Correcting Misinformation on Atmospheric Carbon Dioxide; Pinatubo Study Phase 1 Report

by
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(Contributing editor: Tomer Tamarkin)
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Correcting Misinformation on Atmospheric Carbon Dioxide; Pinatubo Study Phase 1 Report

By: Bud Bromley, May 4, 2022

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Abstract

Digital signal processing technology was used to analyze daily carbon dioxide data from NOAA's Global Monitoring Laboratory. The period surrounding the 1991 eruption of the Pinatubo volcano was rigorously analyzed for slope and acceleration of net global average atmospheric CO_2 concentration and found to be consistent with the theory that Henry's Law, the Law of Mass Action, and Le Chatelier's principle control net global average atmospheric CO_2 concentration rather than human-produced CO_2 emissions. Background and theory are explained. A method of using common physics and math for a novel purpose is presented to compare natural CO_2 emission or absorption with human-produced CO_2 emission. The claim that human-produced CO_2 emission is causing increasing global CO_2 concentration and climate change is shown to be without scientific merit.

Key words: carbon, CO_2, climate, warming, Impulse, Pinatubo, Henry's Law, Mauna Loa

Introduction

William Henry tested and documented his series of experiments on different gas and liquid combinations under various conditions which were published in 1803. (Henry, W., 1803)   Today, the coefficients he developed are now available in tables in reference books and software which are used routinely by chemists and chemical engineers. This stable science is known today as Henry's Law and is a foundational science for several large industries. Though it is not common knowledge among the public and only rarely found in climatology literature, Henry's Law is the foundational science for the multi-billion dollar per year scientific instrumentation industry of gas chromatography, which is one of the methods used to measure atmospheric gases and most chemicals. It is also a foundational science underlying chemical engineering in gas, oil and coal refining and the beer and carbonated beverage industries.   Further, it is one of the major variables

in the absorption and emission exchanges of oxygen and carbon dioxide and other gases in the lungs and gills of all animals.

Photo of Pinatubo eruption by Dave Harlowe, USGS (public domain)

Global surface temperatures declined for a few years following the massive Pinatubo volcanic eruption. "On June 12, the volcano's first spectacular eruption sent an ash column 19 km (12 mi) into the atmosphere. Additional explosions occurred overnight and the morning of June 13. Seismic activity during this period became intense. When even more highly gas-charged magma reached Pinatubo's surface on June 15, the volcano exploded, sending an ash cloud 40 km (25 mi) into the atmosphere." ..." The powerful eruption of such an enormous volume of lava and ash injected significant quantities of aerosols and dust into the stratosphere… This very large stratospheric injection resulted in a volcanic winter, a reduction in the normal amount of sunlight reaching the Earth's surface by roughly 10% (see figure). This led to a decrease in Northern Hemisphere average temperatures of 0.5–0.6 °C (0.9–1.1 °F) and a global decrease of about 0.4 °C (0.7 °F).[21][22] At the same time, the temperature in the stratosphere rose to several degrees higher than normal, due to the absorption of radiation by the aerosol. The stratospheric cloud from the eruption persisted in the atmosphere for three years." (Wikipedia) The event and its causes and effects are the subjects of many studies, for example, Stenchikov et al, 2021.

An excerpt from Science News at the time (Hoppe, 1992):

Ellsworth G. Dutton, a meteorologist [sic] with NOAA's Climate Monitoring and Diagnostics Laboratory in Boulder, Colo., traced the effects of Pinatubo's cloud with ground-based instruments that directly measure the strength of sunlight. Dutton says his results show a 20 to 30 percent decline in the amount of solar radiation that reaches the ground without being scattered or reflected, and a 2 to 4 percent decline in total solar radiation.

Temperatures have already started to drop, both at ground level and in the lower atmosphere, says James K. Angell of NOAA in Silver Spring, Md. Angell told Science News his analyses of weather balloon data show that the first half of 1992 was 0.4 [degrees] C cooler, overall, than the first half of 1991. He notes that the volcano's effect may be greater than suggested by these observed temperature shifts, since this year's El Nino warming would normally raise average temperatures by 0.2 [degrees] C (SN: 1/18/92, p.37).

Weather satellites confirm cooling in the lower atmosphere, recording a global drop of more than 0.5 [degrees[C since last June, with this June being 0.2 [degrees] C cooler than average, according to John Christy of the University of Alabama at Huntsville and Roy Spencer of NASA's Earth Science Lab at the Marshall Space Flight Center in Hunstsville [sic]. Christy says their data indicate that the greatest cooling, 1.0 [degrees] C, occurred in the northern middle latitudes -- an area that includes the continental United States -- while temperatures in the southern hemisphere have dropped by only 0.3 [degrees] C.

Mauna Loa Observatory Atmospheric Transmission
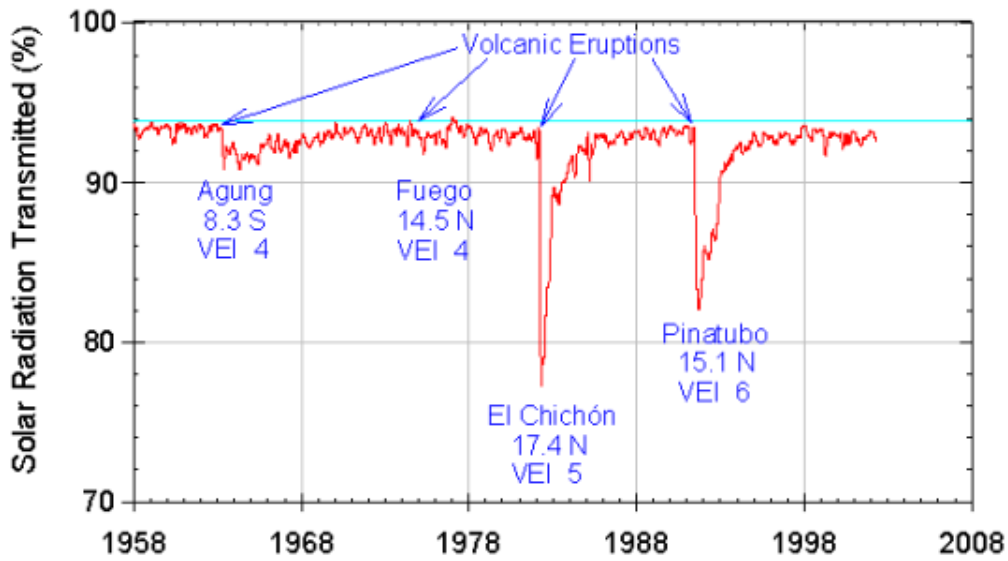
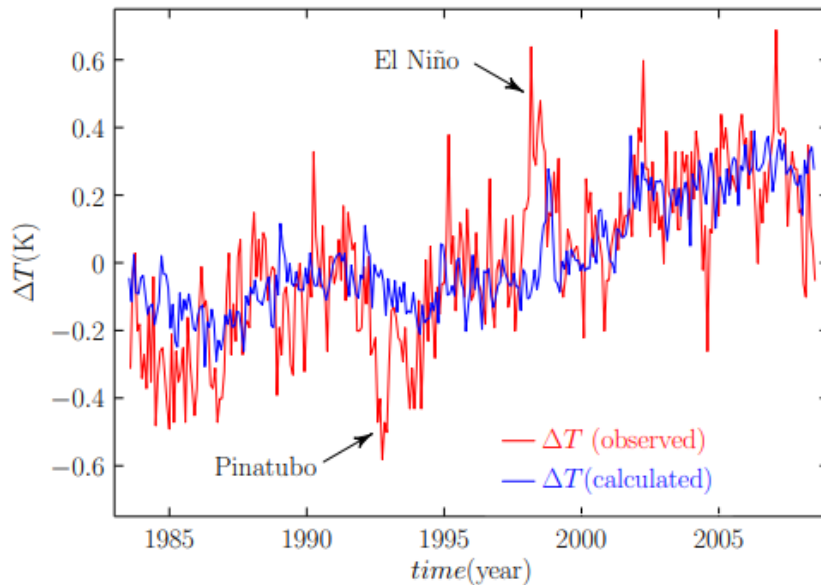https://en.wikipedia.org/wiki/File:Mauna_Loa_atmospheric_transmission.png

Figure 3. [2] Global natural temperature anomaly (blue) superimposed on the observed (red) temperature anomaly. The blue anomaly is derived using the observed low cloud cover data. Kauppinen & Malmi, 2019.

Pinatubo was the largest or second largest volcanic explosion observed on Earth in the last 100 years. The explosion resulted in a belt of clouds, dust, various gases, and particles encircling and spreading in the atmosphere around Earth's tropical zone, which is about 20 degrees latitude both north and south of the equator. In this large zone, ocean surface temperature averages 25 C (77 F) year-round, in contrast to average ocean temperature of 17 C.

On average, ocean surface above 25 C is a net emitter of CO_2 gas, day and night, year-round. That is, more CO_2 is being released from ocean surface than is absorbed from among the CO_2 molecules which are continuously colliding with ocean surface. The belt of clouds, gases, and particles, etc., encircling the tropics is assumed by all known reports to have reduced short wave solar insolation reaching the surface; incoming sun light around 400 to 700 nanometer wavelength was shaded, blocked, absorbed, reflected, scattered, or otherwise obfuscated. Consequently, tropical ocean surface cooled. Higher latitude ocean surface cooled also.

Short wave infrared radiation from the sun is not absorbed by CO_2. It is absorbed by ocean, soil, and biosphere.
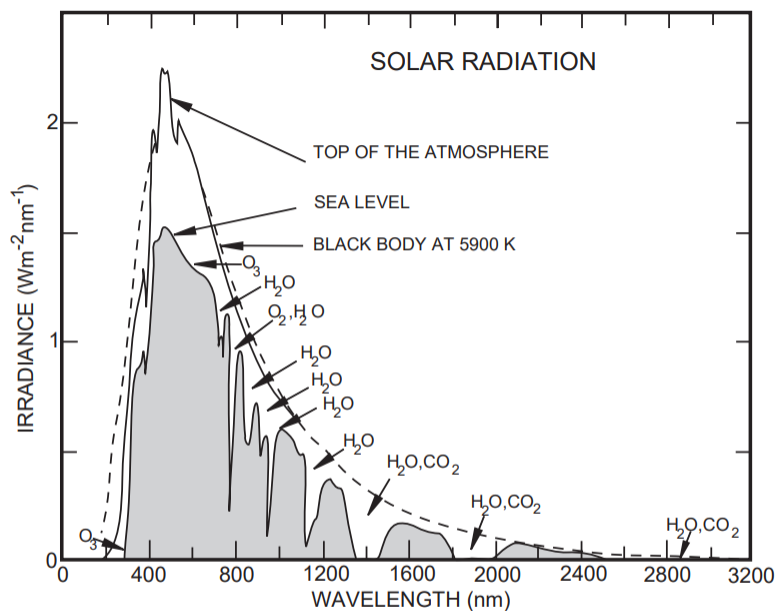
Figure 8.2 Spectrum of SW radiation at the top of the atmosphere (solid) and at the Earth's surface (stippled), compared against the emission spectrum of a blackbody at 6000 K (dashed). Individual absorbing species indicated. Adapted from Coulson (1975).

