Diamond Trees (Tropostats): A Molecular Manufacturing Based System for Compositional Atmospheric Homeostasis

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Abstract. The future technology of molecular manufacturing will enable long-term sequestration of atmospheric carbon in solid diamond products, along with sequestration of lesser masses of numerous air pollutants, yielding pristine air worldwide ~30 years after implementation. A global population of 143 x 10^9 20-kg "diamond trees" or tropostats, generating 28.6 TW of thermally non-polluting solar power and covering ~0.1% of the planetary surface, can create and actively maintain compositional atmospheric homeostasis as a key step toward achieving comprehensive human control of Earth's climate.

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1. Active Compositional Atmospheric Homeostasis

Chemical substances released into the atmosphere as a result of industrial and other human activities can remain aloft for a long time. Eventually the air becomes contaminated with gaseous and particulate waste materials that may not be optimal for human or ecological health. This is simply the problem of air pollution that has been known for many decades.

But let us instead view the atmosphere as a slowly shifting population of atoms (Table 1), grouped via chemical combination into molecules. These atoms are held in temporary storage in Earth's gravitational field, arriving from sources on land and sea and later returning to sinks in land and sea after a series of slow chemical transformations that maintain an equilibrium between products and reactants with atmospheric residence times ranging from days to millennia. If we regard individual molecules (containing various atoms) as objects that we can handle and manipulate one by one, then the problem of air pollution reduces to the problem of continuous management of the shifting inventory of pollutant molecules (hence atoms) resident in the atmosphere of the Earth.

Atmospheric	Molecular Atmospheric		Mass of Air	
Molecular	Weight	Concentration*	Component*	
Component	M _w (gm/mole)	P (atm)	M _{aircomp} (kg)	
Nitrogen $(N_2)^{\dagger}$	28	7.80840 x 10 ⁻¹	$3.8774 \ge 10^{18}$	
Oxygen $(O_2)^{\dagger}$	32	2.09460 x 10 ⁻¹	$1.1887 \ge 10^{18}$	
Argon (Ar) [†]	40	9.340 x 10 ⁻³	6.626 x 10 ¹⁶	
Carbon Dioxide (CO ₂)	44	3.870 x 10 ⁻⁴ (& rising)	3.02×10^{15}	
Neon (Ne) [†]	20	1.818 x 10 ⁻⁵	$6.45 \ge 10^{13}$	
Helium (He) [†]	4	5.24 x 10 ⁻⁶	3.72×10^{12}	
Methane (CH ₄)	16	1.79 x 10 ⁻⁶	$5.08 \ge 10^{12}$	
Krypton (Kr) [†]	84	1.14 x 10 ⁻⁶	$1.70 \ge 10^{13}$	
Hydrogen $(H_2)^{\dagger}$	2	5.50 x 10 ⁻⁷	$1.95 \ge 10^{11}$	
Nitrous Oxide (N ₂ O)	44	3.20 x 10 ⁻⁷	$2.50 \ge 10^{12}$	
Carbon Monoxide (CO)	28	$1.50 \ge 10^{-7}$	$7.45 \ge 10^{11}$	
Xenon (Xe) [†]	131	8.70 x 10 ⁻⁸	2.02×10^{12}	
Ozone (O_3)	48			
Stratosphere [†]		$2-8 \ge 10^{-6}$ (stratosphere)		
Surface		$0-7 (\sim 2.66) \ge 10^{-8} (surf.)$	$\sim 2.26 \text{ x } 10^{11}$	
Formaldehyde (H ₂ CO)	30	2.4 x 10 ⁻⁹	$1.28 \ge 10^{10}$	
Ethane (C_2H_6)	30	2.0 x 10 ⁻⁹	$1.06 \ge 10^{10}$	
Hydrogen Chloride (HCl)	36	$1.0 \ge 10^{-9}$	6.38 x 10 ⁹	
Methyl Chloride (CH ₃ Cl)	51	$7.0 \ge 10^{-10}$	6.33 x 10 ⁹	
Carbonyl Sulfide (OCS)	60	$6.0 \ge 10^{-10}$	6.38×10^9	
Acetylene (C_2H_2)	26	3.0×10^{-10}	1.38 x 10 ⁹	
Sulfur Dioxide (SO ₂)	64	$3.0 \ge 10^{-10}$	3.41 x 10 ⁹	
Nitric Oxide (NO)	30	$3.0 \ge 10^{-10}$	1.60 x 10 ⁹	
Hydrogen Peroxide (H ₂ O ₂)	34	$2.0 \ge 10^{-10}$	1.21×10^9	
Hydrogen Cyanide (HCN)	27	$1.7 \ge 10^{-10}$	8.14 x 10 ⁸	
Nitric Acid (HNO ₃)	63	$5.0 \ge 10^{-11}$	5.59 x 10 ⁸	

Table 1. List of significant molecular gases and their typical concentration in the ambient U.S. standard dry atmosphere, and their total mass in Earth's air [1, 2]

Ammonia (NH ₃)	17	5.0×10^{-11}	$1.51 \ge 10^8$
Nitrogen Dioxide (NO ₂)	46	2.3 x 10 ⁻¹¹	$1.88 \ge 10^8$
Hypochlorous Acid (HOCl)	52	7.7 x 10 ⁻¹²	$7.10 \ge 10^7$
Hydrogen Iodide (HI)	128	$3.0 \ge 10^{-12}$	6.81×10^7
Hydrogen Bromide (HBr)	81	$1.7 \ge 10^{-12}$	2.44×10^7
Hydroxyl radical (OH ⁻)	17	$4.4 \ge 10^{-14}$	1.33×10^5
Hydrogen Fluoride (HF)	20	$1.0 \ge 10^{-14}$	3.55×10^4
Chlorine Monoxide (ClO)	51	$1.0 \ge 10^{-14}$	$9.04 \ge 10^4$
Formic Acid (HCOOH)	46	$1.0 \ge 10^{-14}$	8.16 x 10 ⁴
Carbonyl Fluoride (COF ₂)	66	$1.0 \ge 10^{-14}$	$1.17 \ge 10^5$
Sulfur Hexafluoride (SF ₆)	146	$1.0 \ge 10^{-14}$	$2.59 \ge 10^5$
Hydrogen Sulfide (H ₂ S)	34	$1.0 \ge 10^{-14}$	6.03×10^4
Phosphine (PH ₃)	34	1.0 x 10 ⁻²⁰	6.03 x 10 ⁻²
Total, Dry Atmosphere	28.956	1.00000	5.1354 x 10 ¹⁸
<u>.</u>			17
Water vapor $(H_2O)^{\dagger}$	18	$\sim 4.0 \text{ x } 10^{-3} \text{ (whole atm.)}$	$\sim 1.277 \text{ x } 10^{16}$
		$1-4 \ge 10^{-2}$ (at surf.)	

^{*} PV = nRT, so the concentration by partial pressure (P) is proportional to molar concentration (n). This can be converted to mass of air component by multiplying dry atmospheric mass by the pressure concentration times the ratio of the air component's molecular weight (M_W) to the dry atmosphere molecular weight; e.g., $M_{aircomp} = (1.77345 \times 10^{17}) M_W P$.

[†] Not regarded as a "pollutant".

Beyond conventional air pollutants, more recently it has been determined that atmospheric concentrations of carbon dioxide are rising unusually rapidly by historical standards. This rise appears to have a significant anthropogenic component (e.g., caused by human industrial activities, automobiles, worldwide agriculture, Amazon basin deforestation, and the like). It has also been hypothesized that the rise in atmospheric CO_2 levels might have negative long-term effects on regional and global mean temperatures, rainfall, wind velocities, polar ice coverage, and so forth (i.e., climate change [3]). If this hypothesis is correct, then CO_2 may be regarded as an additional "climate pollutant" gas in Earth's atmosphere.

Since implementation of globally-effective regulations to reduce carbon and other pollutant emissions at their many sources faces significant economic and political challenges, there have been numerous suggestions for sequestration approaches in which, for example, carbon-rich pollutant gases that have already been released into the atmosphere would subsequently be extracted from the atmosphere and isolated in some form of long-term storage [4]. The bestknown examples of carbon sequestration are active aforestation or reforestation programs [5] that seek to sequester carbon as cellulosic biological matter in long-lived plants such as trees. While workable in theory, trees can all too easily be cleared by humans, felled by disease, burned by fire, or die of old age after a few decades, returning the sequestered carbon to the air. Another well-known biosequestration proposal is to seed the ocean surface with bulk quantities of ironrich compounds, stimulating plankton growth that removes CO₂ from the air and carries the sequestered carbon to the ocean floor when the blooms later die off and sink [6, 7], though the effectiveness of this method has been questioned [8]. Oceanic phosphorus seeding is a related possibility [9]. Burial of biochar (anaerobic charcoal) [10] and manufacture of CO₂-enriched concrete [11, 12] and "carbonate cement" (similar to marine cement) [13] are under active investigation, and carbon capture and storage (CCS) [14] from coal-fired power plant

smokestacks is being tested. Others have proposed the direct capture of airborne CO_2 and permanently burying it deep underground [15] or at sea [16]. Free-standing scrubbing towers employing conventional chemistry have been proposed by Zeman and Lackner [17], and their team is working to build a laboratory prototype at Global Research Technologies in Tucson, Arizona [18]. A \$25M Virgin Earth Challenge prize [19] promises to reward the first inventor who demonstrates a practical way to remove a billion tons per year of CO_2 from the atmosphere.

