An Approach to Removing Large Quantities of Atmospheric Greenhouse Gases

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To cite this article: John B. Cook, Svetlana R. Amirova, Edwin A. Roehl Jr., Paul A. Comet, Tamara V. Tulaykova. An Approach to Removing Large Quantities of Atmospheric Greenhouse Gases. American Journal of Environmental Protection. Special Issue: New Technologies and Geoengineering Approaches for Climate. Vol. 5, No. 3-1, 2016, pp. 21-25. doi: 10.11648/j.ajep.s.2016050301.14

Received: March 24, 2016; Accepted: March 27, 2016; Published: May 10, 2016

Abstract: A method for removing atmospheric carbon dioxide (CO₂) and water vapor is proposed. The method sprays clouds with alkaline compounds to significantly increase the solubility of CO₂ in the cloud water, providing for much higher than normal levels of CO₂ to be absorbed by rain droplets. The CO₂ is transported to the ground for sequestration in surface and/or ground water, and available for carbon fixation by plants and organisms. Presented calculations estimate that 38 gigatonnes of atmospheric CO₂ could be removed per year by applying the process over 0.08% to 2.4% of the Earth’s surface. Laboratory experiments that grew multiple edible plant species irrigated with the modified rainwater indicated yield benefits. A concept for removing atmospheric methane (CH₄) is also presented. Powerful lasers would ionize the CH₄ to form CO₂ that could then be removed by the alkaline-enhanced rainfall method.

Keywords: Climate Change, Greenhouse Gas, Carbon Dioxide, Methane, Water Vapor, Removal, Alkali, pH Adjustment, Precipitation, Cloud Seeding, Laser

1. Introduction

Current global emissions of greenhouse gases are exceeding the Earth’s assimilative capacity, causing them to accumulate in the atmosphere [1], [2]. Water vapor comprises 95% of all greenhouse gases [3], however, carbon dioxide (CO₂) and methane (CH₄) are of greater concern. Higher greenhouse gas concentrations are widely believed to contribute to climate change, extreme weather events, rising sea levels, and other marked changes, such as the acidification of surface waters and soils.

Over the past century the carbon dioxide (CO₂) concentration rose from 280 to 400 parts per million (ppm), the methane (CH₄) concentration rose from 0.9 to 1.8 ppm, and both continue to rise rapidly [4], [5]. The oceans’ natural alkalinity allows them to store a large amount of CO₂, including more than a quarter of that produced anthropogenically. This has increased ocean acidity ~26% from preindustrial levels, which corresponds to a decrease in pH from an average of 8.2 to 8.1, or less. A further decrease of ~0.3 units by 2100 is likely unless CO₂ emissions are reduced rapidly. Higher ocean acidity negatively impacts marine ecosystems and the economic benefits they provide [6], [7]. Similarly, rains in industrial regions since the mid-20th century have caused soil deterioration due to higher acidity, with current pH ≈ 3 – 4 [8], reducing alkalinity in the environment.

The development of methods that can efficiently remove greenhouse gases already in the atmosphere would be beneficial. Precipitation enhancement methods, which de facto remove water vapor, have been developed primarily for agriculture, water supply, and reducing air pollution [9], [10]. Typically, aircraft, rockets, or other projectiles are used to disperse hygroscopic or glacial particles to alter cloud microstructure, inducing precipitation [11], [12]. Seeding
along a narrow flight path can be sufficient to restructure an entire cloud. Acoustic wave generators have been investigated as an alternative means to inducing precipitation [13], [14].

A new method proposed here expands the purpose of precipitation enhancement to include climate modification through the removal of large amounts of under-cloud CO$_2$. The solubility of CO$_2$ in water is highly sensitive to pH [15], [16], so the first step is to disperse an alkaline compound such as potassium hydroxide (KOH) inside clouds over selected areas to increase the pH of the clouds’ constituent microscopic water droplets to 10 – 11. The alkaline particles should be consistent in size and composition, and dispersed uniformly inside clouds to produce droplets formed by nucleating water vapor which are uniform in size and pH.

The method’s second step is to induce rain, allowing the high pH rain to absorb substantially more CO$_2$ than a normal pH rain or a two-dimensional (2-D) patch of surface water whose specific surface area is less than rain’s three-dimensional (3-D) droplets. The second step would be unnecessary if alkalis having strong hygroscopic properties are used. Once on the ground, the dissolved CO$_2$ is carbonic acid, H$_2$CO$_3$, and CO$_2$ is hydrogen ion to determine pH, and HCO$_3^-$ and CO$_3^{2-}$ are bicarbonate and carbonate ions.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &= \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 &= \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- &= \text{CO}_3^{2-} + \text{H}^+ 
\end{align*}
\]

where the equilibrium concentrations of H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$ at a neutral pH = 7.0 are approximately 0.71, 3.3, and 0.001 milligrams per liter (mg/l), respectively [17]. CO$_2$ solubility increases as pH increases due to an increasing H$^+$ concentration, with HCO$_3^-$ and CO$_3^{2-}$ concentrations increasing by one and two orders of magnitude, respectively, for each unit change in pH. The fractions of carbon in the molar masses of H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$ are 0.1935, 0.1967, and 0.2, respectively, so all fractions are equal to or approximately equal to 0.2.

