seek to reduce global warming by reflecting sunlight, for example using stratospheric sulfate aerosols.

• Carbon reduction & storage via forestation (our low cost & low tech project).
The Carbon Cycle

- Burning fossil fuels and decomposition of dead plants and animals inject CO₂ into the atmosphere.

- Organic carbon production via forestation provides useful short term organic carbon sequestration.

- Semi-arid forests remove atmospheric carbon dioxide, fixing it underground long term as inorganic carbonate salts.
• $^{13}$C and $^{14}$C are tracers for precipitation reaction. Continuous exchange between DIC and solid sediment in USZ as rainwater flows down. DIC concentration decreases with depth.
• $\delta^{13}$C in solid marine calcite is a result of exchange between DIC and relict marine calcite ($\delta^{13}$C=0), and precipitation onto marine calcite surface, while DIC enriched from -20 (C3 plants).
• $^{13}$C data show continuous exchange and precipitation along path from DIC into solid sediment.
• $\Delta^{14}$C in DIC depleted with depth, while solid enriched from -1000 (no $^{14}$C).
• $^{14}$C exchanges demonstrate that CO$_2$ precipitates out of DIC as calcite. Atmospheric $^{14}$CO$_2$ via roots is only radiocarbon source.
• Measure DIC (as CO$_2$) from CO$_2$ mass & liters of water ($L_w$) extracted from USZ wet sediment by vacuum distillation (~250 mg CO$_2$ $L_w^{-1}$ at Yatir).

• Porosity (~53%), Humidity (~12%), Dry sediment density (1.24 g cm$^{-3}$) → A Liter of sediment has 0.47 L solid + 0.12 L water + 0.41 L gas.
Green Walls are being built/proposed over extensive geographical areas (Sahel, China, India, etc.) that have thicker USZ’s than Yatir.

But forests have reduced albedo; and therefore a warming effect. Forests can cool by evapotranspiration (ET), but do dry semi-arid forests have sufficient soil moisture?

Further study needed to evaluate possible net climate benefits of semi-arid forestation due to carbon sequestration.