A new approach relies on the likely availability of the future technology of molecular manufacturing [20, 21] and its ability to achieve long-term sequestration of atmospheric carbon either in the form of solid diamond, for example via "aerovores" [22] or the widespread global distribution of personal nanofactories [23], or in the form of "glossy graphite pebbles" via nanotech-based "cleanup devices" [24].* In this scenario, molecular manufacturing techniques including diamondoid mechanosynthesis (DMS) [25] and diamondoid nanofactories [21] would be used to build macroscale "diamond trees" or "tropostats" incorporating atomically-precise diamondoid nanomachinery that can filter pollutant molecules out of the troposphere – the lowest portion of Earth's air containing \sim 75% of the atmosphere's mass and \sim 99% of its water vapor and aerosols. Tropostats break out the oxygen contained within the pollutant molecules and return that gas to the atmosphere as a beneficial effluent, then excrete the residuum as solid bricks of almost pure diamond (or other form of densely compacted carbon) entrained with trace quantities of other pollutant atoms. These bricks could be employed as bulk building materials, or as recyclable material for the manufacture of useful high-value consumer or industrial products, or they could be harmlessly buried in landfill or at sea. In all such cases, the mostly carbon atoms comprising the bricks would be permanently sequestered from natural biogeochemical action (e.g., the carbon cycle) because diamond is extremely strong and chemically inert, and can only be chemically broken down by extreme natural processes occurring at the elevated pressures and temperatures found beyond 10-100 km deep in Earth's mantle.

* Hall's Weather Machine [26] is a "programmable greenhouse gas" for managing solar insolation built using molecular manufacturing. It would consist of a large population of airborne 1-10 mm diameter hydrogen-filled spheres incorporating remote-controlled mirrors but no onboard chemical processing capability beyond the electrolysis of water vapor, requiring a worldwide total system mass of 1×10^{10} kg. By comparison, one optical mass of 550-nm diameter aerovores [22] possessing sophisticated onboard chemical processing capability has a total system mass of 37×10^{10} kg. The proposed global population of 143 x 10^9 tropostats has a system mass of 286 x 10^{10} kg (Section 4.8).

The primary objective of this paper is to parameterize the mission design of a hypothetical artificial molecular manufacturing based air-cleaning mechanism called a tropostat that is capable of active continuous management of the concentrations of all relevant pollutant molecular species in the atmosphere (Section 3). The purpose of a global network of tropostats is to maintain all specified air constituents at programmed concentrations that are regarded as ideal for human health, proper ecological maintenance, and human esthetics, thus achieving active compositional atmospheric homeostasis. In this paper, system specifications are dominated by the requirement for massive sequestration of carbon.

2. Optimal Levels of Atmospheric Constituents

What is the optimal ambient concentration of all the molecular constituents of the air that we would like to control? This is a complex issue whose details lie beyond the scope of this paper. For instance, in the case of SO_2 pollutant, is it desirable to reduce the concentration of this gas all the way to zero, or is there some intermediate but low level that is tolerable to human health? Is

there some level of this pollutant that is actually necessary for a healthy ecosystem – given that biology requires some sulfur atoms for natural biochemical processes and given that natural biology has evolved to tolerate certain background levels of this gas, e.g., from volcanoes? In the case of "climate pollutant" molecules, a proper detailed analysis should include, for example, a weighting of each atmospheric component by its heat-trapping efficiency as a greenhouse gas to determine its ideal atmospheric concentration.

It is clear from Table 1 that the performance specifications for the tropostats will be strongly dominated by the requirement for CO₂ removal from the atmosphere. For purposes of the present analysis, it will be naively assumed that permanently rolling back CO₂ concentrations to near-preindustrial levels of 300 ppm (leaving 2340×10^{12} kg, or 2340 petagrams (Pg), of CO₂ in the atmosphere) should suffice to eliminate any possible anthropogenic influence on global climate change from that source. Such a rollback requires removing 680×10^{12} kg of CO₂ from the air. But CO₂ emissions from human sources are slowly rising over time and the rate of that increase is also rising over time (Figure 1). In 2009, roughly 11.8 x 10^{12} kg (~2.3 ppm) of anthropogenic CO₂ was added to the global load, far larger than the 0.130-0.230 x 10^{12} kg/yr normally added from volcanic sources [27]. Linearly extrapolating the historical rate rise of 1 ppm/yr in 1970 to 2 ppm in 2000, the rate of increase reaches 3 ppm/yr by 2030 and 4 ppm/yr by 2060.

Figure 1. Left: The Keeling Curve, atmospheric CO₂ concentrations as measured at Mauna Loa Observatory [28]. Right: Yearly increase of atmospheric CO₂ during 1960-2007 (<u>http://en.wikipedia.org/wiki/File:CO2_increase_rate.png</u>) [29].



Figure 2 shows three possible scenarios for future global CO_2 management. In Scenario 1, there is no sequestration and carbon emissions continue to grow at current rates, allowing CO_2 levels rise to 521 ppm by 2070. In Scenario 2, a global network of ground-based tropostats capable of removing 42 x 10^{12} kg/yr (42 Pg/yr) of CO_2 is built and begins extraction operations at full capacity in 2030, resulting in a peak at 422 ppm in 2029 and a reduction to the target 300 ppm level by 2070. In Scenario 3, the tropostat network is more realistically linearly ramped from 10% of maximum CO_2 extraction capacity in 2030 to full capacity at 50 x 10^{12} kg/yr (50 Pg/yr) by 2039, producing a peak at 424 ppm in 2032 and a reduction to 300 ppm by 2067. In each case, the CO_2 content of the atmosphere in a given year is calculated as the content in the previous year plus the net mass added in the current year less the mass extracted by tropostats in the current year, converted to ppm concentrations.

Figure 2. Three scenarios for global CO_2 management: (1) no sequestration, (2) 42 Pg/yr tropostat network runs continuously during 2030-2070, and (3) 50 Pg/yr tropostat network ramps up linearly during 2030-2039, then runs continuously thereafter.



This paper presents a preliminary scaling study for Scenario 3: a global network of artificial diamond trees powerful enough to extract up to $M_{extract} = 50 \times 10^{12} \text{ kg/yr}$ (50 Pg/yr) of CO₂, sufficient to return Earth's atmosphere expeditiously to pre-industrial carbon levels and thereafter to maintain the atmosphere in this condition indefinitely – even assuming that the current anthropogenic carbon footprint continues growing on its present course without any abatement throughout the 21st century, which seems unlikely for various reasons. This calculation also assumes that there are no sudden massive releases of carbon into the atmosphere such as might occur in the aftermath of a supervolcano eruption or a thermonuclear war. A 50 Pg/yr removal rate should also suffice to accommodate possible slow outgassing from the oceans, where another ~150,000 x 10^{12} kg of dissolved CO₂ is stored as carbonic acid and in other forms such as -10^{19} kg of carbon [2] sequestered as carbonates in rocks takes place over even longer timescales and can safely be ignored in this analysis.

Methane is another greenhouse gas of possible concern. At present, 5.08×10^{12} kg of CH₄ are present in the atmosphere with a net lifetime of ~8 yr, compared to ~100 yr for CO₂. Even if all methane was removed from the air, the mass removed would be only a small fraction (<1%) of the total mass of CO₂ that must be scrubbed out. The concentration of CH₄ appears to be rising at a rate of about 5 ppb/yr from all sources [30] or ~0.014 x 10^{12} kg/yr, which is again only a small fraction (~0.1%) of the CO₂ influx that must already be extracted. There may be as much as 20,000 x 10^{12} kg of additional methane stored in frozen ocean-bottom clathrates [31]), but this is generally regarded as a well-sequestered inventory.

Nitrous oxide (N₂O) is another significant greenhouse gas, but appears to be rising at only ~0.8 ppb/yr [32] or ~0.006 x 10^{12} kg/yr, hence requires negligible additional atmospheric scrubbing capacity compared to that required for CO₂ removal. The total masses of various CFCs and other greenhouse gases to be extracted also appear negligible in comparison to CO₂.