The mass of carbon M$_c$(pH) in the dissolved CO$_2$ in a rainfall volume equivalent $U_w = h_wA$ is estimated from (2), where $h_w$ and A are the volume’s height and cross-sectional area. For brevity, the H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$ concentrations are referred to as C$_1$, C$_2$(pH), and C$_3$(pH).

\[
M_c(pH) = U_w[0.2 \{C_1 + C_2(pH) + C_3(pH)\}]
\]

The concentration of atmospheric carbon C$_{at}$ in an air volume with a height h and a unit (1 m$^3$) cross-section can be estimated from (3), which is derived from (2). The vertical mixing ratio of CO$_2$ is estimated to be constant for altitudes of interest. The fraction of carbon in the molar mass of CO$_2$ is $12/44 = 0.27$. For a cloud at an altitude of 1 km, the cloud water pH should be increased from a typical 5.6 to 10.3 for complete CO$_2$ removal ($C_{at} = 420$ ppm).

\[
C_{at} = (h_w/h)[0.2(C_1 + C_2(pH) + C_3(pH))/0.27]
\]

The deployment of KOH in a liquid water aerosol is used to illustrate how to estimate the amount of an alkali needed to raise the pH of cloud water to an effective level. The dissociation reaction of KOH in water represented by (4) indicates that the molar concentrations of KOH and OH$^-$ are equal.

\[
\text{KOH} = \text{K}^+ + \text{OH}^- (4)
\]

An alkali facilitates the dissociation of ionic species in water according to the constant $K_w = 10^{-14}$ at 20°C [17]. According to (4) and (5), the KOH mass concentration $n_{KOH}$ needed to raise the pH of the cloud water from 5.6 to 10 is $10^4$ mol/l, or $56\times10^5$ g/l when converted to a molar mass. For an example 1 km$^3$ cloud having a liquid water concentration of 1 g/m$^3$, the mass of KOH to be dispersed would only be 5.6 kg. Note that little of the KOH would be spent within the cloud over a short period prior to rainfall inducement due to the small resident concentration of CO$_2$ molecules (~400 ppm).

\[
\text{KOH} = \text{H}^+ + \text{OH}^- (H^+ + \text{OH}^- = \text{H}_2\text{O}, K_w = [H^+] [\text{OH}^-])
\]

The volume of water precipitated by a cloud $U_1$ is estimated by (6), where $I$ is the rainfall rate, $A_s$ is the 2-D receiving area on the Earth’s surface, and $T$ is the duration of the rainfall event. The number of spherical droplets $N$ having a radius $r_d$ in $U_1$ and the droplets’ total surface area $A_d$ are estimated by (7) and (8) respectively.

\[
\begin{align*}
U_1 &= I A_s T \\
N &= 3U_1 / (4\pi r_d^3) \\
A_d &= N\times4\pi r_d^2
\end{align*}
\]

If given a moderate rainfall characterized by $A_s = 1$ km$^2 = 10^6$ m$^2$, $I = 6$ mm/h, $T = 1$ hour, and $r_d = 0.5$ mm, then $U_1 = 6,000$ m$^3$, $N = 10^{13}$, and $A_d = 3.6\times10^7$ m$^2 = 36\timesA_s$. Alternatively, the Marshall-Palmer approximation accurately estimates droplet radii spectra for drizzle, rain, or storm events, and can be applied to perform more detailed droplet surface area estimates [18], [19]. The parameters and measurement methods used to characterize precipitation inside clouds and atmosphere volumes are described in [20]–[22].
Rapid CO₂ saturation of droplets is made possible by their small size and slow speeds. The terminal speed of a droplet \( V_g \) is estimated by (9) by equating the forces of gravity and air resistance, where \( \rho_d \) and \( \rho_a \) are the densities of air and water respectively, and \( g \) is the acceleration due to gravity. A droplet having \( r_d = 0.5 \text{ mm} \) falling from an altitude \( h = 1 \text{ km} \) has a \( V_g = 2.9 \text{ m/sec} \) (\( \rho_a = 1.2 \text{ kg/m}^3 \) at 12°C). The travel time \( t_b = 350 \text{ seconds} \) is estimated by (10).

\[
V_g = \left(\frac{2r_dg\rho_a}{\rho_d}\right)^{1/2} \tag{9}
\]

\[
t_b = \frac{h}{V_g} \tag{10}
\]

The time \( t_{sw} \) needed for a droplet to become saturated with CO₂ depends on the ratio of the droplet’s aerated volume to its surface area, and is estimated by (11), where \( k_{aw} \) is a measured constant, called the gas transfer velocity, for air and water molecules.

\[
t_{sw} = \frac{r_d}{3k_{aw}} \tag{11}
\]

### 2.1. Impact on Plants

![Fig. 1. First crop plants after 19 days (a) and 31 days (b) days. The blue pot (left) was irrigated daily with distilled water. The brown pot (right) was irrigated with an alkaline solution.](Image)

A potential benefit to plant growth is illustrated by results from indoor bench-scale experiments [27] in which two simulated crops were irrigated with and without alkaline-enhanced water for a period of one month (Figs. 1 and 2). The blue pots were irrigated daily with distilled water, and the brown pots were irrigated using the same regime with a stable KOH-distilled water solution having a pH=12. For the first crop both pots were identically planted with beetroots (10 grains), carrots (20 grains), and parsley (2 grams). For the second crop the pots were planted with dill (20 grains) and cucumber (5 grains). As shown, both crops responded favorably to the alkaline-enhanced irrigation.