Figure 8.2 from Salby, 2012, page 206. https://climatecite.com/physics-of-the-atmosphere-and-climate-pt-1/ Our theory is that Henry's Law controls net global average atmospheric CO_2 concentration and human CO_2 emission from all sources only temporarily perturbs net global average atmospheric CO_2 concentration and its rate of change. There are other science groups and individuals who support this theory. But

this theory is rarely studied or found in climate literature and rarely funded in government environmental work. Generally, papers concerning Henry's Law and climate are found only in less well-known journals.

Henry's Law is a reproducible, well-documented law of chemistry and physics which defines the ratio of any gas in contact with any liquid. Each gas and liquid combination has a specific Henry's Law coefficient, denoted k_H. The coefficient is not a constant; k_H varies with temperature at the gas – liquid interchange surface. The coefficient varies with (a) temperature of the surface (b) salinity of the liquid including certain minerals which are dissolved in the liquid not only sodium chloride, (c) alkalinity or pH or the liquid, (d) partial pressure of the gas in the space above the liquid and (e) partial pressure of the gas in the liquid. Concentration of CO_2 gas in seawater is inversely proportional to sea surface temperature. High diligence is needed in sampling procedures to control (a), (b), (c), (d) and (e).

Henry's Law has limitations on its application.

1. Henry's Law only applies when the concentration of the unreacted gas in the liquid is minor and when the concentration of gas being measured in the gas volume above the liquid (i.e., its partial pressure) is minor relative to the other gases in the volume. An oversaturation condition is observed in chromatography by an abnormal, non-Gaussian peak shape. Henry's Law is applicable to CO_2 gas since it is a trace gas in both the atmosphere and in the ocean even at 10 times current concentrations.

2. Henry's Law only applies to the gas in the liquid which has <u>not</u> reacted with the liquid; that is, Henry's Law only applies to the reversible phase-state equilibrium reaction [CO_2 (gas)] <-> aqueous [CO_2 (gas)]. Henry's Law does not apply to ionized CO_2 gas, that is, hydrated CO_2, nor to any of the ions or unionized carbonic acid that are products of aqueous CO_2 gas reacting with water known collectively as dissolved inorganic carbon (DIC).

The total concentration of dissolved inorganic carbon is: (Cohen and Happer, 2015)

$$[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

Most of the CO_2 in seawater is in DIC form, which, according to most sources, is on the order of estimated 38,000 gigatonnes (Gt) of DIC; that is, dissolved, reacted CO_2 in deep seawater. Meanwhile 1000 Gt is in surface seawater and 850 Gt in air. (One Gt is 1000 billion kilograms, that is, 1 followed by 12 zeros.) Figure 2 in Cohen and Happer (2015) illustrate the relative molar stoichiometric concentrations of the DIC species in ocean as atmospheric CO_2 concentration changes. Barely visible, the fine dotted green line slightly above the horizontal axis, the concentration of the CO_2 species of DIC in ocean and the concentration of the bicarbonate species in ocean is increasing as atmospheric CO_2 concentration. Simultaneously, the carbonate ion [CO_3^{2-}] of carbonic acid is decreasing, along with alleged problems of so-called "ocean acidification."
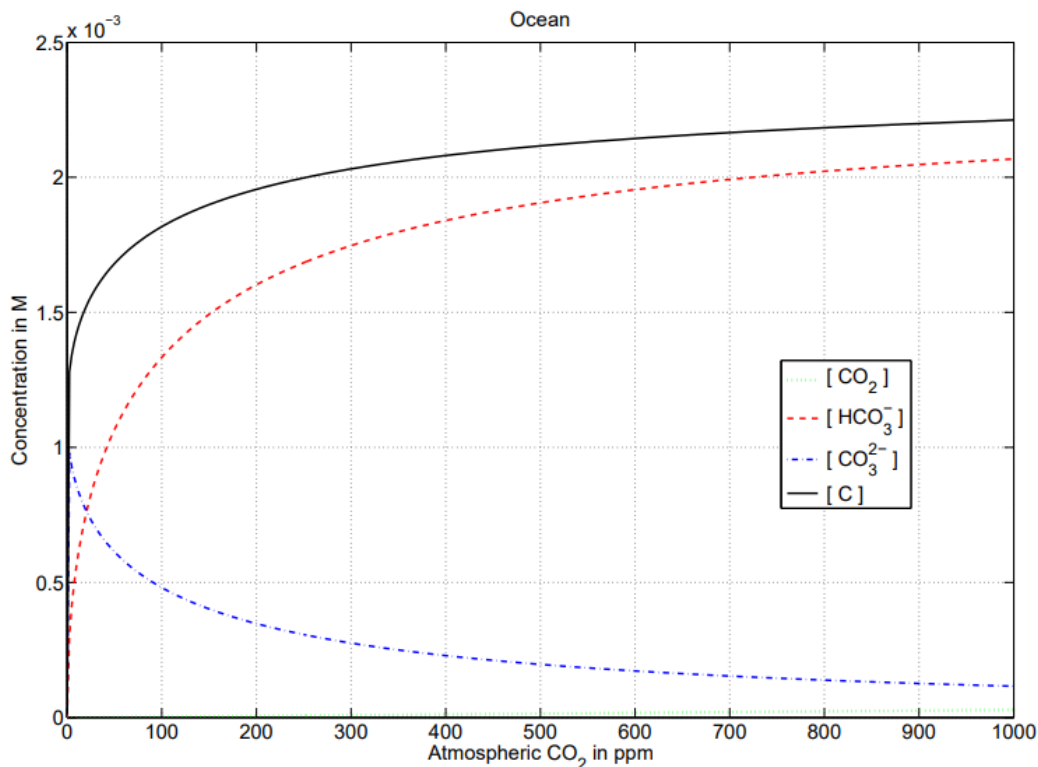
Figure 2: Inorganic carbon in ocean water: uncharged $[CO_2]$, bicarbonate $[HCO_3^-]$, carbonate $[CO_3^{2-}]$ and total $[C]$ of (18) versus concentration of CO_2 in the atmosphere. Calculated with (20), (17), (14) and (11), under the assumption of complete chemical equilibrium. The ocean alkalinity is $[A] = 2.3 \times 10^{-3}$ M and the temperature is $T = 25$ C.

As we demonstrate in this paper, CO_2 gas generated from DIC in ocean surface is rapidly absorbed into sea surface when the surface cools. Ocean surface demonstrates the capacity to rapidly absorb orders of magnitude more CO_2 than humans produce, and then recover to trend. It is imperative to recognize that these reactions of ionized CO_2 (DIC) are rapidly reversible reactions. We do not rely on estimates of CO_2's air and seawater concentrations to demonstrate this point.

Most CO_2 in seawater is in the ionized form HCO_3^- known as bicarbonate as shown in the Happer and Cohen figure 2 above. Minor changes in ocean surface temperature reverse the CO_2 hydration reaction and aqueous CO_2 gas is formed. Aqueous CO_2 (gas) <-> H^+ + HCO_3^-. Colder water pushes this reaction to the right. Warmer water pushes the reaction to the left. Once in its aqueous CO_2 gas form, then Henry's Law dynamic equilibrium applies: for a given seawater surface temperature, there is a fixed ratio of CO_2 gas concentration in air versus CO_2 gas concentration in seawater surface which is in contact with the air. Depending on changes in surface conditions, aqueous CO_2 gas could react with H_2O to become H_2CO_3 (carbonic acid), or it could react with H_2O to become HCO_3^- (bicarbonate) plus hydrogen ion (hydronium), or it could remain in

the water matrix as aqueous CO_2 gas, or it could be emitted to the atmosphere as CO_2 gas.

Cohen and Happer (2015) explain that transition of only a single proton (a hydrogen ion), determines bicarbonate versus carbonic acid species. The carbon species are surrounded in the seawater matrix by hydrogen ions and hydroxide ions. CO_2 gas molecules and DIC ions are not required to move in the seawater matrix. Both bicarbonate ion and carbonic acid are separate reaction products of the aqueous CO_2 gas hydration reaction with H_2O, as well as reversible with each other, as shown in the next graphic. In seawater surface these reactions can reverse in seconds due to changing surface temperature, or agitation by waves, buoys and moving ships, or a sampling procedure, or by an upwelling water current dense with DIC (e.g., an El Nino current). As upwelling seawater dense with DIC comes to the surface, it warms, and aqueous CO_2 gas in the surface becomes oversaturated, out of balance with the Henry's Law ratio for the temperature at the surface, resulting in CO_2 gas being emitted to the air and a rebalancing the Henry's Law dynamic equilibrium for that temperature.