Leaving aside greenhouse gases, the largest atmospheric pollutants appear to be CO, O₃, various sulfur and nitrogen oxides, a variety of hydrocarbons and volatile organic compounds, and other trace substances totaling ~1.3 x 10^{12} kg, less than 0.2% of the mass of CO₂ that must be removed. Additionally, the worst cities have >2.5 µm particulate levels as high as 100-400 micrograms/m³ [33], but levels of ~10 micrograms/m³ (~10⁻⁸ kg/kg air) are considered safe and likely represent an upper estimate for the whole-atmosphere mean. If we assume an average of ~10 micrograms/m³ throughout the entire global air mass and specify that we want to filter it all out of the air, then the total mass of particulates that must be removed should approximate (~10⁻⁸ kg/kg air)(5.1352 x 10¹⁸ kg air) ~ 0.0513 x 10¹² kg, which again is just a tiny fraction of the total mass of CO₂ to be removed. The relative mass of new particulates entering the atmosphere normally is similarly negligible, though these aerosols may play a significant role in climate change [63].

Barring cataclysmic natural or man-made disasters, a ground-based gas-scrubbing tropostat system capable of selectively filtering out ~50 x 10^{12} kg/yr of material – mostly CO₂ (~98% by mass), CH₄ (~1%), and all other greenhouse gases, conventional air pollutants, aerosols and >2.5 µm particulates (~1%) – from the air should suffice to maintain Earth's atmosphere in pristine, pre-industrial, esthetically- and ecologically-ideal perfection more or less indefinitely, following a few decades of initial cleanup activity.

3. Energy Considerations for the Tropostat Network

The primary purpose of the tropostat is to: (1) extract CO_2 from the atmosphere, (2) use the carbon atoms to build solid rectangular bricks of diamond, diamond-like carbon (DLC), crystalline graphite or graphene, or densely-packed glassy or amorphous carbon, and (3) release gaseous O_2 into the air as a beneficial effluent. The solid bricks need not be flawless transparent crystalline diamond, but could be flawed-lattice diamond or polycrystalline diamond if these prove significantly cheaper to fabricate. The bricks could incorporate carbon nanotubes, yielding a strong and highly fracture-resistant composite material, and could be made with interlocking geometries to facilitate their use in architectural applications. Methane is also removed from the atmosphere, its carbon converted to diamond and its hydrogen used to passivate the surfaces of the diamond bricks. All other gases, aerosols and pollutants (~1% by mass of the total) can either be chemically transformed and covalently incorporated here and there throughout the interior structure of the diamond bricks, or simply entrained without chemical processing into small deeply-buried voids within the diamond brick structure.

3.1 Energy Requirements for Chemical Transformations

In principle, any feedstock molecule containing carbon atoms can be used as a carbon source for the fabrication of diamondoid objects via mechanosynthesis. Diamond is essentially a large hydrocarbon molecule, so it should not be surprising that chemically similar hydrocarbons are the most efficient precursor material. Oxygen-rich carbon feedstock generally requires much more energy to convert to diamond than hydrogen-rich feedstock. Dealing with noncovalent feedstocks (e.g., ionic-bonded minerals such as calcium carbonate) would present additional

complications. Table 2 shows the net energy required to complete several mechanosynthetic reactions, each yielding a single molecule of adamantane (the smallest possible chunk of diamond) among the products, starting from a variety of feedstock (reactant) molecules. A negative energy indicates that the net reaction is "exoergic" and readily moves downhill across the potential energy landscape, releasing surplus energy overall. A reaction with positive energy is "endoergic" and must be forced uphill by adding energy from outside. (Reaction energies were calculated using Gaussian98/DFT at the B3LYP/6-311+G(2d,p) // B3LYP/3-21G(d) level of theory with uncorrected zero point corrections, on fully converged structures with no imaginary frequencies except for CaCO₃.)

Table 2. Net Mechanosynthetic Reactions to Produce an Adamantane Molecule (C10H16)				
Eqn.	Mechanosynthetic reaction for making adamantane	Energy (kcal/mole)	% C by wt	% C by #
1	$5C_2H_2+3H_2\rightarrow C_{10}H_{16}$	-261.9	92.3%	50.0%
2	$5C_2H_4 \rightarrow C_{10}H_{16} + 2H_2$	-58.8	85.7%	33.3%
3	$(10/3)C_3H_8 \rightarrow C_{10}H_{16} + (16/3)H_2$	+66.9	81.8%	27.3%
4	$5C_2H_6 \rightarrow C_{10}H_{16} + 7H_2$	+88.7	80.0%	25.0%
5	$10CH_4 \rightarrow C_{10}H_{16} + 12H_2$	+172.5	75.0%	20.0%
6	$10\text{CO}_2 + 8\text{H}_2 \rightarrow \text{C}_{10}\text{H}_{16} + 10\text{O}_2$	+1,360.7	27.3%	33.3%
7	$10CaCO_3+8H_2 \rightarrow C_{10}H_{16}+10CaO+10O_2$	+1,654.9	12.0%	20.0%

Table 2 reveals that unsaturated hydrocarbon feedstocks have the highest carbon content per molecule, the best energetics, and leave behind the fewest post-reaction discard atoms as waste products when used to build diamond. These are the highest-quality feedstocks for diamond mechanosynthesis in an efficient molecular manufacturing facility. Employing saturated hydrocarbons of increasing chain length (CH₄, C₂H₆, C₃H₈, ...) as feedstock also somewhat improves net reaction energy, whereas using CO₂ as the carbon source costs 8 times more input energy than for natural gas (CH₄) feedstock, or 20 times more input energy than for propane (C₃H₈).

Nevertheless, at the cost of some energy inputs to move the endoergic mechanosynthetic reaction forward, CO₂ can be used as a carbon feedstock for a nanofactory building diamond products. Some standard heats of combustion (enthalpy of formation) for diamond and graphite [34] include:

C (diamond) + O_2 (gas) \rightarrow CO ₂ (gas) + 94.49 kcal/mole (657.3 zJ)	(8)
C (graphite) + O_2 (gas) \rightarrow CO ₂ (gas) + 94.04 kcal/mole (654.2 zJ)	(9)
$CH_4 (gas) + O_2 (gas) \rightarrow C (diamond) + 2H_2O (liq) + 118.1 \text{ kcal/mole} (821.7 \text{ zJ})$	(10)

The first two reactions, (8) and (9), can be driven in the reverse direction via mechanically forced chemical reactions (mechanosynthesis) to produce solid diamond and free oxygen gas while consuming carbon dioxide gas, at the cost of significant energy consumption (+94.49 kcal/mole). To accomplish this a specific sequence of mechanosynthetic reactions must be devised in which oxygen atoms are mechanically pulled from the CO_2 molecule one by one, after which the carbon is installed in a diamond lattice. This may require using small numbers of water molecules as a hydrogen source for Reaction 6 in the Table, after which the hydrogen (and water) is recovered when temporarily hydrogenated diamond surface is dehydrogenated to allow the placement of

additional carbon in the growing lattice. One proposed method in conventional bulk chemistry for converting CO_2 into hydrocarbons would operate a fuel cell in reverse, with sunlight and a catalyst splitting water into hydrogen ions and oxygen gas, whereupon the ions cross a membrane and react with the CO_2 to create hydrocarbons [35] – a class of materials that includes diamond.

Note that methane can be exoergically combined with oxygen (which will be plentiful due to the breakdown of CO_2 elsewhere in the tropostat) to produce diamond (or graphite) with net energy production, but we conservatively ignore this potential additional energy source and rely solely upon solar power to provide energy to the tropostats. The net energy requirements both to process CH_4 into diamond (~1% of pollutant mass) and to modify or entrain the other climate gases and conventional pollutants (~1% mass) are conservatively taken as equal to the energy required for CO_2 processing in the energy scaling analysis that follows.

The minimum thermodynamic requirement for converting carbon dioxide to diamond is 657.3 zJ per molecule of CO₂ consumed, and thus also 657.3 zJ per carbon atom laid down in the form of diamond (or 654.2 zJ for graphite). Since 1 kilogram of diamond consists of 83.33 moles or 5.019×10^{25} atoms of ¹²C, the conversion of 83.33 moles of CO₂ gas (3.67 kg, ~1868 liters at STP) to 1 kg of solid diamond and 83.33 moles of O₂ gas (2.67 kg, ~1868 liters at STP) requires the input of at least 32.99 megajoules. Thus we require E_{CO2} ~ 8.99 MJ/kg(CO₂) to sequester the carbon dioxide gas in solid diamond form, which equates to an energy cost of E_{diamond} ~ 32.99 MJ/kg(diamond) to produce the solid diamond bricks.

