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An Approach to Removing Large Quantities of Atmospheric Greenhouse Gases

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Abstract: A method for removing atmospheric carbon dioxide (CO_2) and water vapor is proposed. The method sprays clouds with alkaline compounds to significantly increase the solubility of CO_2 in the cloud water, providing for much higher than normal levels of CO_2 to be absorbed by rain droplets. The CO_2 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 CO_2 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 (CH_4) is also presented. Powerful lasers would ionize the CH_4 to form CO_2 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 (CO_2) and methane (CH_4) 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 (CO_2) concentration rose from 280 to 400 parts per million (ppm), the methane (CH_4) 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 CO_2, 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 CO_2 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 sequestered in surface and/or ground water, and available for carbon fixation by plants and organisms.

Below are calculations that estimate the efficiency of the proposed method for atmospheric CO_2 removal, and results from laboratory experiments that grew different crop species irrigated with the modified rainwater. Also described is a concept that uses laser-induced oxidation to convert atmospheric CH_4 into CO_2 that can then be removed by the alkaline-enhanced rainfall method.

2. Atmospheric CO_2 Removal

The typical pH of normal rainwater ranges from 5.6 to a neutral 7.0, at which the concentrations of dissociated ions are relatively small. The insoluble and dissociated portions of the weak acid that remains after attaining the equilibrium of saturation for water by CO_2 are described by (1), where H_2CO_3 is carbonic acid, H^+ is hydrogen ion to determine pH, and HCO_3^- and CO_3^{2-} are bicarbonate and carbonate ions.

$$\begin{aligned} CO_2 + H_2O &= H_2CO_3 \\ H_2CO_3 &= HCO_3^- + H^+ \\ HCO_3^- &= CO_3^{2-} + H^+ \end{aligned} \tag{1}$$

The equilibrium concentrations of H_2CO_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_2CO_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 $U_w = h_w A$ is estimated from (2), where h_w and A are the volume's height and cross-sectional area. For brevity, the H_2CO_3, HCO_3^-, and CO_3^2 concentrations are referred to as C_1, $C_2(pH)$, and $C_3(pH)$.

$$M_C(pH) \approx U_w\{0.2\ [C_1 + C_2(pH) + C_3(pH)]\} \tag{2}$$

The concentration of atmospheric carbon C_{a-} in an air volume with a height h and a unit (1 m^2) 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_{a-} = 420 ppm).

$$C_{a-} \approx (h_w/h)[0.2(C_1 + C_2(pH) + C_3(pH)]/0.27 \tag{3}$$

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.

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 $56x10^{-4}$ 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).

$$KOH = K^+ + OH^- \tag{4}$$

$$H^+ + OH^- = H_2O,\ K_w = [H^+]\ [OH^-] \tag{5}$$

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

$$U_I = I\ A_s T \tag{6}$$

$$N = 3U_I / (4\pi r_d^3) \tag{7}$$

$$A_d = N \times 4\pi r_d^2 \tag{8}$$

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_I = 6,000 m^3, N = 10^{13}, and A_d = 3.6×10^7 m^2 = $36\times A_s$. 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 CO_2 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 ρ_a and ρ_w are the densities of air and water respectively, and g is the acceleration due to gravity. A droplet having $r_d = 0.5$ mm falling from an altitude $h = 1$ km has a $V_g = 2.9$ m/sec ($\rho_a = 1.2$ kg/m^3 at 12°C). The travel time $t_h = 350$ seconds is estimated by (10).

$$V_g = (2r_d g\rho_w / \rho_a)^{½} \quad (9)$$

$$t_h = h / V_g \quad (10)$$

The time t_{aw} needed for a droplet to become saturated with CO_2 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 [23]–[26]. For $k_{aw} \approx 0.5\times10^{-4}$ m/sec and $r_d = 0.5$ mm, $t_{aw} = 6$ seconds, indicating that the much longer travel time $t_h \approx 350$ seconds is sufficient for nearly complete removal of under-cloud CO_2 molecules.

$$t_{aw} = r_d / 3k_{aw} \quad (11)$$

2.1. Impact on Plants

a

b

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.*

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-enhanceme irrigation.

Fig. 2. *Second crop plants after 19 days.*

2.2. Global Application

Table 1. *Estimated Outcomes of Global Application.*

pH	5.6	10	10.5	11
M_C^1 (kg/m^2)	1.6×10^{-4}	0.849	4.05	26.5
$M^A{}_C$ (kg)	8.2×10^{10}	4.3×10^{14}	2.1×10^{15}	1.4×10^{16}
$M^A{}_{CO2}$ (kg)	3×10^{11}	1.6×10^{15}	7.7×10^{15}	5×10^{16}
A_p (%)	-	2.4	0.5	0.08
Q_{KOH} (kg)	-	6.9×10^{10}	4.8×10^{10}	2.3×10^{10}

pH = pH of induced rainfall, M_C^1 = mass of atmospheric carbon removed by 1 meter of rainfall per m^2 of the Earth's surface, $M^A{}_C$ = mass of global atmospheric carbon removed, $M^A{}_{C02}$ = mass of global CO_2 removed, A_p = percentage of the Earth's surface area needed to completely remove annual global CO_2 emissions (E_A), and Q_{KOH} = mass of KOH needed to remove E_A each year.

Table 1 provides statistics that estimate outcomes of applying the method globally. The Earth's surface area $A_E = 5.1\times10^8$ km^2, the average global annual rainfall $h_A = 1$ m [28], and the annual global CO_2 emissions $E_A \approx 3.8\times10^{13}$ kg [29]. Using (2), row 2 gives the masses of atmospheric carbon M_C^1 removed by 1 meter of annual rainfall per m^2 of the Earth's surface at the different pH levels shown in row 1. Row 3 gives the global masses of carbon removed $M^A{}_C$ per (12). Row 4 gives the global masses of CO_2 removed $M^A{}_{C02}$ per (13), 0.27 being the carbon ratio of CO_2. 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 19×10^{10} kg of nitrogen, phosphorous, and potassium (N/P/K) fertilizers used globally in 2014 [30].

$$M^{A}_{C} = M_{C}^{1}\ A_{E} \quad (12)$$

$$M^{A}_{C02} = M^{A}_{C} / 0.27 \quad (13)$$

$$A_{p} = 100 \times E_{A}/M^{A}_{C02} \quad (14)$$

$$Q_{KOH} = n_{KOH}\ h_{A}\ A_{E}\ A_{p} \quad (15)$$

3. Atmospheric CH_4 Removal

A concept is also proposed that would use lasers to enhance the conversion of atmospheric CH_4 into 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 λ = 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 λ = 288 nm due to the Planck–Einstein relation $\lambda E = hc$ = 1240 eV–nm, where h is the Planck constant and c is the speed of light [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 λ = 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 gigatonnes 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.

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