Daniel Mazza explains on pages 16 and 17, Reversible Reactions of Higher Order. (Mazza, Daniele, 2020)

At any given temperature, the value of Keq remains constant no matter whether you start with A and B, or C and D, and regardless of the proportions in which they are mixed. Keq varies with temperature because k1, and k2 vary with temperature, but not by exactly the same amount.
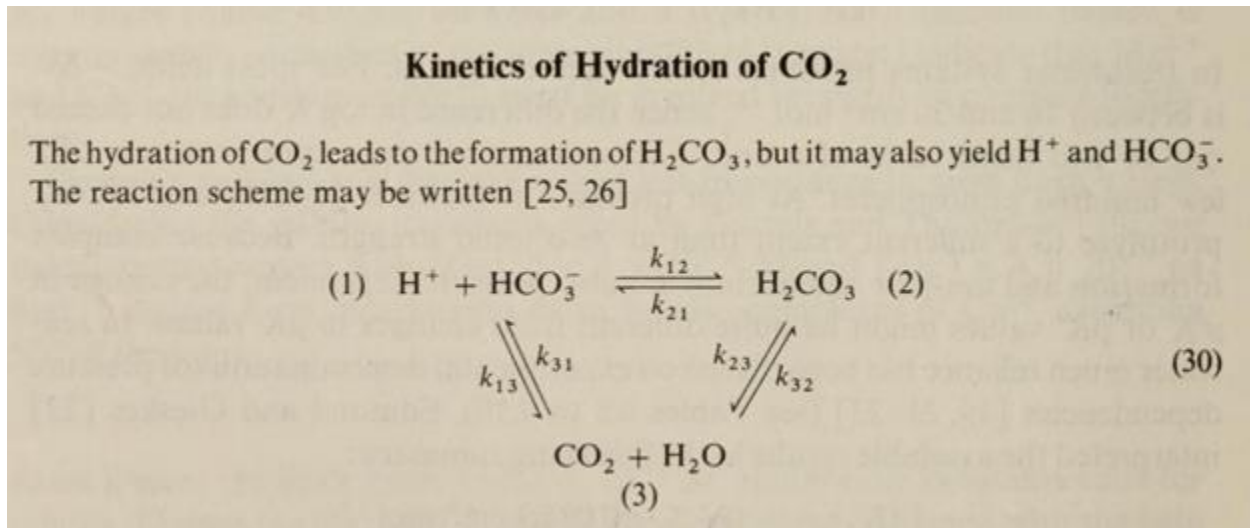
… the general formulation of the law of mass action (Guldberg-Waage, 1864) that states: in a chemical system at equilibrium and constant temperature, the ratio between the product of the concentrations of chemicals formed (each elevated to its stoichiometric coefficient) and that of the reagents is a constant value.

The reactants and products of the carbonate chemistry in seawater are difficult to sample and quantify with precision because the reactions are so rapid and only very minor changes in surface conditions are required to change the dynamic equilibrium. Taking a sample affects the reactions. Special methods and systems must be used for these analyses at the thin layer at ocean surface. Journal and online articles report years or hundreds of years are required to move large amounts of CO_2, allegedly because migration of CO_2 vertically or horizontally in the water matrix is slow. There are such slow changes, with El Ninos and La Ninas being prime examples. However, simultaneously, second by second, bulk CO_2 gas is continuously in flux into and out of millions of square kilometers of ocean surface, driven by SST change. CO_2 is converting in seconds from one ionic species to another and aqueous CO_2 gas is either released to air or hydrated to carbonic acid or bicarbonate. Slower or continuous changes such as human emissions are anomalous perturbations to the trend of the dynamic equilibrium for the local surface temperature. Adding or subtracting CO_2 from

any source or for any residence time or emission rate results in reset of the relative concentrations to the Henry's ratio for a given temperature.

Demonstrating an example of this bulk sea surface reaction and its enormous quantity and rate in the natural environment as observed in the Mauna Loa data is a primary objective of this study.

The cyclical hydration reaction of aqueous CO_2 gas with H_2O is described in the following graphic:

Kinetics of Hydration of CO_2

The hydration of CO_2 leads to the formation of H_2CO_3, but it may also yield H^+ and HCO_3^-. The reaction scheme may be written [25, 26]

$$(1) \quad H^+ + HCO_3^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} H_2CO_3 \quad (2)$$

$$k_{13} \Big\Vert k_{31} \qquad k_{23} \Big/ k_{32} \qquad\qquad (30)$$

$$CO_2 + H_2O$$
$$(3)$$

Stumm and Morgan. 1996. p192.

Changes in kinetics force the reactions forward or backward, changes in kinetics are changes in motion of molecules. Those kinetic changes result from heating, cooling or agitation of the sea surface by waves, ships underway and buoy motion, currents, storms, gas and water sampling procedures, etc. For example, warm tropical sea surface that is normally continuously emitting CO_2 gas can be depleted of CO_2 gas by wind, storms, hurricanes, typhoons, etc. such that the undersaturated sea surface is absorbing CO_2 from air instead of emitting. Significant sampling problems in actual sea water include CO_2 gas added or subtracted by the biology - living and dead - in the sea, currents of CO_2 dense seawater upwelling from deep ocean to the surface, and sampling sea surface when the necessary representative sample is only the top centimeter or less thin layer.

Simultaneously with the portion of the carbonate chemistry described above, calcium ions (Ca^{2+}), which are readily available in seawater in great excess to carbon, react with bicarbonate ions (HCO_3^-) producing calcium carbonate ($CaCO_3$). This reaction is not included in the Henry's Law equilibrium, and not included in the estimated 38,000 Gt of DIC, and not included in the estimated 1000 Gt of DIC in sea surface, although it is accumulated inversely proportional to temperature into the largest CO_2 sink by orders of magnitude. As Richard E. Zeebe and Dieter A. Wolf-Gladrow remind us, aqueous CO_2 gas as well as solid precipitant calcium carbonate are produced, "at surface water

conditions… counterintuitively.. during $CaCO_3$ precipitation CO_2 is liberated…by only ~0.03 µmol per µmol $CaCO_3$ precipitated." (Zeebe and Wolf-Gladrow) The famous white cliffs of Dover and Sussex, England, limestone caves around the world, the famous marble quarries of Italy are examples of enormous $CaCO_3$ deposits. Ultimately, when the Henry's ratio for CO_2 is out of balance, the DIC and Ca^{2+} reactions move to the right, towards products and excess CO_2 in converted to rock. The calcium reaction is another source of CO_2 in sea water while at the same time it removes bicarbonate.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

CO_2 gas dissolved in ocean surface is estimated to be 30 to 40 times more concentrated than in air, results from multiple reactions, yet still a minor component of sea surface water. But this estimate is many meters of ocean surface. In this report, we are concerned with the CO2 in the thin layer at the sea-air interface. This report and project do not rely on estimates of CO_2 concentration. Demonstrating measurements of CO2 absorption and emission and their rates in comparison to human emissions is the purpose of this project.

Additional background on Henry's Law and the carbonate chemistry: (Cohen and Happer, 2015). (Stallinga, P. and Khmelinskii, I. 2018) (Stallinga, P. 2018.) (Harde, 2019). (Zeebe and Wolf-Gladrow.) (Mazza, Daniele, 2020.)

Our theory assumes net global atmospheric CO_2 concentration will remain in a dynamic equilibrium that is constantly re-balancing CO_2 concentration in the atmosphere and ocean surface, a re-balancing based primarily on the change in relative surface area of Earth above or below 25 C. Flux is not the same as flow or flow rate. Flux is the mass of material flowing through a surface per time interval. Average ocean and or air temperature yield incorrect Henry's Law calculations. Many factors affect ocean surface temperature in addition to insolation.

In the following graphic, we see that CO_2 concentration changes rapidly <u>follow</u> changes in sea surface temperature. Changes up and down in the blue line (representing rate of change of sea surface temperature) are <u>followed by</u> changes in rate of CO_2 change per month at MLO. CO_2 concentration changes rapidly in response to changes in sea surface temperature. The response occurs in months.

Comparing Rates of Change (*Derivatives*): Global Tropical Sea Surface Temperature versus the Mauna Lau CO_2 Concentration

Method

The first phase of this study sought to determine if we could detect, in the "gold standard" data for global CO_2 concentration, an inflection point in the slope of the daily CO_2 concentration measurements before, during or after a single major climate event, the explosive volcanic eruption of Pinatubo on the island of Luzon in the Philippines in June 1991. Proprietary software for digital signal processing was used to analyze the publicly available daily CO_2 concentration data reported by the Earth Monitoring Laboratory of the U.S. government's National Ocean and Atmospheric Administration (NOAA). We defined an inflection point as a change in sign of the slope of CO_2 concentration after the eruption of Pinatubo. Hypothetically, if we are able to detect these inflection points with statistical confidence, then, to support our theory, we can use the same data set and software to produce evidence from many different climate, weather and environmental events and a global CO_2 calibration curve. We would be able to measure changes in CO_2 concentration which resulted from other volcanoes, El Ninos, La Ninas, storms, human CO_2 emissions, and other events which reportedly affect net global average atmospheric CO_2 concentration. In a sense, we are iterating William Henry's experiments for CO_2 gas and water at the global scale with various climate and environmental conditions but using only measured global data. Instead of unreliable computer climate models with too many estimates and theories, we would have data experiments using empirical data from the natural environment to correct the pervasive misunderstanding of CO_2 which is curated in popular culture and education.

The Mauna Loa data from the U.S. National Oceanic and Atmospheric Administration's (NOAA) Global Monitoring Laboratory was selected because it is widely recognized and reported to be the gold standard reference measurement for net global average atmospheric CO_2 gas concentration. The lab is located about 11,000 feet above sea level on northwest facing flank of Mauna Loa volcano on the Big Island of Hawaii. This data set was selected because it is accessible to the public and it has been diligently measured and curated since the 1970s. We selected their set of daily CO_2 measurements. The data are reported in micromoles of CO_2 gas per mole of air, which is equal to parts per million (ppm) CO_2 in air. We are grateful to NOAA's scientists, authors and administration for making these data available to the public. (See acknowledgments and Thoning et al 2021 reference for details and access to the data.)

The software toolset for this initial phase of the study was designed and operated by Shahar Ben-Menahem, PhD (physics, Stanford) and Abraham Ishihara, PhD (Aeronautics & Astronautics, Stanford) through their company Modoc Analytics LLC under contract with EnergyCite (https://energycite.com/) and its sister company ClimateCite (https://climatecite.com/).

Using these software tools, if these data were found to be responsive to a geographically remote event such as Pinatubo, then potentially it would not be necessary to examine many different CO_2 data sets nor to employ laboratories to validate our theory. Our theory assumes sea surface temperature (SST) directly affects

the ratio of atmospheric CO_2 gas concentration versus CO_2 gas concentration in sea surface, following Henry's Law, while human CO_2 has no effect on that ratio.

Care must be taken with Henry's Law since it can be expressed in many forms for different uses. Here we use its dimensionless form. The Henry's Law coefficient k_H = c(aqueous)/c(gas) where c is concentration in moles. For example, 400 micromoles of CO_2 per mole of air (which is 400 ppm CO_2 concentration in air) is in equilibrium with 333 micromoles of CO_2 per mole of seawater in sea surface at 298 K and a solution density of 997 kg/m^3. Dimensionless k_H = 0.8317. (Sander, 2015) Concentration of CO_2 in seawater is directly proportion to depth due to higher density (kg/m^3) and inversely proportional to temperature.