In addition, we assume that mechanosynthetic processing is only $\sim 60\%$ efficient, comparable to the efficiency of the chemomechanical myosin motor in biology, somewhat increasing the actual energy cost above the minimum chemical energy costs estimated above.

3.2 Energy Scaling of Global Tropostat Network

A global ground-based gas-scrubbing tropostat network capable of selectively filtering out $M_{extract} \sim 50 \times 10^{12} \text{ kg/yr}$ of CO₂ gas would produce ~434 metric tons/sec (13.6 x 10^{12} kg/yr) of solid diamond worldwide, or ~3.88 billion m³/yr – roughly one-half of the current 7.8 x 10^9 m^3 /yr worldwide production of concrete [36]. The tropostat network would require a continuous systemwide power draw of $P_{DMS} \approx M_{extract} E_{CO2} / \tau_{yr} = (50 \times 10^{12} \text{ kg}(CO_2)/\text{yr}) (8.99 \times 10^6 \text{ J/kg}(CO_2)) / (3.14 \times 10^7 \text{ sec/yr}) = 14.3 \times 10^{12} \text{ W}$ to cover energy dissipation from mechanosynthetic processes. The power requirement to implement a basic planetary atmospheric pollutant management system may be estimated as $P_{network} = P_{DMS} + P_{other}$, where P_{other} includes nonmechanosynthetic power draw plus compensation for mechanosynthetic inefficiencies. Budgeting $P_{other} = P_{DMS}$ for computational convenience, then $P_{network} = 28.6 \times 10^{12} \text{ W} (28.6 \text{ TW})$. This is about 14 times the worldwide electricity consumption of ~2 x 10^{12} W in 2008 but only about twice the total worldwide energy consumption of ~15.04 x 10^{12} W for 2008 [37].

Although 28.6 TW seems like a lot of power by present-day standards, worldwide biomass traps ~100 TW via photosynthesis [38] and the entire disk of the Earth receives 1370 W/m² of continuous solar illumination or ~175,000 TW (1.75×10^{17} W). Grid-connected photovoltaic electricity is now the fastest growing energy source, growing on an exponential curve (Figure 3) with a Moore's Law-like doubling time of ~2 years – e.g., installations of all photovoltaics increased by 83% between 2006 and 2008, bringing the total installed capacity to ~15 GW.



Figure 3. Annual (red) and cumulative (black) world photovoltaic installations, 1998-2008 [39]

If capacity doubles every two years, then after 11 doublings or 22 years (i.e., by the year 2030) the installed solar capacity would reach 30.7 TW. Following this same curve, by two years later in 2032 another 30.7 TW would be built, and successive 30.7 TW generating capacity increments would be built out in the following 1-year, 0.5-year, etc. intervals as long as the exponential growth rate continues. It is unknown whether an exponential growth rate in solar capacity can be maintained over the next two decades. But if it can, then sometime within the decade of the 2030s the world may become predominantly solar powered (possibly some of it space-based). A 28.6 TW tropostat network may then represent only a very modest and quite reasonable percentage of total global electrical capacity. Of course, tropostats would generate their own power and thus need not withdraw any energy from the existing global supply.

3.3 Tropostat Network Waste Heat Generation

Since the global tropostat system can run entirely on solar power that is intercepted before it hits the ground, the waste heat released by the tropostats will not exceed the heat that would otherwise have been re-radiated by the now-shadowed ground underneath the machines. Thus even a closely-packed field of tropostats should produce no localized heat-island effects.

Note also that the 28.6 TW energy demand for the entire global tropostat network is several orders of magnitude smaller than the estimated global hypsithermal limit of ~1000 TW believed necessary to trigger serious worldwide ecological disruptions [40]. Hence the net effect of the tropostat system on the planetary thermal ecological balance would still be small even if all power were provided from additive sources other than thermally-neutral ground-based solar such as fossil fuel, nuclear, or space-based solar, assuming this additional waste heat is adequately geographically dispersed.

3.4 Tropostat Solar Energy Supply

In one possible design called the "tree" configuration" (Section 4.1), an individual tropostat would consist of a large spherical shell of radius R_{tropostat} covered with high-efficiency photovoltaic (PV) collectors, perched atop a flexible stalk analogous to the trunk of a tree. The question of whether the general spherical shape might be more efficient if structured with a more dendritic (multiscale branching) sphere-filling configuration is not addressed in this paper.

Even when buffeted by winds into various different orientations, the PV shell could always collect solar power at the average rate of $P_{tropostat} = \pi R_{tropostat}^2 I_{net}$, where I_{net} is the 24-hour average solar insolation that reaches the planetary surface, net of cloud cover, seasonality, pointing geometry and day-night cycles. Solar insolation of 1370 W/m^2 strikes the upper atmosphere but the topmost surface of a ground-based PV collector receives less than half of this amount due to atmospheric reflection, absorption, scattering, and the like. Power is maximum for PV cells pointing to zenith at noon on the equator, but is less at higher latitudes, earlier or later in the day and on cloudy days, and falls essentially to zero at nighttime. Figure 4 shows the net solar power potentially available worldwide over a full 24-hour period under normally prevailing weather conditions. A few sites in Africa, Australia and elsewhere are capable of providing a net usable solar power influx of 300-350 W/m². For properly sited tropostats, and assuming only presentday conventional (pre-nanotechnology) commercial photovoltaic conversion efficiencies of $\sim 20\%$ [41], each tropostat collector shell should be able to generate 60-70 W/m^2 of power, net over a full 24-hour cycle (1.4-1.7 Kw-hr/day/m²). Taking $I_{net} \sim 63$ W/m² and $R_{tropostat} = 1$ m, each tree yields a power of $P_{tropostat} \approx 200$ W. Hence the entire 28.6 TW tropostat network consists of $N_{\text{tropostat}} = P_{\text{network}} / P_{\text{tropostat}} \approx 143 \text{ x } 10^9 \text{ individual tropostat "diamond trees" worldwide.}$

The network of 143 x 10⁹ tropostats having total cross-sectional area of $A_{netC} = \pi R_{tropostat}^2 N_{tropostat} = 449,250 \text{ km}^2$ will cover a total ground surface area of $A_{net} = L_{tropostat}^2 N_{tropostat} = 572,000 \text{ km}^2$, since spheres of radius $R_{tropostat}$ can be packed into a square grid of cell edge $L_{tropostat} = 2 R_{tropostat} = 2 m$. This sounds like a lot of land area but is just a square 756 km (469 mi) or ~7 deg of latitude on an edge (~0.1% of world area), only ~1/7th of the area of U.S. farmland, or approximately the land area of any one of California, Cameroon, Morocco, Papua New Guinea or Turkmenistan. Given that the most intense sunlight in the world appears to fall in the poor North African countries of Chad and Sudan (Figure 4), just 1/7th of the land area of these two countries (largely uninhabited desert) would support the entire global atmosphere control network. The required ~\$364B/yr tropostat construction and replacement investment (Section 4.8) could quadruple the GDP of these two countries in perpetuity. Siting the entire network in poorest (and politically corrupt) Chad, covering the barren Saharan lands in the northern 2/5ths of the country with tropostats, would increase that nation's GDP by twentyfold, possibly boosting per capita annual income from \$1700 to as high as \$30,000. (Of course, the people may still remain poor unless viable political solutions are found.)

Local winds (Figure 5) must provide adequate mixing and re-entrance of unprocessed air. The exact geographical distribution of tropostats for optimum atmospheric processing deserves further detailed study, although siting half of the network in each of the northern and southern hemispheres might be more efficient due to the relatively slow mixing across the equator between the two hemispheres. A network consisting of a dozen widely-separated smaller sites might prove more robust against geological- or weather-related disturbances or political disruptions.

Figure 4. Map colors show local solar irradiance averaged over 3 years from 1991-1993 for 24 hours/day, taking into account the cloud coverage available from weather satellites (<u>http://en.wikipedia.org/wiki/File:Solar_land_area.png</u>); solar areas defined by the dark disks could provide more than the world's total primary energy demand in 2009, assuming 8% conversion efficiency. Below: The most energy-intense land sites are Chad and Sudan.





Figure 5. Global atmospheric circulation displaying Hadley cell, Ferrell (mid-latitude) cell and polar cell wind flows (http://en.wikipedia.org/wiki/File:Earth Global Circulation.jpg).

Note also that in a practical system, tropostats will operate at higher power levels during daylight hours and at near-zero power levels during darktime, unless the design includes provision for onboard energy storage or can tap into feeds from a global electricity grid at night.

4. Design Parameters for the Tropostat

In the "tree" configuration, a large population of individual tropostats, each consisting of a large spherical photovoltaic shell perched atop a flexible stalk analogous to a tree trunk, is collected into a regular surface array resembling a large grove of trees. A complete tropostat design is beyond the scope of this paper but some general conclusions can be gleaned from the following basic scaling calculations.

