*Engineering Photochemical Smog
Through Convection Towers*

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ENGINEERING PHOTOCHEMICAL SMOG THROUGH CONVECTION TOWERS

by

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ABSTRACT

Propositions for engineered, post hoc solutions to atmospheric pollution phenomena span all terrestrial scales from the global downward. Urban smog has been the subject of several studies. Most recently, reverse convection towers have attracted attention as a medium for cleansing modern cities. Evaporation of an aqueous mist injected at the tower opening could generate electrical power by creating descent, and simultaneously scavenge unsightly and unhealthful particulates. The study offered here assesses the influence to tower water droplets on the photochemical component of Los Angeles type smog. The primary radical chain initiator OH is likely removed into aqueous phases well within the residence time of air in the tower, and then reacts away rapidly. Organics do not dissolve, but nighttime hydrolysis of N_2O_5 depletes the nitrogen oxides. A lack of HOx would slow hydrocarbon oxidation and so also ozone production. Lowering of NOx would also alter ozone production rates, but the direction is uncertain. SO_2 is available in sufficient quantities in some urban areas to react with stable oxidants, and if seawater were the source of the mist, the high pH would lead to fast sulfur oxidation kinetics. With an accommodation coefficient of 10^{-3} , however, ozone may not enter the aqueous phase efficiently. Even if ozone is destroyed or its production suppressed, photochemical recovery times are on the order of hours, so that tower processing must be centered on a narrow midday time window. The cost of building the number of structures necessary for this brief turnover could be prohibitive. The increase in humidity accompanying mist evaporation could be controlled with condensers, but might otherwise counteract visibility enhancements by recreating aqueous aerosols. Quantification of the divergent forcings convection towers must exert upon the cityscape would call for coupled three dimensional modelling of transport, microphysics, and photochemistry.

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Introduction

Concepts for technological intervention into large scale atmospheric pollution problems are appearing with increasing frequency in the scientific literature (Cicerone et al., 1992). Propositions directed toward the greenhouse effect or ozone depletion have sometimes been of global extent (Stix, 1989; Broecker, 1990). Hemispheric and regional ozone engineering concepts have also been presented (Cicerone et al., 1991; Heicklen, 1981a). Following initial scrutiny such remediation plans have generally fallen into one of two categories. They have invariably proven to be either inordinately expensive (Bullock et al., 1992), or else dangerous (Pitts et al., 1977; Elliott et al., 1994).

The current work examines photochemical ramifications of a new concept for remediation of urban air pollution. M.L. Prueitt and coworkers have suggested that reverse convection towers designed for generating electrical power could be modified to remove particles from city air (Glanz, 1992). In the original plan, water pumped to the tops of the towers was to be misted, and droplet evaporation would create a down draft through a set of turbines (Carlson, 1975). However, mist properties could also be manipulated to provide effective scavenging of urban aerosols (Glanz, 1992; Prueitt et al., 1993), potentially improving atmospheric visibility and health characteristics. The dominant urban pollution problem of modern times is Los Angeles type smog (Haagen-Smit et al., 1951; Haagen-Smit, 1952)), which possesses an important photochemical component in addition to undesirable particulates. Here we ask what effects the interactions of city air with convection tower mists might have on smog photochemistry.

Our analysis is for the moment conducted at a qualitative level only. The goal is to outline modelling strategies which would be required for a full assessment. We begin with a detailed discussion of the development of the convection tower proposition. Next, we trace the chemical events taking place in an air parcel which is pulled into a tower and then comes in contact with the artificial droplets. We conclude that daytime scavenging of the hydrogen oxide radicals

(HOx) may stabilize organics, leading to brief reductions in ozone production, while at night removal of N_2O_5 lowers nitrogen oxide concentrations (NOx). The influence of altered NOx on oxidants the following day cannot be predicted without full photochemical calculations. There is thus some chance for a reduction in key criteria species. The photochemical recovery times, however, are on the order of minutes to hours. For cleansing to be effective, it may be necessary to process all city air during a tight time window corresponding to midday pollution episodes. The cost of such fast transport could be prohibitive. The sea is one likely source of the mist water, so that droplets could be of high pH. Reaction with sulfur IV removes ozone rapidly from alkaline solutions, but we estimate that transfer through the gas phase is rate limiting. Although removal of existing particulates seems feasible, mist evaporation would raise the local humidity. At elevated RH ammonium sulfate and nitrate particles would swell and degrade visibility.