If this first phase data experiment worked, then the overall scientific complexity, effort, and expense of our project would be greatly reduced. The most difficult data experiment was done first: could we detect the Pinatubo perturbation in the MLO data.

We calculate a not-to-exceed amount of human-produced CO_2 based on measured data rather than assuming estimates of human-produced CO_2 based on estimates of fossil fuel production and cement production from spurious and dubious sources. This is not to doubt the diligent and careful curation of the data by Oakridge National Laboratories, for example. But the data they are handed comes from some sources which have been dubious over the years, for example Soviet Union, Nigeria, Iran, Venezuela, OPEC, to mention a few major oil producers.

This first phase of our project analyzed daily CO_2 data from Mauna Loa (MLO) to determine if the changes in CO_2 due to the Pinatubo eruption were present in the data. Is the data set responsive to remote events? Could the software and skills of our scientists detect a reduction in the CO_2 concentration and an inflection point in rate of change of concentration due to cooling of tropical ocean surface by the Pinatubo cloud belt. Velocity and acceleration of net global average CO_2 concentration were calculated based on measurements.

The raw daily MLO data (as raw as available publicly) from the 1970s through 2020 was used as input for our sequence of algorithms. This "raw" time-series data set was only changed by us to fill in days with missing data.

Block Diagram of Algorithms Applied To Mauna Loa CO2 Data
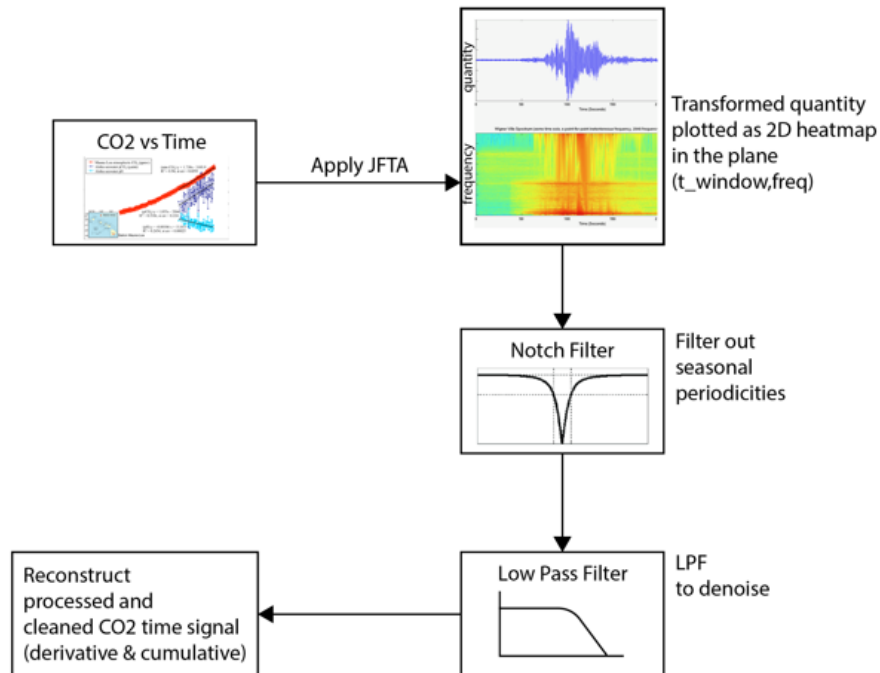
Data for days for which no real CO_2 data were available from MLO, marked as 999 in the MLO data file, but for which data were available for days both preceding and following the block of missing-data day(s), were interpolated accordingly.

Data for days (at the beginning of the recording period — early 1970s) for which no real data were available and no earlier data with valid data were available — were replaced by constant nominal values in the low 300's. This block of data is limited to the early 1970s and does not affect our Pinatubo results.

The following mathematical procedures (as summarized by boxes in the block diagram) are then applied to this "raw CO_2 level data" time series wherein time is given in fractional Gregorian years and CO_2 levels are given in ppm.

A JTFA ("Joint Time Frequency Analysis") is performed. Those skilled in the art of time-series digital signal processing (DSP) will recognize that this term refers to a class of methods, wherein a quantity-vs-time series is analyzed for its frequency content (such as PSD = Power Spectrum Density) as a function of time. While there are many JTFA techniques, the simplest one is performing a Fast Fourier Transform analysis (FFT) in a moving ("swept") time window and computing the complex FFT coefficients as a function of both window start-time and in-window frequency index. This type of JTFA transformation, however, is not easily invertible.

One of the simplest sub-classes of JTFA methods which is easily invertible, is the Gabor Transform. The Ben-Menahem- Ishihara proprietary analysis method used in this investigation was based on combining the Gabor Transform and FFT.

In the quantity-vs- time-frequency analyzes raw data result of our JTFA, we then remove the seasonal (1-year period) frequency-band peak via a notch filter, and also suppress the high-frequency band ("low-pass filtering"). Those skilled in the art of DSP or analog filtering in EE and other branches of physics-based engineering will readily recognize these terms and techniques.

After the notch- and low-pass filtering of the JTFA-produced data — represented by the relevant boxes in the Block Diagram — the filtered JTFA transform is then inverted. This computation yields the output (lower-left) box of the Block Diagram — the processed CO_2 vs. time signal (and its time derivative).

Then with these data we introduce a proven and well-known math and physics calculation to compare natural CO_2 absorption into the environment with human emissions. The calculation is used thousands of times each day to make decisions which mean life or death to a few million people each day.

RESULTS:

Raw and Fully Processed CO2 Concentration

——— raw data

——— processed version

Mauna Loa data acquisition time
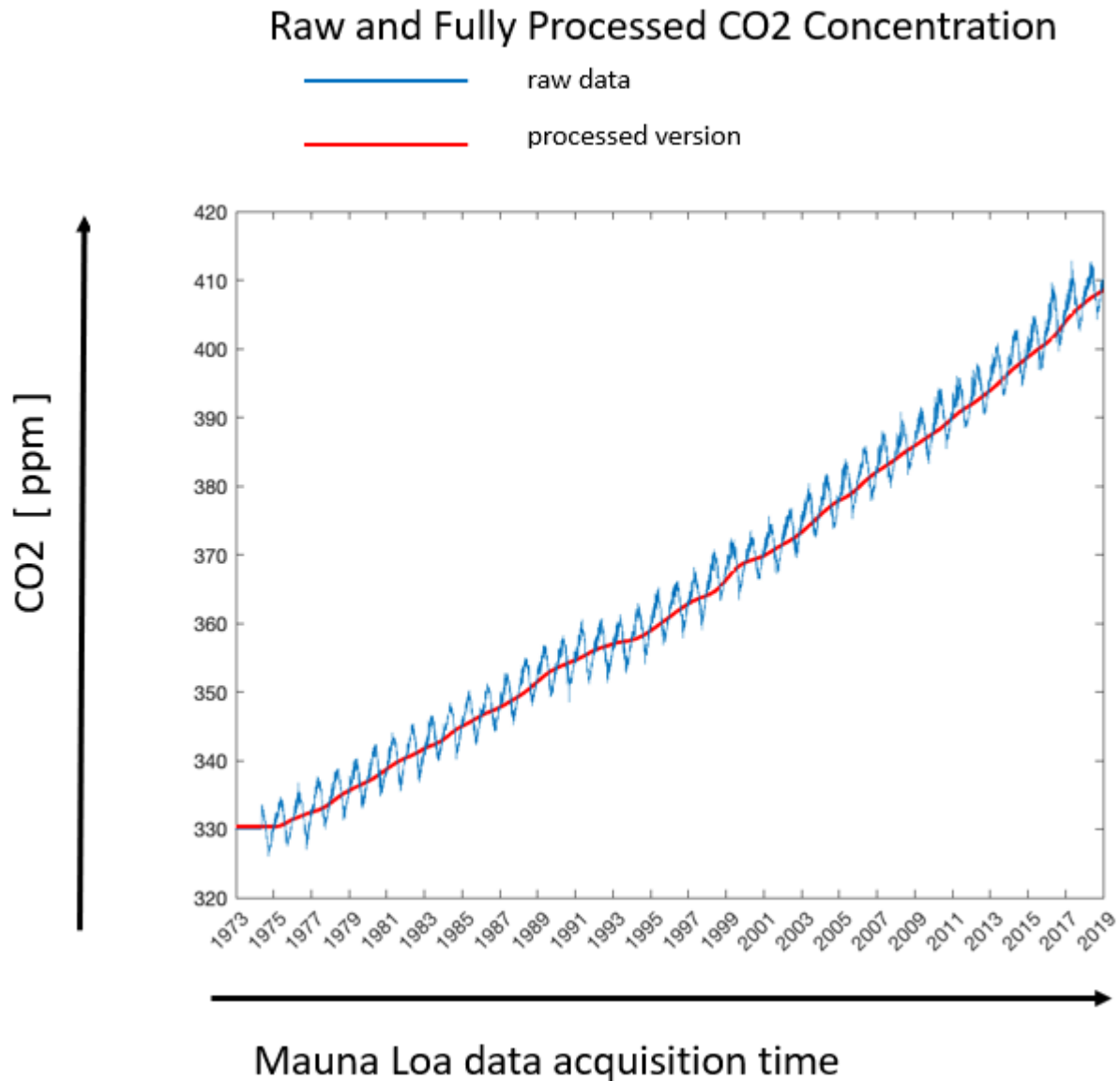
The graph above is plotted over the entire Mauna Loa recording epoch (circa 5 decades) with both the "raw" (as defined above) and processed (as defined above) CO_2 levels, vs. time. The graph appears very similar to the graphs typically produced by NOAA which appear frequently in media, education, politics and online.