4.1 Photovoltaic Shell

In the "tree" design, the main body of an individual tropostat consists of a large spherical shell ~6 feet in diameter ($R_{tropostat} = 1$ m) that is covered with photovoltaic (PV) collectors. At an ideal minimum mechanosynthetic power level of 100 W, each tropostat unit can process $m_{CO2} = 1.11 \text{ x}$ 10^{-5} kg/sec of CO₂ extracted from the air, requiring 1.89 x 10^{-2} kg/sec of air to pass through the unit, a volume of $V_{air} = 1.47 \text{ m}^3$ /sec at STP. CO₂-rich air enters the sunward-oriented $A_{hemi} = 4\pi R_{tropostat}^2 / 2 \sim 6.28 \text{ m}^2$ hemispherical side of the tropostat sphere through small shadowed gaps in the photovoltaic array while O₂-rich air is discharged through the opposite hemisphere, the flow traveling across the average ~1 m separation between the two hemispheres at a net velocity of $v_{flow} = V_{air} / A_{hemi} = 23.4 \text{ cm/sec} (~0.5 \text{ mph})$. The mass of a spherical photovoltaic array having wall thickness $w_{PV} \sim 100 \text{ }\mu\text{m}$ is $M_{PV} = 4\pi R_{tropostat}^2 w_{PV} \rho_{diamond} \sim 4.4 \text{ kg}$.

The photovoltaic array has a transparent diamond coating to prevent scratching or pitting from abrasive windborne sand particles. Self-cleaning mechanisms (analogous to but more durable than current methods [62]) should also be provided to remove fine dust and biological debris from the photovoltaic surface and to keep the airflow channels clean of sand and other clogging materials; 2 kg of system mass and 5 W of continuous power are allocated for these mechanisms, along with a small additional allocation for network communications and control circuitry.

4.2 Support Stalk

A flexible hollow stalk made of strong composite diamond material with Young's modulus $Y_{diamond} = 1.05 \times 10^{12} \text{ N/m}^2$ and measuring $L_{stalk} = 4 \text{ m}$ in length, $R_{stalk} = 1.25 \text{ cm}$ in outside diameter, and $r_{stalk} = 1.15 \text{ cm}$ in inside diameter (1 mm wall thickness), physically supports the sphere and extends from the sphere's center point to 1 meter below ground level, anchoring the device and placing the bottom surface of the sphere a full 2 meters (~6 feet) above ground level. The Euler buckling force for a hollow tube of this shape is $F_{buckle} = \pi^3 Y_{diamond} (R_{stalk}^4 - r_{stalk}^4) / 4 L_{stalk}^2 = 3522 \text{ N}$, equivalent to a mass of 359 kg >> 20 kg, the actual aerostat mass which the stalk must support. The mass of the stalk is $M_{stalk} = \pi (R_{stalk}^2 - r_{stalk}^2) L_{stalk} \rho_{diamond} = 1.06 \text{ kg}$.

4.3 Sortation Module

After the initial CO_2 -rich air passes into the sphere, almost all CO_2 content should be extracted and transported to the mechanosynthesis subsystem. There are many possible bulk separation technologies that could in principle be employed, ranging from differential solvation and cold trapping to diffusion sortation or centrifugation cascades, or even molecular sieving (since CO_2 molecules have a different size and shape than N_2 or O_2 molecules). A detailed comparative analysis of the full panoply of energy-efficient molecular separation technologies is beyond the scope of this paper. However, a simple example of a sortation module that uses molecular sorting rotors [42] illustrates the magnitudes of the relevant design parameters.

A sorting rotor is a wheel with mechanically reversible binding sites for a particular molecule – in this case, carbon dioxide – positioned around its rim. As the wheel rotates, target molecules are selectively captured and transported through the barrier wall in which the wheel is embedded, acting, in effect, as a single-molecule pump. Each rotor is made of diamondoid materials and its overall dimensions, including the housing but not the power or gearing mechanisms, are about 7 nm x 14 nm x 14 nm, $M_{rotor} \sim 2 \times 10^{-21}$ kg, throughput rate $n_{CO2} \sim 10^4$ CO₂ molecules/sec at the air

concentration of ~10⁻⁵ CO₂ molecules/nm³ (which assumes a ~99% CO₂ binding site occupancy), while consuming up to $P_{drag} \sim 10^{-16}$ W to overcome drag resistance and $E_{sort} \sim 10-40$ zJ/molecule to perform the sortation process on small molecules [42]. Thus the sortation module in each tropostat unit contains $N_{rotors} = (M_{extract} N_{avogadro} / \tau_{yr} N_{tropostat} M_{W,CO2} n_{CO2}) = (50 \times 10^{12} \text{ kg}(CO_2)/\text{yr}) (6.023 \times 10^{23} \text{ molecules/mole}) / (3.14 \times 10^7 \text{ sec/yr}) (143 \times 10^9 \text{ units}) (0.044 \text{ kg/mole}) (10^4 CO_2 \text{ molecules/rotor-sec}) = 1.52 \times 10^{16} \text{ rotors/unit having total volume } V_{rotors} = (7 \text{ nm x 14 nm x 14 nm}) N_{rotors} = 20.9 \text{ mm}^3/\text{unit, total mass } M_{totrot} = M_{rotor} N_{rotors} = 3.04 \times 10^{-5} \text{ kg/unit, a collective drag power of } P_{totdrag} = P_{drag} N_{rotors} = 1.52 \text{ W/unit, and a collective sortation power draw of } P_{totrot} = P_{totdrag} + E_{sort} n_{CO2} N_{rotors} = 1.52 \text{ W} + (40 \times 10^{-21} \text{ J/molecule}) (10^4 CO_2 \text{ molecules/rotor-sec}) (1.52 \times 10^{16} \text{ rotors/unit}) = 7.60 \text{ W/unit}.$ The total input air-exposed facial area of the rotor field is $A_{rotfield} = (7 \text{ nm x 14 nm}) N_{rotors} = 1.49 \text{ m}^2$. Allowing generous 1 cm wide channels separating adjacent surfaces of the rotor field to keep airflow resistance very low gives a rotor field volume of $V_{rotfield} = (1 \text{ cm}) A_{rotfield} = 0.0149 \text{ m}^3$. Liberated O₂ can be discharged in bulk without need for sortation.

Because the mass of sorting rotors is so low, a full reserve set of rotors targeting a multitude of other pollutant gases (e.g., CH₄, N₂O, CO₂, SO₂, etc.) can be included in the sortation module, allowing some or all of the entire pumping capacity of the global tropostat network to be retargeted to these other gases upon receipt of authorized instructions.

4.4 Airflow Channels

The precise architecture of the airflow channels leading from the air-ingress gaps in the photovoltaic array through which CO₂-rich air is funneled to the rotor field volume near the center of the sphere, and the channels leading from the rotor field to the air-egress gaps in the photovoltaic array through which O_2 -rich air escapes from the opposite hemisphere of the sphere. should be selected to allow sufficient residence time of CO_2 molecules in the sortation module to ensure virtually complete extraction of the target gas from the passing air. Airflow channels may resemble a 3D honeycomb-like structure with ~ 1 cm wide passages, with cells made of thin strong graphene sheets, allowing the tropostat to be shipped in a compact folded configuration and then opened on site – perhaps somewhat like a beach umbrella – into the ball-on-a-stick geometry. The pumping power through airflow channels appears minimal. For a 1-cm wide 1-m length tube through which air of viscosity 1.89×10^{-5} kg/m-sec passes at a velocity of 23.4 cm/sec, the required $P_{chan} \sim 3 \times 10^{-5}$ W/channel pumping power uses a pressure differential of only $\sim 10^{-5}$ atm at opposite ends of each channel. This implies that an electronically-gated system of one-way valves might be feasible even with modest ambient prevailing winds. If the total number of such channels in each unit is $N_{channels} \sim 4 R_{tropostat}^3 / 3 R_{channel}^2 L_{channel} = (4) (1 m)^3 / (3)$ $(5 \times 10^{-3} \text{ m})^2$ (1 m) = 5.33 x 10⁴ channels, then total channel pumping power is a very modest $P_{chanpump} = P_{chan} N_{channels} = 1.6 W$. The mass of the airflow channels in each unit, taking wall thickness as $w_{channels} \sim 3 \ \mu m$ with material having failure strength σ_w , $\sim 10^{10} \ N/m^2$ for diamond, is $M_{channels} \sim N_{channels} \rho_{diamond} (4 R_{channel} L_{channel} w_{channels}) / 2 = 5.6 kg.$ Note that these cylindrical airflow tubes would have a bursting strength of $P_{max} = w_{channels} \sigma_w / R_{channel} \sim 59$ atm, sufficiently strong to resist tearing by even the strongest wind-driven forces.

