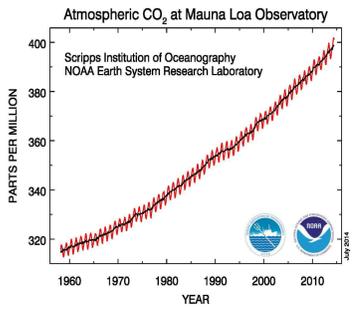


Sequestration of Inorganic Carbon via Forestation

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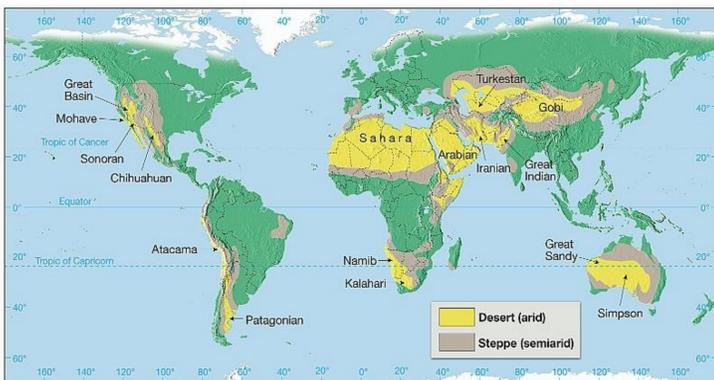
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Carbon dioxide has always been an atmospheric component. However, its concentration and isotopic composition have been changing over time. Long term changes were brought about by chemical weathering and volcanism; while shorter term changes were due to biological activity (on land and in the ocean) by photosynthesis and respiration. Since monitoring of clean air began in the late 1950's, a continuous increase in the CO₂ concentration has been noted. This upward trend is due to the clearing of the forests for agriculture; and more importantly, due to the burning of fossil fuels. Before the Industrial Revolution, the CO₂ concentration was constant.



The carbon cycle is well known and fairly well quantified, as shown in the adjacent table and representative cartoon. No mention is made however how much is retained in the soil as lime (secondary carbonate) nor how much is transferred to the groundwater as carbonate or bicarbonate anions (depending on the pH, and potentially for thousands of years). We studied how carbon and its isotopes evolve in a pine forest (in the semi-arid region of southern Israel) from atmospheric inputs through the relatively thick unsaturated zone until the groundwater table. Semi-arid zones receive between 25 to 50 cm of rain annually. This level of rainfall can support shrubs and small trees, though farming is unstable, subject to periodic drought.

Consider a carbon sequestration model based on forestation of the world's semi-arid areas; and the resulting sequestration of inorganic carbon within the extensive water unsaturated and saturated zones below the resulting semi-arid forested areas. This has advantages compared to sequestration by trees of carbon into biomass, carbon based biological material derived from living, or recently living organisms, composed of a mixture of organic molecules containing hydrogen and other atoms. However, biomass generally returns to the atmosphere (via burning or rotting) when trees dies. The semi-arid zone is an extensive geographical area on the global scale, as shown in the map below. Although marginal for growing crops and for pasture lands, this zone receives sufficient rainfall to sustain tree growth. An example of such an area is the semi-arid Sahel zone in Africa, between the Sahara desert to the north and the Sudanian Savanna to the south. Forestation of such areas can remove significant atmospheric CO₂ annually into groundwater via inorganic (CO₂/HCO₃) sequestration. The rate at which the groundwater flows in semi-arid regions is slow, meters per year. So the CO₂ is held for times ranging up to thousands of years (as in the Judea Group limestone aquifer underlying Jerusalem Hills, the Galilee, and parts of the Negev). Also some of this bicarbonate can precipitate within the aquifer as secondary lime infillings, which removes even more of the atmosphere originating CO₂.

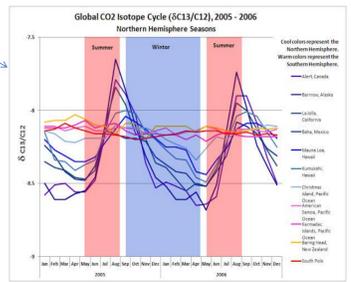
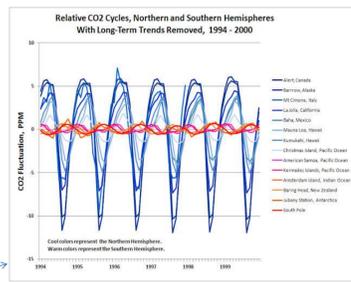