Raw and Fully Processed CO2 Mauna Loa

zoomed to Pinatubo decade, 1990-2000]

——————	raw data
——————	Final (post-LPF) processed version

ML data acquisition time
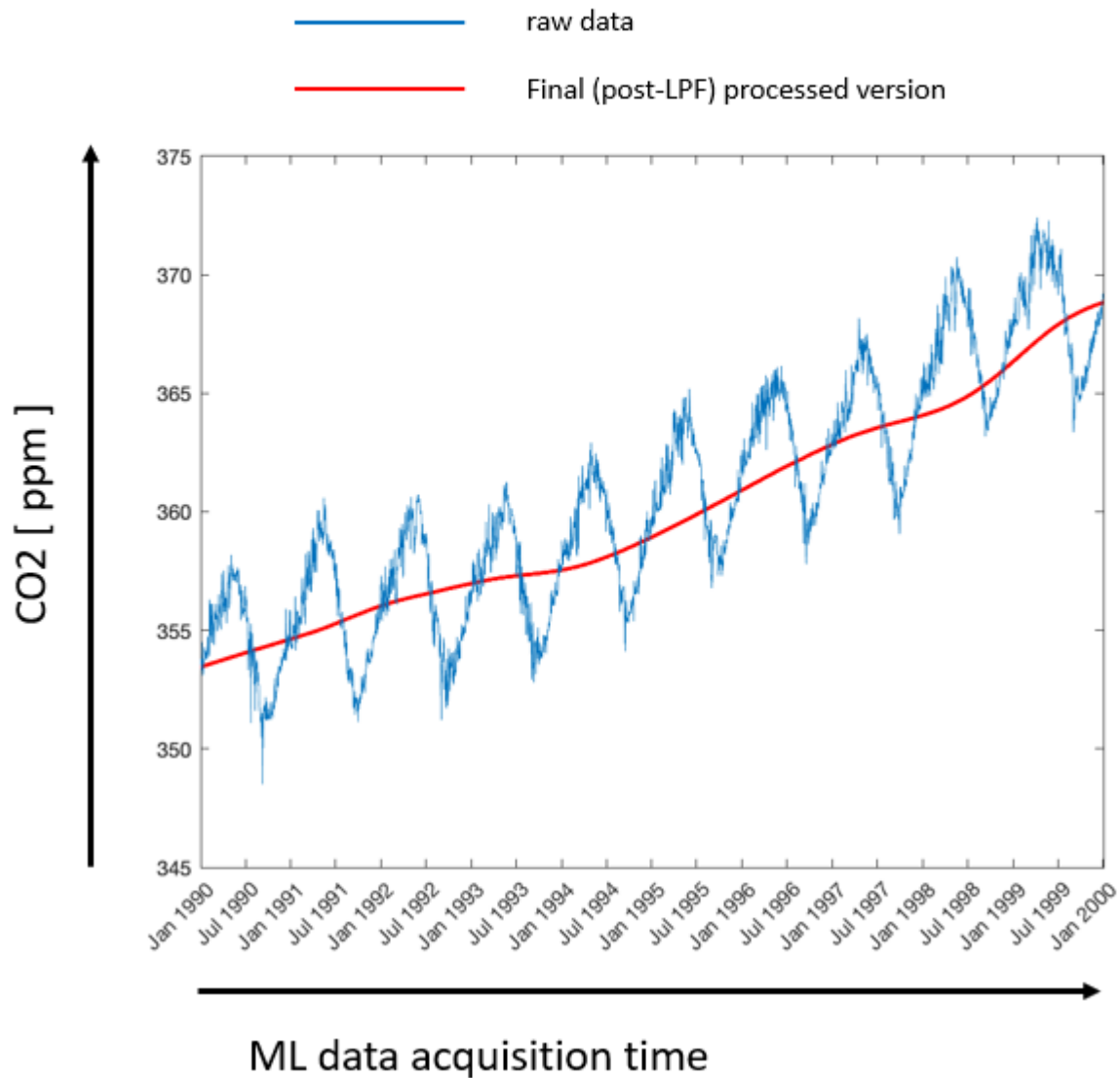
The graph above is processed as in the previous graph and described in the method section above but simply zoomed in to cover only the Pinatubo decade: 1990-2000. The slope of the red line is visibly bending or flattening in July of 1991 into 1994, and then in 1995 the slope turns upward again.

Mauna Loa, Hawaii, United States (MLO)
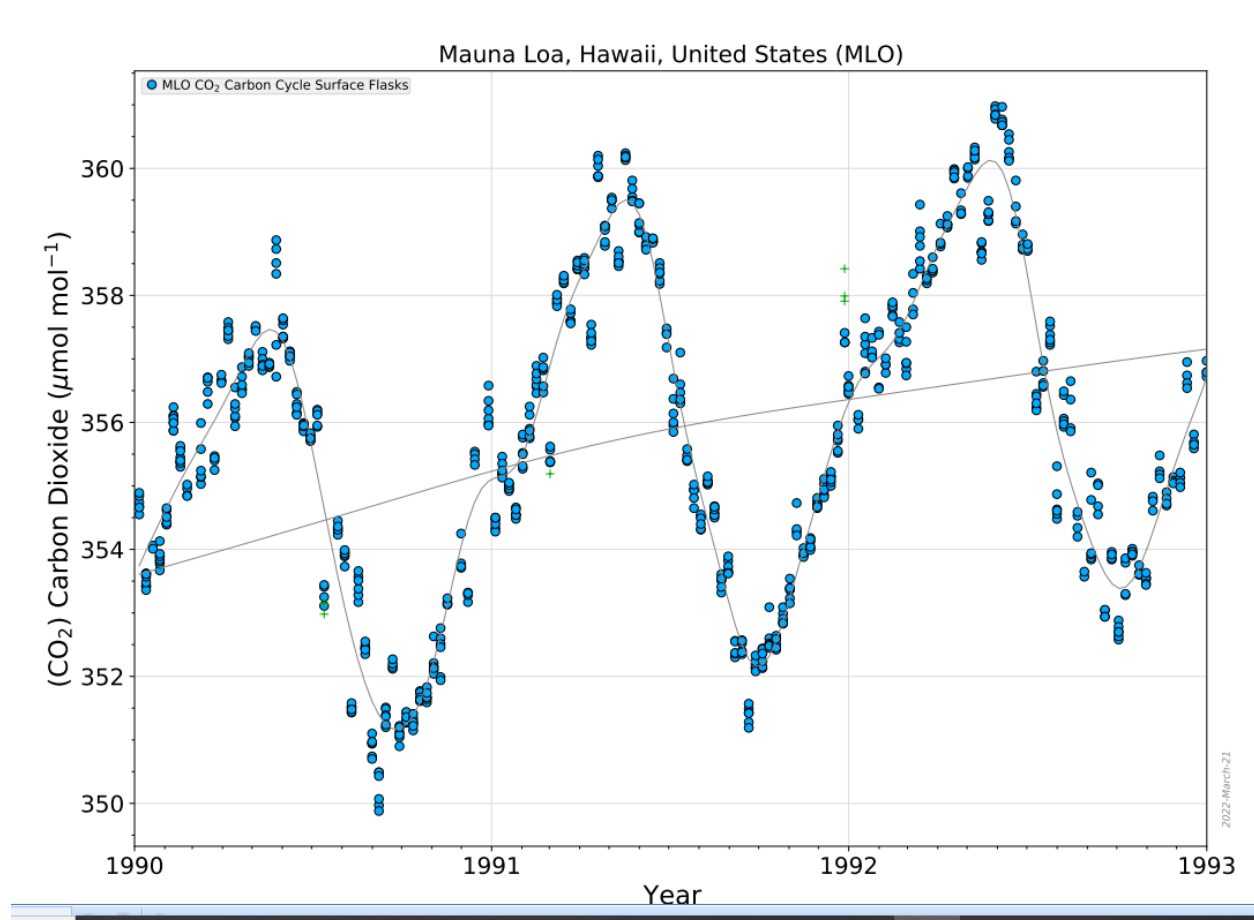
The data in the graph above is again processed as the previous two graphs but here zoomed in to the year of Pinatubo plus the year before and after Pinatubo. The slope (grey line) is slightly bending or flattening after mid-year 1991 when the Pinatubo eruption occurred. Velocity of CO_2 concentration is slowing after mid-year 1991.

No inflection point in the slope of CO_2 concentration was found in the period following the Pinatubo eruption. Slope declined slightly from prior trend but did not turn negative. Large changes in acceleration were detected. In this case, acceleration is the rate of change of slope, or the time derivative of CO_2 ppm per year.
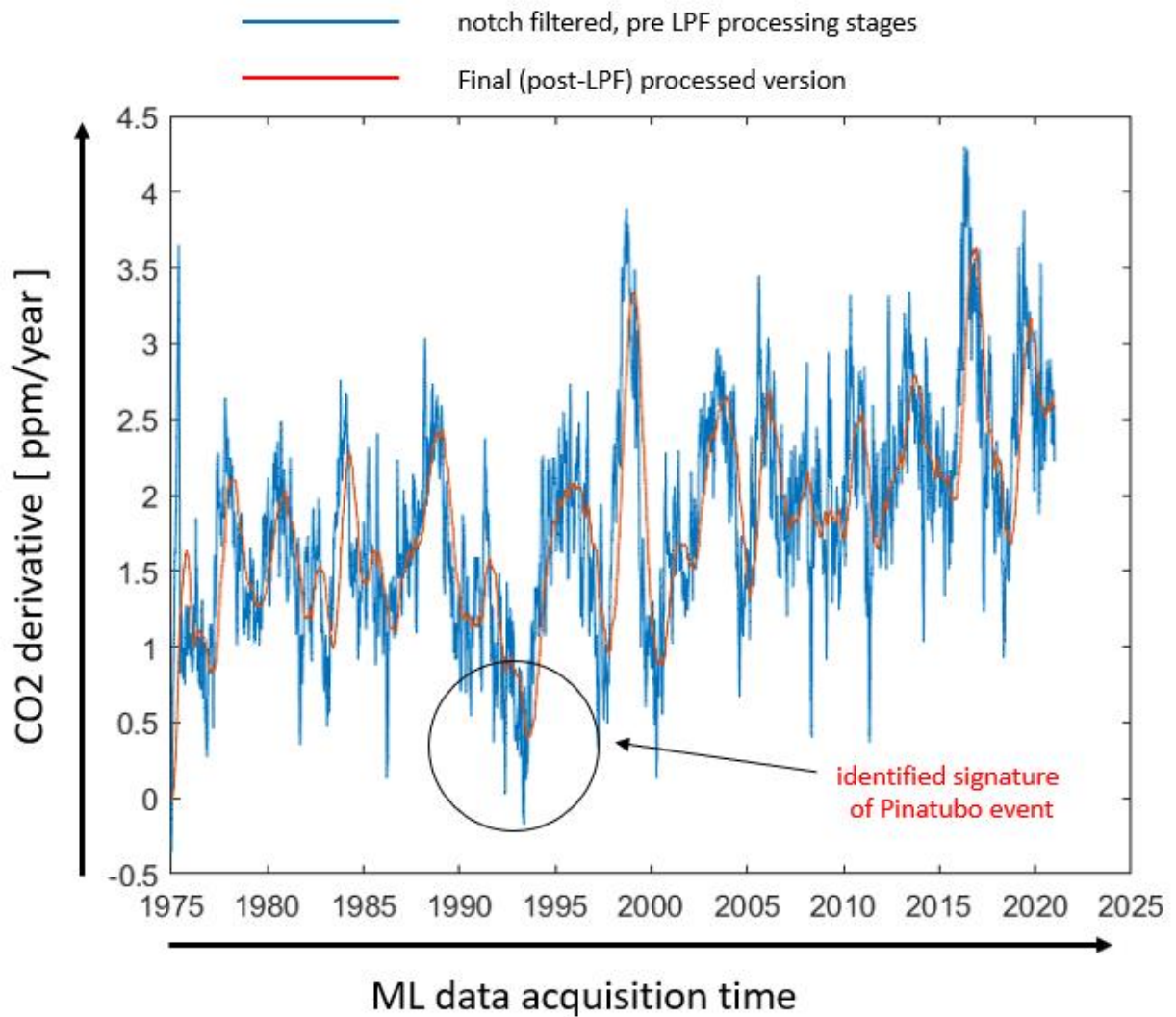
The graph above plots the time derivative of the processed CO_2 ppm/year.