4.5 Nanofactory Module

A small nanofactory module measuring 25 cm x 15 cm x 5 cm resides on the underside of the sphere. The support stalk is affixed to the underside of the nanofactory module. The nanofactory manufactures diamond bricks using power from sunlight collected via the spherical shell and

materials from CO₂ and other gases gleaned from the air via the sorting rotor array. A density of $\rho_{diamond} = 3510 \text{ kg/m}^3$ for diamond implies that each 1 kg diamond brick has a volume of 284.9 cm³ and could have dimensions measuring 20 cm x 10 cm x 1.4245 cm.

Assume there are two diamond brick extrusion ports on the underside of the nanofactory module, located on either side of the stalk, measuring 10 cm x 1.4245 cm. During normal operation, one diamond brick is extruded from each port until the brick reaches 20 cm in length, whereupon it is truncated and released, dropping the short distance to the ground like ripe fruit falling from a tree. These can be collected by human workers or, more likely, by automated harvester machines.

The nanofactory module has a volume of 1875 cm³, a mass of ~3.75 kg taking mean density as ~2000 kg/m³ in accordance with past scaling studies, and a modest power density of 5.3×10^4 W/m³ (comparable to a gasoline-powered automobile). Given a reasonable 60% energy efficiency for mechanosynthetic processing, 100 watts of net mechanosynthetic power would allow each tropostat to remove 1 kg of gaseous CO₂ from the air about every day (89,900 sec/kg) and to produce two 1 kg diamond bricks about every week (329,900 sec/brick).

4.6 Biomass vs. Tropostat Performance

The mass and power budgets for the "tree" configuration tropostats are summarized in Table 3.

Table 3. Mass and power budget for one "tree" configuration tropostat			
Tropostat Component	Mass (kg)	Power Draw (W)	
Photovoltaic shell			
PV cells	4.40	0.0	
Support	2.00	5.0	
Stalk	1.06	0.0	
Sorting rotors	0.01	7.6	
Airflow channels	5.60	1.6	
Nanofactory module	3.75		
Mechanosynthesis @ 100% efficiency		(100.0)	
Mechanosynthesis @ 60% efficiency		166.7	
Unallocated	3.18	19.1	
TOTALS	20.00	200.0	

The ideal performance of diamond trees is roughly comparable to the best theoretical performance of biological systems. For example, Loomis and Williams [43] estimated the maximum quantum yield of a single leaf, photosynthetic photon flux absorption and respiration, and determined a theoretical maximum potential growth rate of 15.4 μ g/cal of total radiation (28.1 kg/yr/m²) at an incident photon flux of 500 cal/day/cm² (242.5 W/m²). By packing plants tightly and growing them in ideal conditions in liquid hydroponics culture with three times more photosynthetic flux than is typical in the field, Bugbee and Salisbury [44] induced wheat plants to add biomass at a 50.4 kg/yr/m² rate, or about 60% of the 84.3 kg/yr/m² theoretical maximum for

that flux. Wheat straw has 47.3% carbon content [45], so the hydroponics wheat added carbon at a 23.8 kg/yr/m² rate which required extracting CO₂ from the atmosphere at an $\varepsilon_{\text{biomass}} = \underline{87.5} \underline{\text{kg}(\text{CO}_2)/\text{yr/m}^2}$ rate (vs. a <u>146 kg(CO₂)/yr/m²</u> theoretical maximum rate). Comparably, the global network of tropostats is estimated to remove $M_{\text{extract}} \sim 50 \times 10^{12} \text{ kg/yr}$ of CO₂ gas using a total network mass and collector area of $M_{\text{network}} = N_{\text{tropostat}} M_{\text{tropostat}} = (143 \times 10^9 \text{ units}) (20 \text{ kg/unit}) = 2.86 \times 10^{12} \text{ kg}$ and $A_{\text{netC}} = \pi R_{\text{tropostat}}^2 N_{\text{tropostat}} \approx 4.4925 \times 10^{11} \text{ m}^2$, respectively, giving a specific CO₂ extraction rate of $\varepsilon_{\text{tropostat}} \sim M_{\text{extract}} / A_{\text{netC}} = \underline{111.3 \text{ kg}(\text{CO}_2)/\text{yr/m}^2} (17.5 \text{ kg/sec/kg})$ for tropostats, or $\varepsilon_{\text{diamond}} \sim (M_{W,C} / M_{W,CO2}) \varepsilon_{\text{tropostats}} = 30.4 \text{ kg}(\text{C})/\text{yr/m}^2 (4.8 \text{ kg/sec/kg})$ for $M_{W,CO2} = 44 \text{ gm/mole}$, $M_{W,C} = 12 \text{ gm/mole}$.

While genetic engineering might improve the best possible performance of biological photosynthetic systems, the analysis so far has also assumed that only present-day commercial (pre-nanotechnology) photovoltaic conversion efficiencies of ~20% [41] are available. However, high efficiency solar cells have already demonstrated experimental efficiencies of ~40% in the lab (Figure 6) [46]. A network of tropostats capable of 40% efficiency instead of 20% might be buildable in half the time, use half the land area, provide twice the specific CO₂ extraction rate, or cost only half as much to deploy. Alternatively, higher-efficiency tropostats could be located in areas having much less intense sunlight than the northern Sahara desert, greatly expanding the siting options. (Plants typically convert light into chemical energy with a photosynthetic efficiency of only 3-6% [47].) The availability of a global electricity grid or space-based solar power could permit nighttime operation, improving tropostat productivity by a factor of 2-3 or more while adding little to the existing thermal pollution burden.



Figure 6. Evolution of photovoltaic cell efficiencies, 1975-2010 [48].

4.7 Wind Velocity and Vertical Convection

Consider a square tropostat field of edge length $L_{net} = A_{net}^{1/2} = 7.56 \times 10^5$ m across which air of density $\rho_{air} = 1.165$ kg/m³ at 30 °C and CO₂ mass fraction $m_{ratioCO2} = 5.881 \times 10^{-4}$ blows at a mean horizontal wind speed of vwindH. Let Hextract be the height of the air column above the tropostat field from which CO_2 can be extracted. A good proxy for $H_{extract}$ is the thickness of the planetary boundary layer - typically ~1000 m [49] - which is the lowest layer of the troposphere nearest the ground where wind is most turbulent and gusty, maximizing convective mixing. In this case the extraction volume $V_{extract} = H_{extract} L_{net}^2 \sim 5.72 \times 10^{14} \text{ m}^3$ and the mass of CO₂ available for extraction in that volume is $M_{CO2} = V_{extract} m_{CO2} = 4.06 \text{ x} 10^{11} \text{ kg}(CO_2)$, where sea-level air contains $m_{CO2} = \rho_{air} m_{ratioCO2} = 7.09 \text{ x} 10^{-4} \text{ kg}(CO_2)/\text{m}^3$ and the CO₂ removal time from the extraction volume $V_{extract}$ is $\tau_{CO2} \sim M_{CO2} / M_{extract} \sim 2.55 \text{ x } 10^5 \text{ sec}$ (~3 days), for $M_{extract} = 50 \text{ x } 10^{12}$ $kg/yr = 1.59 \times 10^{6} kg(CO_{2})/sec$. To allow sufficient time for vertical mixing of fresh air from above with air nearest the surface from which CO_2 has been extracted, the vertical wind speed $v_{windV} \ge (H_{extract} / \tau_{CO2}) \sim 0.39$ cm/sec. The average vertical wind speed (often charted [50] in microbars/sec, roughly equivalent to cm/sec [51]) is downward over most of the Earth's surface at any given time and is typically a few cm/sec [51], so $v_{windV} \sim 1$ cm/sec seems reasonably conservative and appears to satisfy the vertical mixing requirement. Similarly, the horizontal surface wind velocity needed to move replacement air into the extraction volume over the tropostat field is $v_{windH} = L_{net} / \tau_{CO2} = M_{extract} / (H_{extract} L_{net} \rho_{air} m_{ratioCO2}) = 2.96 \text{ m/sec, well below}$ the average surface wind speed of ~ 7 m/sec in the geographical areas of interest (Figure 7).

Figure 7. Worldwide mean horizontal surface wind speeds in January and July (http://commons.wikimedia.org/wiki/File:Wind speed climatology.jpg).