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Many proposals have been made how to reduce the atmospheric carbon dioxide concentration. Engineering proposals include geologic sequestration, putting CO₂ into deep underground geological zones, to be stored over geologic time. A major constraint of these proposals is their high cost. We suggest that **planting trees in semi-arid regions could be a successful climate engineering method. This low-tech, safe, cheap and continuous forestation method could remove and then sequester CO₂ for long periods of time as inorganic carbon.** This sink is not the organic bio-mass of trees above ground, but rather the underground inorganic component that has so far received little attention. The fact is that trees act as pumps, taking in CO₂ through the leaves, building bio-mass via photosynthesis, and then pumping out CO₂ through root respiration underground into the thick water unsaturated zone (USZ). The partial pressure of CO₂ in the soil increases to 10-100 times over the atmospheric concentration. As percolating rainwater passes through the soil, part of this CO₂ is converted to HCO₃ bicarbonate, which is then stored as the dominant anion in groundwater. This CO₂ is thus sequestered and does not return to the atmosphere, considering that the groundwater flow rate in semi-arid regions is very slow.

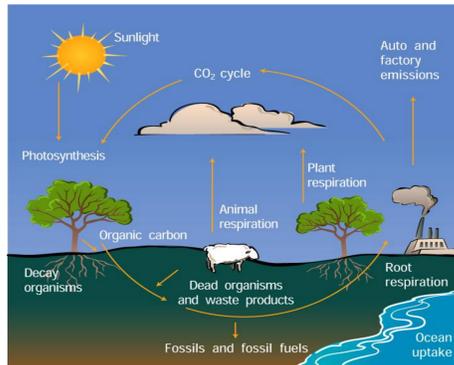
The inorganic carbon may be CO₂ gas or CaCO₃ lime, or DIC Dissolved Inorganic Carbon H₂CO₃*. DIC solution carbonates, denoted as H₂CO₃*, comprise the total dissolved carbon in the form of carbonic acid H₂CO₃ and aqueous carbon dioxide CO₂(aq). Here, we focus on carbon sequestration of inorganic carbon within the extensive unsaturated zone (USZ) and saturated zone (SZ) below semi-arid forested areas. The USZ extends from the top of the ground surface to the water table. The water table is the top of the aquifer, the top surface of the subsurface ground-water, below which soil pore spaces or fractures and voids in rock become completely saturated with water. The depth to the water table varies. Aquifers comprise the saturated zone, and are regions of the subsurface that easily transmit groundwater. The sequestration of carbon in plant biomass starts with CO₂ in the atmosphere. CO₂ taken in by plants is used to build the biomass. But a large amount of this CO₂ is pumped into the USZ, above the water table, where it precipitates as secondary lime, or is retained in soil moisture. Some CO₂ penetrates the underlying SZ including aquifers. Consequently, the water in the SZ beneath the water table can contain significant amount of DIC. This groundwater is semi-arid regions cycles very slowly.

In temperate zones, the average annual rainfall is 800 mm. Leaching of soil lime (CaCO₃) by percolating precipitation is maximal, the unsaturated zone (USZ) is very shallow (perhaps less than 2 meters deep), and the flow rate of water is high, thus temperate zone sequestration would not be nearly as effective as in semi-arid zones



Superimposed upon the continuous upward trend are seasonal oscillations. These correspond to the seasonal periods of growth (summer) when the atmospheric concentrations are reduced, as plants abstract the CO₂ from the atmosphere to build biomass. During dormancy (winter) and the accompanying decay and decomposition of biomass, CO₂ is released into the atmosphere in similar amounts. The standard worldwide C13/C12 isotopic abundance ratio is R₀ = 0.0112. Most plants prefer to take up the lighter C12 during photosynthesis; with the result that carbon compounds so formed have a lower C13/C12 ratio R than R₀. The isotopic ratio $\delta C13\% = 1000 \times (R - R_0)/R_0$ is therefore an indicator of life. The decay of isotopically depleted tree biomass would lead to fairly constant atmospheric $\delta C13\%$ ratios over the long run, if it were not for massive additional amounts of C13 isotopically depleted CO₂ being added continuously throughout the year by the burning of fossil fuels. Atmospheric CO₂ has increased from 270 ppmv with a concomitant $\delta C13 = -6.4\%$ (Craig and Keeling, 1963) at the start of the Industrial Revolution to the present value of almost 400 ppmv CO₂ with $\delta C13 = -8\%$. The decreasing value $\delta C13$ for atmospheric CO₂ is strong evidence the source of the CO₂ increase is due to fossil fuels.

Throughout the Pleistocene, atmospheric CO₂ concentrations, as determined from Greenland and Antarctica ice cores, varied from a low of 170 ppmv (glacial times) to a high of approximately 280 ppmv (interglacial times) in cyclic fashion. It is only since the Industrial Revolution that these values have been exceeded. Plants are important today as in the past for regulating atmospheric inputs. Most obvious is the conversion of CO₂ via photosynthesis into plant bio-mass. There is a cycle of trees growing, whose carbon storage reaches an equilibrium on the order of a few hundred years (depending on the average life span of a tree). Methods are needed now to store the green house gas for periods of thousands of years (we are in an interglacial period at present), at least until the next cyclical global cooling phase returns.