Fully Processed CO2 Derivative curve with estimated pseudo-inflection date markers
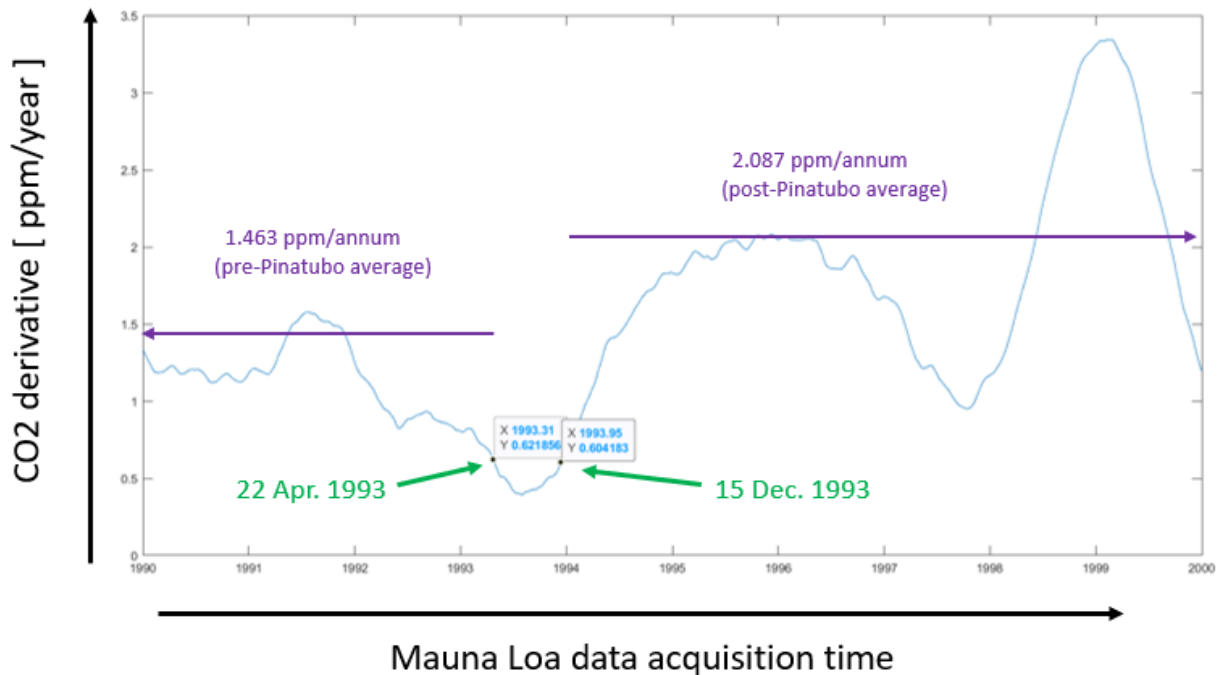
The above plot is the time derivative of the processed CO_2 ppm/year. The estimated "would-be inflection" times bracket the detected "Pinatubo Event" as indicated by arrows and DD/MM/YY date markers. The bracket dates are the points of fastest decline (deceleration) of slope and the fastest increase (acceleration) of slope. On this plot, the mean baseline pre- and post-Pinatubo CO_2 slope are indicated as horizontal lines; the full time period of the Mauna Loa data before or after the "would-be inflection" times were used to calculate the means, 1970's to 2020. The points of minimum and maximum acceleration are used to determine respectively the end point of the pre-Pinatubo mean and the start point of the post-Pinatubo mean. These two points allow assignment of the points where offset is calculated. This offset (or over-recovery) is expected based on Le Chatelier's Principle, basically stated, a perturbed trend will rapidly return to its equilibrium condition plus an offset amount or overcorrection.

DISCUSSION:

Now we have a reliable method based on gold standard measurements of a single climate variable, i.e. CO_2 concentration, which we can use to compare human-produced-CO_2 emissions with changes in net global average atmospheric CO_2 concentration.

The trace gas CO_2 is produced, modified, and absorbed through many and varied natural processes in the environment. Documenting and quantifying all of these with

accuracy and precision into a so-called carbon budget or energy balance is a quixotic task, and approximate at best, yet that is what the public through their governments are paying for in elaborate projects, for example, annually documenting Earth's carbon balance in over 100 pages by dozens of authors, e.g., Friedlingstein et al, 2021, not to mention UN IPCC climate conferences around the world and their thick documents and public relations campaigns. It is climate modelers dream project with no end. These reports use too many estimates in too many models, not measurements of human-produced CO_2.

Meanwhile, net global average atmospheric CO_2 concentration is routinely and diligently measured in micromoles per mole (ppm) of atmosphere at Mauna Loa and a few other locations. It has been observed by many scientists that net global average atmospheric CO_2 emissions vary with temperature. In contrast, the common misunderstanding is that temperature varies with CO_2 concentration and global temperature is increasing because human-produced CO_2 is increasing. While confirming that atmospheric CO_2 gas contributes to Earth's temperature, atmospheric physicist, professor Murry Salby, PhD has educated us that CO_2 varies coherently <u>following</u> temperature change.

"An increase of T_s [surface temperature] introduced by a radiative perturbation dF [dF is the direct radiative forcing] thus leads to an increased emission rate of CO_2, and, hence, cumulatively in CO_2." …"Increased temperature increases net emission of CO_2. Decreased temperature has the reverse effect. It is noteworthy that the positive sensitivity to temperature, dr_{CO2}/dT is not restricted to small perturbations. As is evident in Fig. 1.43, the dependence on temperature applies to r_{CO2} as large as 100%. Also noteworthy is that the correspondence applies to changes of temperature that are clearly of different origin. Following the eruption of Pinatubo, when SW [shortwave radiation emitted by the sun] heating decreased, r_{CO2} decreased by more than 50%. During the 1997-1998 El Nino, when SST increased, r_{CO2} increased by more than 100%. To maintain stability, there must exist a negative feedback in CO_2, one that is sufficiently strong to bridle the enhancement of CO_2 emission by positive feedback from temperature. That negative feedback involves sinks of CO_2 at Earth's surface."

$$\text{Net emission rate of } CO_2, \ r_{CO2} = d/dt \ rCO_2 \ (\text{ppmv/yr})$$
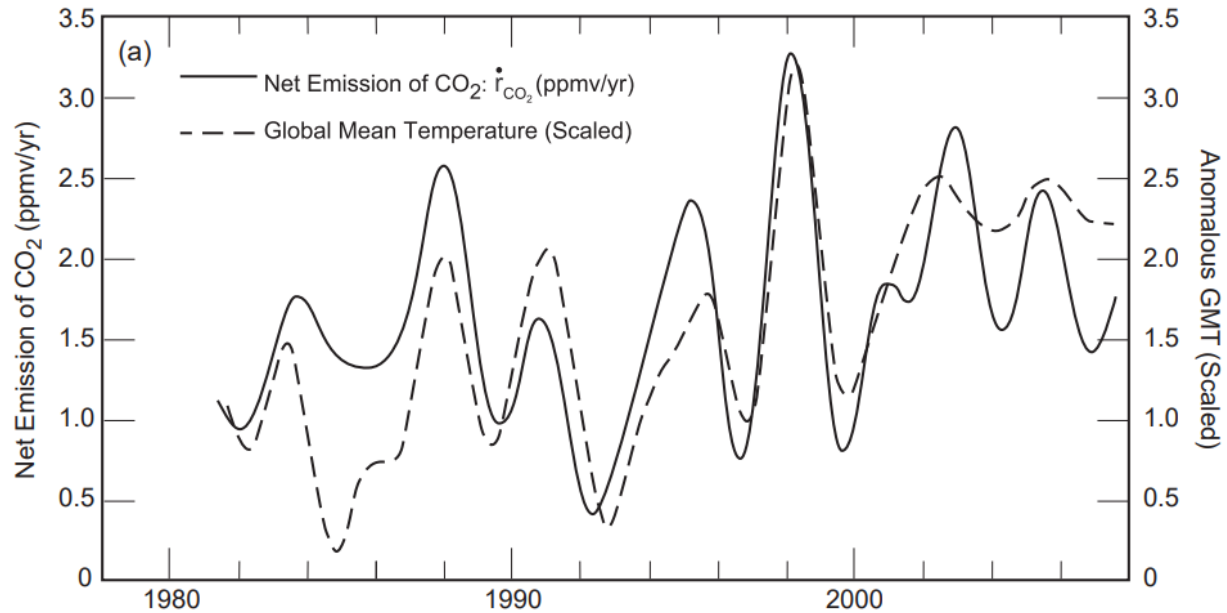
Fig. 1.43 (a) Net emission rate of CO_2, $r\dot{}CO_2 = d/dt\ r_{CO2}$ (ppmv/yr), derived from the Mauna Loa record (Fig. 1.15), lowpass filtered to changes that occur on time scales longer than 2 years (solid). Superimposed is the satellite record of anomalous Global Mean Temperature (Fig. 1.39), lowpass filtered likewise and scaled by 0.225 (dashed). Trend in GMT over 1979–2009 (not included) is ~0.125 K/decade.

(Salby, Physics of Atmosphere and Climate.p252. https://climatecite.com/physics-of-the-atmosphere-and-climate-pt-1/)

As seen in the NOAA graph at the end of the introduction above, the time derivative of CO_2 concentration <u>follows quickly</u> in months the time derivative of sea surface temperature (SST.)