Complete understanding of the effects convection towers would have on Los Angeles type smog requires at the very least the application of a three dimensional chemical-microphysical-transport model of the urban airshed. The calculations entailed are quite expensive both in terms of labor and raw computation. Even if 3D modelling were conducted, there is no guarantee that the answers it produced would be accurate enough to serve as a basis for testing or implementation decisions. Experience with other pollution remediation schemes has shown that the evaluation of feasibility and/or safety can depend sensitively on model parameters which may not be readily identifiable (Cicerone et al., 1991 and 1992; Elliott et al., 1994).

Background: Atmospheric Engineering

The likelihood of global climate change has provided a strong impetus for the development of pollution mitigation strategies (Cicerone et al., 1992; Keith and Dowlatabadi, 1992). Several plans have focussed on countering the global greenhouse effect. Carbon dioxide might be sequestered in the deep sea (Golomb, 1989) or

removed via iron fertilization of surface waters (see series Martin et al., 1990; Broecker, 1990; Peng and Broecker, 1991; Sarmiento, 1991). Stratospheric ozone loss has been another major theme. Stix (1989; NAS, 1992) has discussed multiphoton dissociation of all chlorofluorocarbons in the troposphere through the construction of huge laser assemblages. Cicerone and coworkers modelled the scavenging of chlorine atoms by light alkanes as an approach to rectifying the regional ozone hole phenomenon (Cicerone et al. 1991; Elliott et al., 1994).

Urban pollution has not escaped the attention of atmospheric engineers. The distinguished meteorologist Joanne Simpson suggested as early as the 1950's that local albedo modification might alter flow patterns through the Los Angeles basin, easing the smog problem. Radical chain inhibitors have been investigated as a means to slow photochemical ozone production (Jayanty et al., 1974; Pitts et al., 1977; Heicklen, 1981a and b; Cupitt, 1981; Heicklen, 1985). Even on the urban scale, intervention usually seems too costly or too dangerous (Pitts et al., 1977). The merits of atmospheric engineering studies are the subject of an ongoing and lively debate (Cicerone et al., 1992; Keith and Dowlatabadi, 1992; Elliott et al., 1994). It has been argued both that it is preferable to investigate geoengineering schemes in order to locate their flaws, and that they should be ignored entirely so that research resources can be channeled elsewhere.

Background: Reverse Convection Towers and Smog

The modified convection tower is a recent addition to the urban remediation family. Reverse convection was patented as a power source in 1975 (Carlson), and is being taken quite seriously by developing nations (Coy, 1993). Physical details have been dealt with by Lasier and Jacobs (1983), Krakowski and Miller (1992) and Prueitt et al. (1993). Water is pumped from some convenient source such as the sea, a lake or a river to the tops of hollow cylindrical structures on the order of several hundred meters high. It is then misted, and evaporation of the droplets cools the surrounding air and leads to descent. Turbines placed in the outflow region can harness the

kinetic energy of the moving air mass, and some of that energy can be recycled to supply the pumps. The convection tower is essentially self driven, but is not a perpetual motion machine. The real power source is thermal energy within the atmospheric system, and so ultimately the sun.

Los Alamos National Laboratory has attempted to extend the tower concept to the filtration and cleansing of urban air. Krakowski and Miller (1992) and Prueitt et al. (1993) estimated that a small electrostatic charge applied to the droplets would enable them to scavenge all deleterious smog particulates, even those in the Greenfield gap (Slinn, 1984). A hundred or so towers scattered throughout a smoggy cityscape could process all the urban airshed in on the order of a day, and prevent aerosol buildup. In the present work we investigate the effects of such an engineering feat on the other major component of the smog system, photochemical oxidant production through hydrocarbon oxidation. We also mention some microphysical factors connected with humidity changes.

The tower as cleansing agent has so far been touched upon only in laboratory internal publications and a few popular journals (Glanz, 1992; Dane, 1993). We feel strongly, however, that it is not at all premature to begin assessing real effects. There is a tendency for atmospheric engineering propositions to spend long periods in the draft stages because authors realize that their work will stir controversy. Serious cross examination must sometimes be conducted without the benefit of documentation. The iron fertilization strategy for removal of carbon dioxide to seawater sparked a fascinating dialog in major scientific periodicals (Broecker, 1990; Peng and Broecker, 1991; Sarmiento, 1991) but was never formally delineated by its inventors (Martin et al., 1990). Several of us (SE, RPT) were involved in research on alkane injections into the ozone hole. The alkane plan was both offered and evaluated simultaneously. Our approach is not without precedent, and even if it were would be defensible.