A representative depiction of the carbon cycle



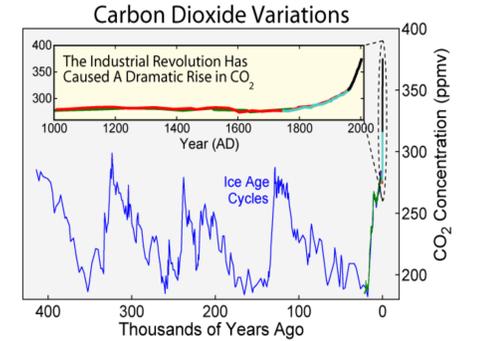
Yatir Forest

The Yatir forest in the northern Negev is an example of reforestation in a semi-arid zone. Yatir is one of our sampling sites for carbon isotopic analyses of atmospheric CO₂, soil-gas, soil moisture, and secondary lime. Our data agree with Hibbard et al. (2001) who found that in the top 10 cm of soil in southwest Texas, soil concentrations of CO₂ increased appreciably when trees replaced grasses. Kattibbard et al. (2001) noted that plant carbon mass increases by an order of magnitude when grass land is replaced by savanna woodland.

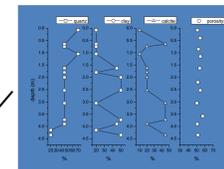
An important transfer route of CO₂ from the atmosphere takes place as the high partial pressure from the root zone respiration recharges the ground water with HCO₃- bicarbonate, the dominant anion of the groundwater. The flow rate of groundwater in Israel is slow, on the order of meters per year. Thus, CO₂ that is converted to HCO₃ is retained beneath the water table for many hundreds or thousands of years.

Another sink is CO₂ stored as bicarbonate anion is stored in ground water in the aquifer directly beneath the USZ, the dominant anion in most Israeli groundwater, having mild alkaline pH. Some is in the recharge water, CO₂(g) + H₂O = H⁺ + HCO₃⁻ (formation of carbonic acid), some is generated by carbonic acid dissolving calcite CO₂(g) + H₂O = H⁺ + HCO₃⁻ (enhanced by high partial pressure of CO₂ from the root zone) as well the oxidation of soil organic matter and silicate weathering. Slightly more than half of the bicarbonate can be traced as coming from the present atmosphere CO₂. In Israel, the HCO₃⁻ concentration of the ground water lies within the approximate range of 250 mg/L to 350 mg HCO₃⁻ for each liter of water. As groundwater flow is slow, 1-10 meters per year the CO₂ taken from the atmosphere is sequestered for long periods of time, ranging from hundreds to tens of thousands of years. There is, as an approximation, on the order of magnitude of 0.30 g HCO₃⁻ per liter of ground water, 1.1x10⁹ meters of groundwater are used annually (taken as approximating annual input)- Therefore, (0.30g/L) HCO₃⁻ * 0.72 (the mole fraction of CO₂ in HCO₃⁻) * 1.1x10⁹ m³ * 10³ L/m³ * 10³ g/L = ~ 2.2x10¹³ g/yr. 120,000 tons CO₂/yr. stored in ground water in Israel may be small compared to the 35 billion tons CO₂ released to the atmosphere globally; but Israel represents less than a thousandth of the land area of the global semi-arid region. **If this value can be taken as representative, then groundwater in all of the semi-arid region can store approximately 0.12 petagrams (1 Pg = 10¹⁵ g) of carbon dioxide per year, which is the same order of magnitude as the rate 0.7 Pg of CO₂/year by which the CO₂ in the atmosphere is increasing.** Thus, this sink, especially when taken with lime precipitation and the tree biomass, can retard the increase by which carbon dioxide is increasing in the atmosphere. Moreover, planting trees would provide many jobs, producing timber and firewood in a region that is otherwise poorly suited to profitable agriculture.

Is there evidence that forestation can efficiently sequester carbon dioxide? Yes! A large increase in atmospheric carbon dioxide occurred during the middle Devonian by volcanism. Atmospheric carbon dioxide was then as high as 15 times present concentrations. During the following Carboniferous period, in which the great forests of that time produced today's great coal fields, the carbon dioxide in the atmosphere was greatly reduced. The carbon in the biomass was not recycled, but was rather preserved within carboniferous coal deposits. Only now is this carbon being returned to the atmosphere as fossil fuels are burned. The transfer of carbon dioxide to plant biomass tapered off with the onset of the late carboniferous Permian Karoo Ice Age. The adjacent figure showing the variability of carbon dioxide in the atmosphere throughout the Phanerozoic. It should be noted that despite the great increase since the Industrial Revolution, the atmospheric levels at present are relatively low on a geological time scale.