4.8 Network Manufacture and Deployment

Tropostats would clearly be the product of a mature diamondoid molecular manufacturing technology, and the construction and deployment of a global tropostat network would require the existence of an extensive global nanomanufacturing industrial base at a time when nanofactories were both efficient and widely available. A detailed cost analysis is not yet possible but the following estimates may suffice for the purposes of this scaling study:

(1) **Manufacturing.** If each unit has a mass of $M_{tropostat} \sim 20$ kg, then the total system mass of $N_{tropostat} = 143 \times 10^9$ tropostat units is $M_{network} \sim 3 \times 10^{12}$ kg. Assuming a typical fully amortized cost of \$1/kg for nanofactory output in an era of mature industrial molecular manufacturing [20, 21, 52] puts the raw tropostat manufacturing cost at \$3T. Manufacturing $(M_{network} / 10) \sim 0.3 \times 10^{12}$ kg/yr over a decade-long implementation time would fully occupy 34.2 million general-purpose 10-kg nanofactories each producing ~1 kg/hr [52], although larger specialty nanofactories would likely be more efficient. If the first general-purpose 10 kg nanofactories of similar type rather than marketable products, then there are 438 nanofactories by 2028, 191,844 nanofactories by 2029 and 84 million nanofactories by 2030, whereupon 34.2 million (~41%) of them can then be employed to build out the global tropostat network in a 10-yr ramp-up through 2040.

(2) **Installation.** If one laborer needs ~1000 sec (~17 minutes) to manually install and erect each "beach umbrella" tropostat unit in the ground, and if 1.37 million people are hired to work 8-hour days (i.e., ~457,666 workers for each of 3 shifts/day), then total installation time is $t_{install} = (143 \times 10^9 \text{ tropostat units}) \times (1000 \text{ worker-sec/unit}) / (457,666 \text{ workers}) = 3.14 \times 10^8 \text{ sec} = 10 \text{ yrs}$ (Scenario 3 in Figure 2). Assuming a pay rate of \$30K/yr (extremely generous by thirdworld standards), hiring 1.37 million people represents an installation labor cost of \$0.411T.

(3) **Shipping.** Even assuming that tropostat units will be installed within a reasonably compact land area, some transportation of finished units from nanofactories to field sites is probably necessary. As a conservative estimate, let us assume that tropostat units must be trucked in along a 500 mile round trip path and that each truck can make 1 round trip per day. Then the driver's pay per truckload is (1 day/truckload) (30K/yr) / (365 days/yr) ~ 82/truckloadfor labor. Each truck also requires fuel. If each truck gets 5 mpg and travels a 500 mile circuit using 100 gallons per trip at 3/gallon, then the fuel cost is -300/truckload. It also costs money to buy each truck. If a new truck costs \$30,000 and can run for 100,000 miles on long hauls before being junked, then each truck can make 200 trips and the amortized cost of each truck is 150/truckload. The estimated cost per truckload is therefore 82(labor) + 300(fuel) + 150(vehicle) = \$532. If a truck can transport 1000 tropostat units (~20 metric tons) on each trip, then a total of $(143 \times 10^9 \text{ tropostat units})/(1000 \text{ units/truckload}) = 143 \times 10^6 \text{ truckloads are needed and}$ the total trucking cost is $(143 \times 10^6 \text{ truckloads}) \times (\$532/\text{truckload}) = \0.076 T . A delivery rate of 143 x 10⁶ truckloads over a 10-year period is 39,178 truckloads/day; running three shifts/day, the delivery fleet needs ~13,000 trucks. Total fuel consumption by this fleet is (100 gallons/trip) x 143 x 10^6 trips/decade) = 1.43 x 10^9 gallons/yr, or ~1% of total U.S. gasoline consumption (1.38) x 10^{11} gallons/yr in 2008 [53]), and solar-energy-based battery- or hydrogen-powered trucks are alternatives to fossil fuels.

(4) **Land.** Data on the price of land in Chad and Sudan is not readily available. As a conservative proxy, the average value of rural farmland in Wyoming (the cheapest in the U.S.)

was \$192/acre in 1995 [54], the last year these data were reported. The network of 143 x 10^9 tropostats will cover a total ground surface area of $A_{net} \approx 572,000 \text{ km}^2 = 141$ million acres, which would cost \$192/acre or a total of \$27.1B if purchased in Wyoming in 1995. Adding 5%/yr price inflation during 1996-2030 raises the total land acquisition cost to \$27.1B (1.05)³⁵ = \$0.149T for the network. More likely, the land would be donated or inexpensively leased from the host nation government in exchange for the permanent jobs and the right to sell some of the diamond bricks.

Summing the four principal expenses, the total buildout cost for the tropostat network may approximate $C_{deploy} = \$3T$ (manufacturing) + \$0.411T (installation) + \$0.076T (shipping) + \$0.149T (land) = \$3.636T. Another important cost factor is the turnover rate – the length of time that tropostat units can operate before they must be repaired or replaced. Assuming a mean lifetime of 10 yrs, $C_{annual} = C_{deploy}/10 \sim \$364B/yr$ must be spent in perpetuity to continually rebuild and maintain the network in good working order. The long-term post-installation cost for CO₂ removal during the 30-yr drawdown phase is $C_{CO2} \sim C_{annual} / M_{extract} = (\$0.3636T/yr) / (50 \times 10^{12} \text{ kg}(CO_2)/yr) = \$7.27/ton of CO_2$, equivalent to a carbon (C) removal cost of \$26.66/ton.

5. Alternative Deployment Scenarios

The discussion thus far has assumed ground-based siting of tropostats configured as groves of diamond trees in flat desert areas receiving intense sunlight. However, several other deployment scenarios are possible.

5.1 Diamond Balloons

In the "tree" configuration (Section 4), tropostats are spheres attached to the end of a short stalk of fixed length. If further investigation reveals that vertical atmospheric mixing is too slow because the tropostat field can extract CO₂ faster than fresh air can be imported (e.g., the system is convection-limited, contrary to estimates in Section 4.7), one solution may be to employ a "balloon" configuration in which individual spherical neutral-buoyancy tropostats are tethered to ground anchors via thin retractable or spoolable cables that allow the spheres to freely move continuously between ground level and ~1 km altitude, thus giving the filtration network direct access to a much larger volume of air. In this configuration, each tropostat is a hollow sphere of slightly larger radius R_{tropostat} = 2 m with wall thickness t_{wall} = 63 microns and material density $\rho_{wall} = 3510 \text{ kg/m}^3$ (diamond) filled with hydrogen gas of density $\rho_{gas} = 0.0899 \text{ kg/m}^3$ (STP) providing net lift in air of density $\rho_{air} = 1.2929 \text{ kg/m}^3$ (STP) for a payload mass (M_{payload}) of:

$$M_{\text{payload}} = (4\pi/3) \rho_{\text{air}} R_{\text{tropostat}}^{3} (1 - \rho_{\text{gas}}/\rho_{\text{air}}) - 4\pi \rho_{\text{wall}} t_{\text{wall}} R_{\text{tropostat}}^{2}$$
(11)

The hydrogen can be provided by electrolysis of 27.1 liters (\sim 7 gallons) of water for each tropostat, which requires 4.3 x 10⁸ J or \sim 6 days to fill the balloon using the \sim 800 W generated by each unit's PV cells.

To preventing bursting of a spherical pressure vessel having working strength $\sigma_w = 10^{10} \text{ N/m}^2$ (diamond), we also require:

$$t_{wall} \ge \Delta P R_{tropostat} / \sigma_w \tag{12}$$

where the maximum environment pressure fluctuation is $\Delta P = 3$ atm which exceeds the maximum possible sound pressure in air. For R_{tropostat} = 2 m, then t_{wall} = 63 microns, M_{payload} = 20 kg, and the material mass of the sphere is 11.1 kg. The retractable cable of radius r_{cable}, length L_{cable} = H_{extract} = 1000 m, density $\rho_{cable} = 3510 \text{ kg/m}^3$ (diamond) and working strength $\sigma_w = 10^{10} \text{ N/m}^2$ (diamond) must possess a tensile strength of F_{cable} = $\pi r_{cable}^2 \sigma_w$ that equals or exceeds the weight of the cable (= M_{cable} g) where M_{cable} = $\pi r_{cable}^2 L_{cable} \rho_{cable}$ and g = 9.81 m/sec₂, plus the maximum wind force exerted on the balloon of F_{wind} = $\pi R_{tropostat}^2 \Delta P$; hence $r_{cable} \geq (R_{tropostat}^2 \Delta P / (\sigma_w - L_{cable} \rho_{cable} g))^{1/2}$ = 122 microns and M_{cable} = 0.16 kg. The mass and power budgets will otherwise be similar to those given in Table 3 for the "tree" configuration tropostats. Note that manufactured tropostat mass rises to 31.2 kg (an 11.1 kg balloon shell provides 20.1 kg of net lift) but four times fewer units are needed due to the radius increase from 1 m to 2 m, hence total network mass actually can decrease by 60% unless additional physical infrastructure is required. Spheres can be ganged and moved in groups to eliminate the possibility of wind-driven tether tangling. No attempt has yet been made to optimize the tradeoff between the size and number of tropostats in a network.