![Fig. 2. Second crop plants after 19 days.](Image)

### 2.2. Global Application

| pH | 5.6 | 10 | 10.5 | 11 |
|----|-----|----|------|----|
| \( M_c \) (kg/m²) | 1.6×10⁴ | 0.849 | 4.05 | 26.5 |
| \( M'_c \) (kg) | 8.2×10¹⁰ | 4.3×10⁸ | 2.1×10⁶ | 1.4×10⁶ |
| \( M_{CO₂} \) (kg) | 3×10¹¹ | 1.6×10⁹ | 7.7×10⁵ | 5×10⁶ |
| \( A_p \) (%) | - | 2.4 | 0.5 | 0.08 |
| \( Q_{KOH} \) (kg) | 6.9×10⁹ | 4.8×10⁸ | 2.3×10³ |

Table 1 provides statistics that estimate outcomes of applying the method globally. The Earth’s surface area \( A_E = 5.1×10^8 \text{ km}² \), the average global annual rainfall \( h_a = 1 \text{ m} \) [28], and the annual global CO₂ emissions \( E_A = 3.8×10^{11} \text{ kg} \) [29]. Using (2), row 2 gives the masses of atmospheric carbon \( M_c \) removed by 1 meter of annual rainfall per m² of the Earth’s surface at the different pH levels shown in row 1. Row 3 gives the global masses of carbon removed \( M'_c \) per (12). Row 4 gives the global masses of CO₂ removed \( M_{CO₂} \) per (13), 0.27 being the carbon ratio of CO₂. Using (14), row 5 gives the percentages \( A_p \) of \( A_E \) needed to completely remove annual emissions \( E_A \), indicating the need is 0.08% – 2.4%. Row 6 gives the mass \( Q_{KOH} \) of KOH needed to remove \( E_A \) each year per (15), indicating that the amount needed is a fraction of the 19×10¹⁰ kg of nitrogen, phosphorous, and potassium (N/P/K) fertilizers used globally in 2014 [30].
\[ M^A_C = M_C^A A_E \] (12)
\[ M^A_{CO_2} = M^A_C / 0.27 \] (13)
\[ A_p = 100 \times E_u / M^A_{CO_2} \] (14)
\[ Q_{COH} = n_{COH} h \lambda A_E A_p \] (15)

3. Atmospheric CH\(_4\) Removal

A concept is also proposed that would use lasers to enhance the conversion of atmospheric CH\(_4\) to CO\(_2\) and water, a process that occurs naturally through the photo-dissociation of CH\(_4\) molecules by sunlight [31]. Once freed, the carbon ions bond preferentially with oxygen [32]. This process can be stimulated by using a powerful laser with an optimized wavelength. Subsequent alkaline-enhanced rainfall would remove the CO\(_2\).

Measurements of atmospheric CH\(_4\) concentrations can be performed at distances of \(8 - 11\) km using pulsed integrated-path differential absorption Lidar in the infrared spectrum at wavelengths \(\lambda = 1.650\) nanometers (nm) [33], [34]; however, the photon energies are too low for ionization. For efficient ionization, the laser wavelength should coincide with a peak absorption frequency at the molecule’s C-H bond dissociation energy of \(E = 4.3\) eV electronvolts (eV) or \(\lambda = 288\) nm due to the Planck–Einstein relation \(\lambda E = hc\) [35]. However, at UV irradiation other gases such as oxygen and nitrogen also could be ionized. Alternatively, multiple-photon excitation achieves photo-dissociation using a laser to bombard gas molecules with multiple photons, increasing their vibrational energy until their chemical bonds are broken [36]. CH\(_4\) has a small absorption peak near \(\lambda = 865\) nm (1.43 eV) [37], suggesting that three or four photons could be sufficient for dissociation to occur.

4. Conclusions

A proposed approach could be effective at removing significant amounts of the main greenhouse gases of concern, i.e., water vapor, CO\(_2\), and CH\(_4\). Estimates show that a method for alkaline-enhanced rainfall could remove more than the \(~38\) gigatones of anthropogenic CO\(_2\) emitted each year if applied over a small portion of Earth’s surface. The next step would be to field test the method’s efficacy. An adjunct method for pre-treating atmospheric CH\(_4\) by laser is also proposed. It would convert the CH\(_4\) into CO\(_2\) for subsequent removal by alkaline-enhanced rainfall.

Acknowledgements

The authors thank Dr. Yakov Ponurovskii and Dr. Imant Vinogradov for sharing information about monitoring greenhouse gases with tunable diode laser spectroscopy and the photo-dissociation of methane with lasers.

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