GLOBAL WARMING: CO ₂ SOURCES		
Where does the human-induced CO ₂ come from?		
Burning the forests:	1.7 PgC	21%
Soil degradation and desertification:	0.8 PgC	10%
Burning fossil fuels (gas, oil, coal):	5.0 PgC	63%
All human food and cooking fuel:	70.5 PgC	76%
TOTAL	8.0 PgC	100%
Volcanic activity	??1.0 PgC/yr	
Photosynthesis + decay on land	60-120 PgC/yr	
Photosynthesis + decay in the sea	40-100 PgC/yr	
What is the standing stock in Carbon units?		
All plants and trees above ground:	600 PgC	25%
All soil organisms, roots, mulch, peat:	1300 PgC	54%
All CO ₂ in the atmosphere:	500-700 PgC	21%
All CO ₂ in the oceans:	37,500 PgC	
CO ₂ in marine sediments	30,000,000 PgC	
CO ₂ in the atmosphere increases 10-20% every 20 years and this rate is still increasing! (0.2 PgC/yr).		



Calculating the precipitation of C in secondary calcium carbonate

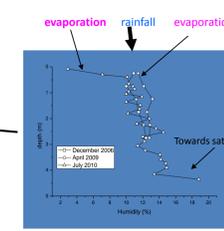
We use the porosity to calculate the proportions of solid and of (water+gas). Then using the humidity(soil moisture or recharge), we calculate the proportions of water and gas. We use the density to calculate the weight of the dry sediment, and then use the sedimentology to calculate carbonate in dry sediment.

Data used:
 Porosity of the sediment 53%
 Humidity(soil moisture)(recharging at 0.11m/yr tritium data) at 2.2m is 12%
 Dry sediment density 1.24 gcm⁻³. Calcite in the sediment at 2.2m is 20%
 DIC at 2.2m is 47mmole liter⁻¹
 Carbonate precipitation from the DIC is 2.9% yr⁻¹

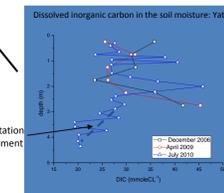
Thus, in 1 liter of sediment we have:
 0.47 liter solid and 0.53 liter water + gas (0.12 liter water and 0.41 liter gas ~500ppm CO₂)
 The solid (0.58 kg dry sediment) contains 1.17 moles calcite.
 The water contains 5.64 mmole DIC (liter sediment)⁻¹

Carbonate precipitation from the DIC on 1 liter of sediment is 0.16 mmole yr⁻¹ (5.64*2.9/100) or ~2 mgC yr⁻¹ (liter sediment)⁻¹.

For a USZ of 1 km² area and 5 m depth, with growing trees on top and roots in the USZ (source of CO₂) the lime precipitation is approximately 10 tons of carbon per year under each km² equivalent to 36.7 tons carbon dioxide. Taking this to be representative of the USZ under all of Israel (22,000 km²) 8 x 10⁹ tons x 10⁶ g/ton = 8 x 10¹¹ g is precipitated as lime each year, solely in Israel.



Moisture content of the USZ (annual precipitation 280mm)



Sampling data from the USZ at Yatir

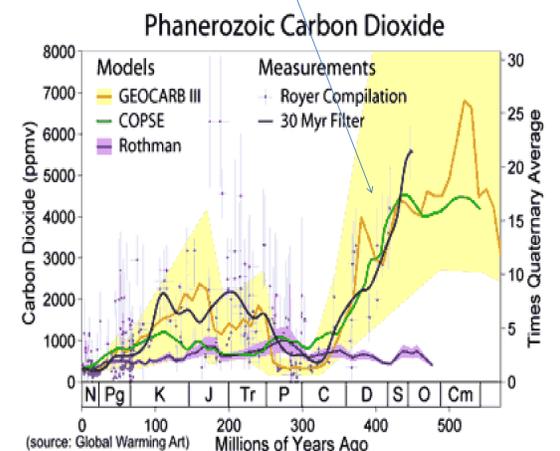
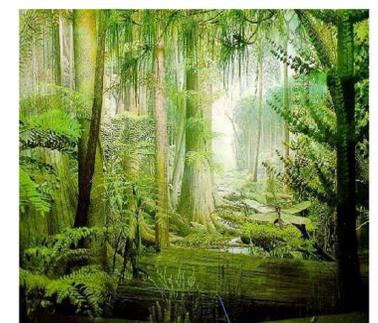


Figure from R.A. Rohde. The estimates have been made from geochemical modeling. The GEOCARB III (Bernier and Kavalala, 2001) COPSE (Bergmann et al., 2004) and Rothman (2001) combined with direct determinations (Royer et al, 2004) calculated from carbon isotopic ratios in phytoplankton, paleosols, and from stomatal density in plant fossils.