5.2 Mountain Siting

Some or all of the tropostat network could be sited in relatively uninhabited mountainous regions or at high altitudes where unassisted human habitation is impossible (Figure 8). Sunlight is more intense at higher altitudes thus reducing the total network footprint on the ground, and few people or other activities would be displaced so impact on human commerce should be minimal. Comparing sunlight intensity (Figure 4) with areal extent of sunny mountain locations (Figure 8) indicates that ideal mountain sites would include first and foremost the Himalayas between China and India, secondarily the central Andes of South America, and thirdly the central Rocky Mountains of North America. The diamond bricks could be allowed to accumulate in these uninhabited sites, or creative means could be devised to remove them.

Figure 8. Global digital elevation model GTOPO30, compiled in 1996 by USGS, shows mountains in red, sea-level areas in dark blue [55].



5.3 Ocean Siting

Another attractive deployment scenario is ocean deployment. Seagoing bargelike tropostats could simply drop their diamond bricks into the pelagic depths, effectively sequestering the extracted carbon (and other atmospheric pollutants) across geological timescales. Storage sites for these chemically inert diamond bricks on the ocean bottom could be chosen where there are the fewest living systems and thus no significant ecological impact, or the dropped bricks could be purposely fabricated with perforate features to encourage, for example, coral growth. A low number density of smooth-surfaced root tendrils embedded with sorting rotors, dangling deep in the water below each tropostat to gather dissolved CO_2 from the sea, could offset possible gas collection limitations due to slow vertical convection in the open ocean without entangling wildlife. The mass-weighted CO_2 concentration in seawater is ~10⁻⁴, comparable to the air concentration. Extraction of this CO_2 would effectively alkalinize seawater, slowly drawing more CO_2 out of the atmosphere (and into the oceans) over a timescale of many decades.

Oceanic tropostats could be allowed to circulate or stationkeep near the center of one of the five major oceanic gyres (Figure 9A). For instance, currents in the North Pacific Gyre (Figure 9B) have trapped exceptionally high concentrations of suspended plastic and other manmade debris in a formation known as the Pacific Trash Vortex (135°-155°W, 35°-42°N, between San Francisco and Hawaii), roughly the size of Texas [56, 57]. The currents of the Sargasso Sea in the North Atlantic Gyre also accumulate a large vortex of non-biodegradable plastic waste (Figure 9C). The central regions of each of these and other Gyres are individually large enough to accommodate the entire tropostat network. Alternatively, oceanic tropostats could be tethered together in large floating mats and anchored to the seabed floor to prevent migration into commercial shipping lanes.

5.4 Airborne Siting

Free-floating airborne tropostats – untethered diamond (or graphene) "blimpstats"– could stationkeep over fixed areas of the planetary surface using solar-powered vertical mobility via buoyancy control combined with active steering based on detailed real-time knowledge of horizontal air currents (Figure 5) that could be provided by satellites and other means. The ideal size for these devices is currently unknown but deserves further study.

Alternatively, large collections of balloon tropostats could be lashed together into floating islands or "airbergs" in the sky, whose travels around the Earth could be at least coarsely steered, tracked and avoided by aircraft. Airbergs could be landed and relaunched from designated ground sites to allow periodic inspection, maintenance and refurbishment as required. Diamond bricks could be accumulated onboard until the tropostats were over open ocean where their loads could be dumped, or alternatively their cargo could be unloaded at product distribution centers on land during each of the periodic ground landings. Figure 9. (A) Top, left: Major ocean gyres, including the North Pacific Gyre (http://en.wikipedia.org/wiki/File:North_Pacific_Gyre_World_Map.png). (B) Top, right: Closeup of the North Pacific Gyre (http://en.wikipedia.org/wiki/File:North_Pacific_Gyre.png). (C) Bottom: Closeup of Sargasso Sea in North Atlantic Gyre (http://en.wikipedia.org/wiki/File:North_Atlantic_Gyre.png).







5.5 Urban Siting

As noted in Section 2, particulates and aerosols [63] can be a serious localized problem in many urban areas. A good case can be made for incorporating particulate collection and recovery systems into building structures in cities and suburban locales. Complementing the gas extraction systems, a significant mass of particulate recovery and sequestration systems could be incorporated into many residential and industrial structures, e.g., on home, office, and factory rooftops and other areas, along with solar energy conversion and storage systems. Creative use of existing artificial structures can reduce the need for new ones.

5.6 Pressurized Storage

Using solar-powered sorting rotors simply to remove CO₂ from the air in order to mechanically store it as a pressurized liquid in underground geological formations, without chemically processing it to extract the C atoms and release the oxygen, would reduce system energy requirements ~ 10 -fold from ~ 30 TW to ~ 3 TW, but would also increase total sequestration volume by \sim 10-fold in a practical system as compared to diamond sequestration (see below). Sequestered liquid CO₂ has additional problems. It must be securely warehoused and constantly guarded because an accidental (e.g., earthquake) or malicious (e.g., terrorist) leak could quickly release the CO₂ back into the air, causing ecological disaster. By comparison, barring significant purposeful effort, it is almost impossible for carbon sequestered in diamond bricks to return to the ecosphere. Diamond bricks can be uniformly distributed over the Earth's surface if desired, whereas CO_2 pressure storage is more practical using much larger volumes such as underground geological formations. (A hybrid approach of storing pressurized CO₂ in smaller diamond pressure vessels that are buried underground or in deep ocean reduces storage volumes but correspondingly increases total energy costs.) Furthermore, diamond bricks or related products would have many applications that can be implemented without risking de-sequestration. By comparison, liquid CO₂ has relatively few industrial uses and virtually all of these uses risk returning carbon to the biosphere.

A related suggestion is to sequester unprocessed CO_2 as pressurized gas inside capped carbon nanotube (aka. "buckytube") pressure cylinders that would be fabricated and filled with gas by the nanofactories. Best for this purpose would be spherical fullerenes which can hold twice the pressure without bursting compared to cylindrical nanotubes. However, scaling laws predict that the highest ratio of stored carbon atoms per unit volume is achieved at maximum wall thickness t_{wall} and minimum tank radius R_{tank} , which occurs when $t_{wall} = R_{tank} - i.e.$, a solid sphere of diamond. This makes sense because CO_2 compressed to 80,000 atm achieves only ~14 C atoms/nm³ and even solid CO_2 reaches only ~21.4 C atoms/nm³, whereas solid diamond stores ~176 C atoms/nm³, providing a tenfold denser sequestration medium than any form of unprocessed CO_2 .

6. Conclusions

The future technology of molecular manufacturing will enable long-term sequestration of atmospheric carbon in solid diamond products, along with sequestration of lesser masses of numerous air pollutants, yielding pristine air worldwide \sim 30 years after implementation. A global population of 143 x 10⁹ 20-kg "diamond trees" or tropostats, generating 28.6 TW of

thermally non-polluting solar power and covering less than 0.1% of the planetary surface, can create and actively maintain compositional atmospheric homeostasis as a key step toward achieving comprehensive human control of Earth's climate.

Once global CO₂ concentration is reduced to 300 ppm, many of the carbon-processing components of the system can be furloughed and held in reserve to combat future unexpected atmospheric challenges such as those posed by major volcanoes or supervolcanoes, massive forest or peat fires, modest asteroid strikes, regional nuclear wars, and the like. For example, the June 1991 eruption of Mt. Pinatubo caused global average temperature to decrease by 0.4 °C in the first year after the stratospheric injection of ~20 x 10⁹ kg of SO₂, some of which remained aloft for up to 3 years. Such pollutant clouds might be cleared in ~10⁶ sec (~2 weeks) using a population of free-floating diamondoid blimpstats having only ~1% the mass and capacity of the proposed ground-based global tropostat network.

The network reserve capacity also provides some initial defense against catastrophic carbon releases. One such event may have occurred 550 million years ago during a period of widespread glaciation extending close to the equator, believed to have ended suddenly when a colossal volcanic outgassing raised the CO_2 concentration of the air to 12%, ~350 times modern levels, causing extreme greenhouse conditions and carbonate deposition as limestone at the rate of about 1 mm/day [58]. Another similar possible event might involve the future rapid release of gaseous methane from seabed methane clathrates into the atmosphere as the oceans warm [59], though this hypothesis currently lacks support [60, 61]. Alternatively, if someday the planet is threatened by an impending ice age, the tropostat network can be used to quickly ramp up the level of greenhouse gases present in Earth's atmosphere under precise human control, providing an offsetting warming effect to oppose the global cooling trend.

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