The link between sea surface temperature and CO_2 concentration also has been noted by government scientists. For example: "At Mauna Loa the results implied that for the period 1970-1985, the season-to-season change would be about 0.2 ppm higher for a +1 degree C deviation in temperature of the eastern equatorial Pacific. A slightly lower figured 0.15 ppm/degree C was found at the south pole for the full record length and about 0.35 ppm/degree C at Barrow (Alaska) for the full record."…"For the cumulative dCO_2 we found a 1 degree C deviation would produce about 0.4 ppm change at Mauna Loa, 0.3 ppm change at the south pole, and 0.8 ppm at Barrow, Alaska." (Elliott and Angell, 1986)

And "…we found as have others, that warming of this region is usually followed by an above average increase in CO_2 concentration." …" At Mauna Loa this increase follows SST by about one season and at the south pole by two seasons." Unfortunately, these scientists usually do not pursue the linkage to its cause but instead, as these scientists did, the linkage or causes are dismissed. They concluded, "We take these results as

further confirmation that the apparent effect of SST on the CO_2 record comes less from changes in the equatorial eastern Pacific than from climate changes throughout the globe." (Ellliott, Angell & Thoning, 1990)

Anthropogenic CO_2 is widely believed to be responsible for the trend of increasing net global average atmospheric CO_2 concentration, and from that that belief is inferred that global temperature is increasing, some claim dangerously. Proponents of anthropogenic CO_2-caused global warming (AGW) believe that reducing human CO_2 emission by stopping use of fossil fuels will reduce net global average atmospheric CO_2 concentration and thereby reduce global temperature. The need to reduce global temperature is an unproven assumption as is the need to reduce human-produced CO_2. Those assumptions are based on computer models where only a few types of data are measurements. Comprehensive climate models have not been able to be validated against real world measured conditions. For example, "The instability of current models to estimate accurately oceanic uptake of CO_2 creates one of the key uncertainties in predictions of atmospheric CO_2 increases and climate responses over the next 100 to 200 years. 60 references." (Peng, et al. 1987)

Climate scientists who support alleged human-caused global warming, for example Ben Santer and Michael Mann with others, authored a peer reviewed paper in the journal Nature Geoscience which acknowledges that their climate models are wrong, although their admission is hidden in technical jargon: "In the early twenty-first century, satellite-derived tropospheric warming trends were generally smaller than trends estimated from a large multi-model ensemble," reads the first line of the abstract the paper. (Santer, et al., 2017) In other words, the actual temperature trends were less than their models. They continued, "Over most of the early twenty-first century, however, MODEL tropospheric warming is substantially larger than OBSERVED." (Santer et al., 2017) (Capital letters are added for emphasis.) In other words, their computer models substantially overestimate the global warming alleged to occur in the real world.

In contrast, the present study, based on measurements not models, simple in scope, analyzed a 2-year period where the rate of increase in slope of net global average atmospheric CO_2 concentration slowed and then stopped momentarily. The acceleration of CO_2 concentration was temporarily halted by the effects of the Pinatubo volcanic eruption. During those same months, CO_2 emissions from human sources continued, CO_2 emissions from natural sources continued (such as rotting soil and biosphere, etc.), the Pinatubo volcano itself added large amounts of CO_2 gas to the atmosphere, and an El Nino event in 1991-1992 added CO_2 to the atmosphere. According to the results of this study, the second derivative (i.e., the acceleration) of CO_2 concentration dropped precipitously in the 2 years following Pinatubo to its lowest point in the pre-Pinatubo Mauna Loa record, despite the CO_2 additions by humans, natural sources, a volcano and an El Nino. Nature rapidly absorbed the added CO_2 and then more rapidly accelerated again to reset its CO_2 concentration to trend.

The Law of Mass Action states that the rate of a chemical reaction is directly proportional to the concentrations of the reactants, applicable under any circumstances. In this case, the chemical reaction is the Henry's Law phase-state equilibrium reaction of CO_2 occurring in millions of square kilometers of tropical seawater surface cooled by the effects of the Pinatubo eruption.

To give the amounts of CO_2 perspective, Earth's "…forests provide a "carbon sink" that absorbs a net 7.6 billion metric tonnes of CO2 per year…" (World Resources Institute, 2021). Cooler surface in the two years following Pinatubo absorbed net 2778 billion metric tons of CO2, and then in the next two years emitted that amount plus an additional increment.

The rate of change of the slope of net global average atmospheric CO_2 concentration in this analysis dropped momentarily below zero. A large, global scale, decrease in CO_2 emission is consistent with an oceanic source of CO_2 and the rapid rate of change of slope is consistent with estimates of the size of absorption and emission fluxes of CO_2 gas. By elimination, there is no other known, logical or physically possible sink for such a large amount of CO_2 to be absorbed and emitted so rapidly other than ocean surface. The Henry's global CO_2 equilibrium ratio was abruptly perturbed by cooling SST. CO_2 emissions decreased precipitously after millions of square miles of tropical ocean surface cooled. For a period of about 2 years, the rate of CO_2 absorptions into the environment greatly exceeded the rate of CO_2 emissions from all sources. The slope CO_2 concentration had been on average 1.4 ppm per year since mid-1970s. For a period of about 2 years, that slope decelerated and briefly reached below zero even though human emissions were continuing, the Pinatubo eruption had added large amounts of CO_2 to the atmosphere, Earth's biosphere was continuing to emit CO_2 as usual, and a El Nino event was adding CO_2 to the air.

Annual mean global growth rate of CO_2
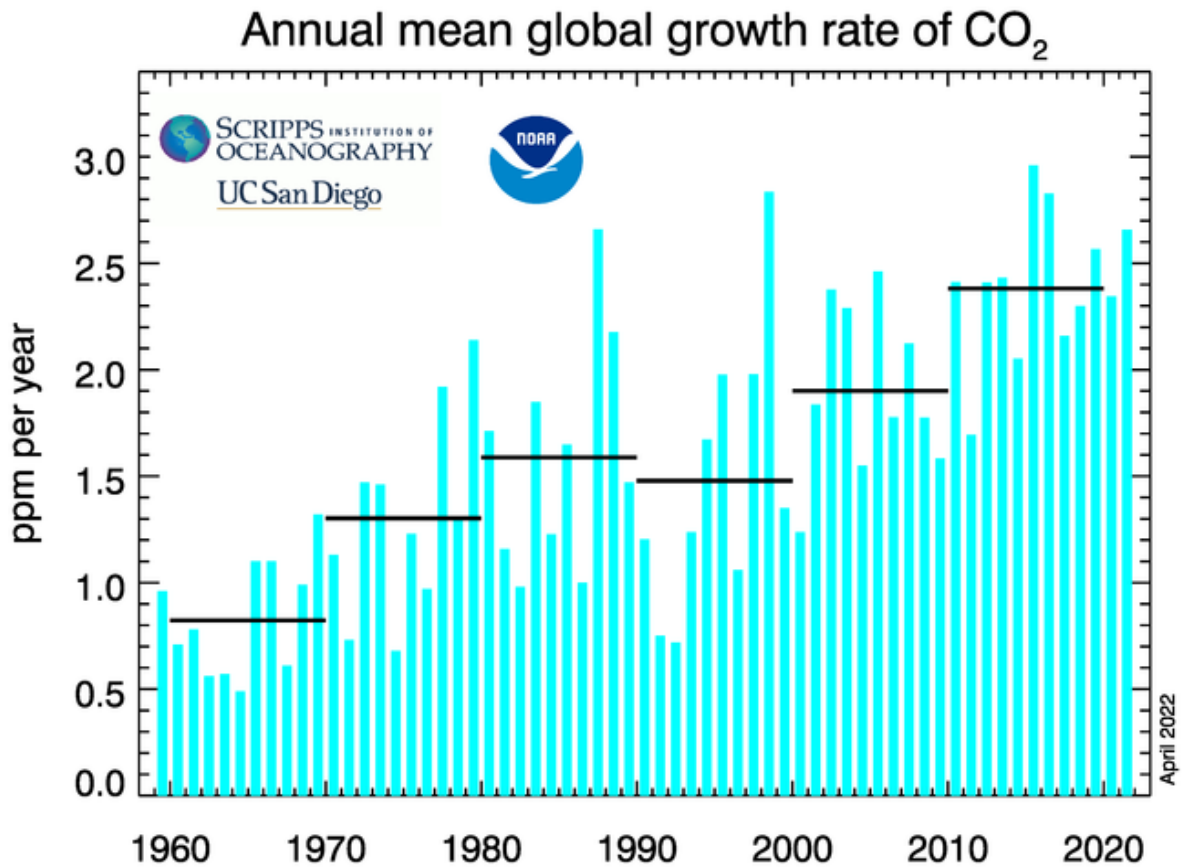
https://gml.noaa.gov/webdata/ccgg/trends/co2_data_gl_anngr.png

The decrease in CO_2 slope after 1991 followed by its recovery are clearly seen in the graph above. This NOAA/Scripps graph is CO_2 slope versus time, i.e. ppm per year or velocity of net global average CO_2 atmospheric concentration. 1 ppm is 7.76 Gt of CO_2.

Atmospheric CO_2 at Mauna Loa Observatory

Examining closely the NOAA/Scripps graph immediately above. A slight decrease or flattening is visible after 1991. This graph is CO_2 concentration versus time.

In addition to the CO_2 added to the atmosphere by Pinatubo, and the continuing CO_2 emissions by humans from all sources, and the continuing natural emissions of CO_2 by the biosphere, there was an El Nino event in 1991-1992. El Nino events add large amounts of CO_2 to the atmosphere. "The equatorial Pacific is the largest oceanic source of carbon dioxide to the atmosphere and has been proposed to be a major site of organic carbon export to the deep sea… The data establish El Nino events as the main source of interannual variability." (Murray, et al, 1994) The historical series of El Nino and La Nina perturbations are beyond the scope of this document, but we hope these major CO_2 and temperature perturbations can be examined in the next phases of this study.

During the period 1990 to 1995, there were major additions of CO_2 to the atmosphere, positive perturbations of the established CO_2 slope. Yet the net results measured at Mauna Loa and revealed in our analysis are a temporary flattening or decrease in slope

of CO_2 concentration and a sharp temporary deceleration in CO_2 concentration followed by rapid recovery acceleration back to and slightly beyond the pre-Pinatubo trend.

Where did that CO_2 go? Where did that recovery CO_2 come from? It was and is in the ocean. And it was there in enormous quantity, as will be illustrated next.

We studied the period of the Pinatubo perturbation. A natural perturbation to the diligently measured ~20-year trend of CO_2 concentration occurred. This Pinatubo perturbation period is an example, in both size and rates, of the capacity of the natural environment to emit and absorb CO_2. Human-CO_2 emissions are also a perturbation to the same net global average CO_2 concentration trend, but tiny by comparison to Pinatubo's perturbation.

The CO_2 absorbed was over two orders of magnitude larger than the perturbation due to human CO_2 emissions in the same period, as now will be shown. The slope of net global average CO_2 concentration rate averaged 1.463 ppm/year prior to Pinatubo. Concentration decelerated to near zero ppm/year/year, then accelerated steeply to an average slope of 2.087 ppm/year post Pinatubo. This recovery to trend with an offset above previous trend, an over recovery, is expected from Le Chatelier's principle.

Rather than estimate natural and human emissions based on computer modeling, carbon budgets and proxy data from pre-industrial times, and dubious fossil fuel data sources, we will compare CO_2 measured diligently by the Mauna Loa laboratory.

On June 15, 1991, net global average CO_2 atmospheric concentration (Mauna Loa data) was 358 ppm.

One ppm equals 7.76 gigatons (Gt) of CO_2.

358 ppm * 7.76 = 2778 Gt CO_2. (1 ppm CO2 = 2.12 Gt carbon. 2.12 Gt carbon * 3.66 tonnes CO2 per tonne carbon = 7.7592 Gt CO2.)

The specific impulse calculation can be used to compare forces in the environment.

Imagine a fully loaded 747 airplane with a mass of 2778 Gt on the runway ready to depart. How did the jet engine and aircraft designers and later the pilots know that the engines could produce enough force to accelerate the airplane to sufficient velocity to liftoff before the end of the runway? This calculation is the impulse calculation. It gives us a reliable, well known and trusted calculation to compare human-produced CO_2 with natural CO_2. Assume our 747 is rolling along at velocity of 1.4 miles/year and accelerating at about 0.73 miles/year/year, and then it hits a bump in the runway and decelerates. Then our 747 accelerates again.

This study provides the values for impulse calculations for the mass, velocity and acceleration of CO_2 in atmosphere during the time period following the Pinatubo eruption.

The mass of CO_2 is calculated from the MLO ppm concentration on the day of eruption.

m = 2778 Gt CO_2 in air, which is equal to 358 ppm CO_2 in air (June 15, 1991.)

dt is change in time = 2 years following Pinatubo eruption

a = dv/dt Acceleration a is the change in velocity divided by the change in time

a = 1.463 ppm/yr divided by 2 years = 0.73 ppm/yr/yr

F is force. F = m * a

F = 2778 Gt CO_2 * 0.73 ppm/yr/yr = 2027.94 Newton-years.

A Newton is the unit of force in the International system of units (SI). It is represented by the symbol N. Sir Isaac Newton devised the three Laws of Motion. The impulse-momentum theorem is logically equivalent to Newton's second law of motion. Impulse is the measure of force over time. Impulse is denominated by the symbol J. J is always directional one-way (i.e. a vector).

J = F * dt Impulse = force * change in time

J = 2028 Newtons * 2 years

J = 4056 Newton-years.

4056 Newton-years is the specific impulse of CO_2 that was removed from the atmosphere in 2 years after Pinatubo.

For comparison, let's assume human CO_2 was equal to 100% of the CO_2 that was added to the atmosphere between 1990 and 1991, the year preceding the Pinatubo eruption. Calculating from MLO data, the measured average rate of change (or velocity) of net global atmospheric CO_2 concentration for 1990 to 1991 was 1.5 ppm per year. How much CO_2 is that? Thus 1.5 ppm/yr * 7.76 Gt/ppm = 11.64 Gt of total change in CO_2 concentration in the year 1990 to 1991; this exceeds maximum possible human emission because it includes all sources and sinks of CO_2, not only human emission. But for our comparison here, we will attribute 100% of that CO_2 to humans. Let's also assume that 100% of the average velocity of CO_2 concentration in the Mauna Loa record from the 1970s to Pinatubo in 1991 was entirely due to humans. Our scientists calculated that average velocity in the pre-Pinatubo dataset period was 1.463 ppm/year.

Repeating the specific impulse J calculation:

11.64 Gt of "human" CO_2 * 0.73 ppm/year/year acceleration * 2 years = an impulse J of 16.99 Newton-years.

17 Newtons-years is J, the maximum possible specific impulse due to "human"-produced CO_2 that was added to the atmosphere during the 2-year Pinatubo deceleration period. It is the maximum amount impulse because we assume (for the purpose of this comparison only) that all of the CO_2 increase since the 1970s is due to humans.

The result of this comparison is exculpatory evidence. We have 4056 Newton-years versus 17 Newton-years.

The environment, mostly ocean surface (since ocean about 71% of Earth's surface,) demonstrated rapid CO_2 absorbance capacity which is 239 times larger than maximum possible net human emissions. We conclude that net human emissions are trivially minor, negligible, and absorbed and re-emitted along with the 239 times larger change in natural CO_2.   One 747 has 239 times the impulse to take off than another 747. Which would you fly?

Recall that deceleration of net global average CO_2 concentration dropped to near zero ppm/yr/yr. CO_2 concentration, both natural and human, is cumulative over time. Impulse is cumulative over time. Thus, the impulse is suitable and logical for this comparative analysis. Integration of cumulative CO_2 concentrations would also be a correct method for comparison, but the math is less well known. Airliners would not be taking off without the impulse calculation. When we attribute 100% of the changes in CO_2 concentration to humans, the impulse due to "humans" is negligible, not enough to stop CO_2's rapid deceleration. The human-produced-CO_2 climate change story does not fly.

CONCLUSION:

The environment demonstrated a measured impulse to absorb 239 times the human-produced CO_2 impulse when very conservatively calculated. Simply said, the natural environment is controlling CO_2 concentration. Human CO_2 emissions are not causing the increase in atmospheric CO_2. CO_2 concentration in the natural environment is controlled primarily by global temperature, most immediately by surface temperature, primarily sea surface temperature. These temperatures are controlled by various natural forces. Since an amount greatly exceeding all possible human CO_2 emissions was absorbed rapidly by the environment, then no net warming or net cooling can be attributed to human CO_2 emissions. Human CO_2 emission is a minor perturbation which is rapidly returned to trend along with the much larger CO_2 changes.

Scientist Peter Stallinga, Ph.D., concluded, "The correlation between temperature and [CO_2] is readily explained by another phenomenon, called Henry's Law: The capacity of liquids to hold gases in solution is depending on temperature. When oceans heat up, the capacity decreases and the oceans thus release CO_2 (and other gases) into the atmosphere. When we quantitatively analyze this phenomenon, we see that it perfectly fits the observations, without the need of any feedback [1]. We thus now have an alternative hypothesis for the explanation of the observations presented by Al Gore. The greenhouse effect can be as good as rejected and Henry's Law stays firmly standing. We concluded that the effect of anthropogenic CO_2 on the climate is negligible and the effect of the ocean temperature on atmospheric [CO_2] is exactly, both sign and magnitude, equal to that as expected on basis of Henry's Law." (Stallinga, P., 2018, Stallinga, P., 2020)

Where did the CO_2 go after Pinatubo? It was held in the oceans primarily, but also in cooler soils and in biosphere. The Henry's equilibrium is adjusted downward due to the lower sea surface temperature, resulting in much less CO_2 being emitted from the cooled tropical ocean, soils and biosphere; meanwhile, normally colder water in higher latitudes was even colder due to the Pinatubo effects. Ocean surface increased absorbance of CO_2 in these higher latitudes. Thus the CO_2 slope declined and acceleration rapidly declined. Then, about 2 years after Pinatubo, when the cloud belt had partially dissipated and insolation of tropical oceans increased, the deceleration of net global average atmospheric CO_2 concentration reversed sign and recovered, surpassing the average slope prior to Pinatubo. Professor Murry Salby provides calculations and graphs showing that the observed long-term slope of CO_2 concentration is explained by a series of offsets such as Pinatubo and El Ninos. And, "There is no evidence of a systematic trend in temperature." [referring to the actual mean global UAH satellite record for global anomalous temperature.] (Salby, 2018, beginning about 16:30 time mark in the video.).

Concerning the Pinatubo perturbation, Stallinga and Khmelinski write, "In total, the natural contribution is negative 50% of the anthropogenic emissions (i.e., a sink; Sabine et al. estimate 48% (Sabine, C.L. et al, 2014), plus fluctuations, with these fluctuations being of the same order of magnitude as the anthropogenic emissions… We have thus direct proof of Henry's Law that predicts such effects of temperature on the carbon-dioxide content in the atmosphere. Oceans undeniably outgas and absorb CO_2 from the atmosphere and they govern the dynamics, the correlation of [CO_2] with temperature." (Stallinga, P. and Khmelinski, I. 2018)   In other words, human emissions are absorbed by nature.

Kauppinen and Malmi explain, "Low cloud cover controls practically the global temperature." "The IPCC climate sensitivity is about one order of magnitude too high, because a strong negative feedback of the clouds is missing in climate models. If we pay attention to the fact that only a small part of the increased CO_2 concentration is anthropogenic, we have to recognize that the anthropogenic climate change does not exist in practice. The major part of the extra CO_2 is emitted from oceans [6], according to Henry's law. The low clouds practically control the global average temperature. During the last hundred years the temperature is increased about 0.1°C because of CO_2. The human contribution was about 0.01°C." (Kauppinen & Malmi, 2018)

Since most of Earth's surface around the equator that was obfuscated by the Pinatubo cloud belt was tropical ocean, we confidently infer that the rapid deceleration of CO_2 concentration was caused by cooling of millions of square kilometers of tropical ocean surface. This resulted in a net CO_2 gas absorption impulse over 230 times larger than net human emission impulse during same period. We expect that continuing this study into its next phases will yield a matrix of supporting evidence and, theoretically, a calibration curve for human-CO2 emission, based on measurements rather than estimates, so that the pernicious claims of global climate change due to human-produced CO_2 can be summarily dismissed.

The argument that human-CO_2 emission is causing global climate change is shown to have no scientific merit.

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Glossary

An extensive glossary of names, terms, & scientific principles used in this paper may be found online at: https://pinatubostudy.com/glossary.html

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A Complete Glossary of Terms, Principles, and Names appears
at: https://pinatubostudy.com/glossary.html