Since the tower filtration system has only been described in the grey literature, we will review it in depth here. The Los Alamos internal publications provide the results of fluid dynamical simulations of reverse convection towers as power generators. Typical water

droplet radii were on the order of 20 microns, and their concentrations were around 100 per cubic centimeter. The size distribution is thus similar to that of a dense cloud (Pruppacher and Klett, 1978; Lelieveld et al., 1989; Lelieveld and Crutzen, 1991). The velocity of flow through the structure reached about 10 meters per second, for a residence time of about 20 seconds. In a coastal city the most convenient source of liquid water would be the sea, and we will focus on seawater as an aqueous phase here, with its pH of 8 and high concentrations of dissolved metals. Freshwater supplies could be tapped for inland cities. In order to complete removal of undesirable particulates, the scavenging droplets would be extracted from the air flow at the tower bottom. This could be accomplished either through a spray of larger water drops, or by attaching an electrostatic demister. By passing the moist air over pipes containing cold water, perhaps obtained below the ocean surface, the humidity rise created during evaporation could be counteracted and fresh water condensed from the original salty source. Pumping seawater from colder layers would require at least some further energy expenditure, however, and the possibility of significant water vapor increases must be accounted for in the outflow.

Photochemical and Microphysical Factors

Air chemistry in a smoggy city undergoes a well known archetypal diurnal cycle (Finlayson-Pitts and Pitts, 1977; Tuazon et al., 1978 and 1981; Hanst et al., 1982; Crutzen, 1988). Morning brings injections of nitrogen oxides and hydrocarbons from motor vehicles. Irradiation of ozone produces the excited singlet D oxygen atom (O^1D), which abstracts hydrogen from water vapor to form the chief atmospheric oxidant, the hydroxyl radical. The hydroxyl in turn attacks the organics, and as they break down oxygen molecules attach themselves to exposed carbon atom sites to form peroxy radicals. Reaction of NO with the peroxy species gives NO_2 , which photolyzes rapidly to generate the ground state triplet P oxygen atom (O^3P). Ground state oxygen recombines in the termolecular sense with the O_2 molecule yielding O_3 . The sequence of chemical events following morning

perturbations has been observed carefully in smog chamber experiments. A sketch of typical chamber results is shown in Figure 1. Ozone levels often rise well into the afternoon. At night, the solar energy source has been turned off and radical chains terminate. The nitrogen oxide radicals successively abstract oxygen atoms from ozone to form NO₂ and NO₃, and the latter two species combine to form N₂O₅. The nitrogen oxides NO₂, NO₃ and N₂O₅ enter into thermal equilibrium at nighttime.

To construct our preliminary analysis of photochemical effects, we trace a few typical air parcels as they move through hypothetical reverse convection towers. As air enters the top of the structure, it comes into contact with droplets in the artificial mist and remains with them for on the order of 10 to 100 seconds. There are several formulations which can be used to estimate the time constant for gases to impact or enter drop surfaces. Wagner (1982) writes for the gas kinetic regime

$$F_k = \alpha \pi r^2 v (n - n_{vp}) \quad (1)$$

for the flux of molecules to a spherical particle. Subscript k signifies kinetic conditions, α is the accommodation coefficient, r is the droplet radius, v is the molecular thermal velocity, n is a number density and subscript vp indicates a vapor pressure just above the condensed phase surface. In the continuum regime

$$F_c = 4 \pi r D (n - n_{vp}) \quad (2)$$

where D is the gas phase diffusion coefficient. The quantity D can be expressed as $v\lambda/3$, where λ is the mean free path. Kinetic and continuum transport are bridged by the combined formula

$$F = F_k (1 + 3\alpha/4K)^{-1} \quad (3)$$

in which K is the Knudsen number λ/r . Turco et al. (1989) and Drdla et al. (1993) have recently applied these quantities to stratospheric

microphysics problems. Lelieveld and Crutzen (1990, 1991) give the related expression

$$(\tau)^{-1} = L((r^2/3D) + (4r/3v\alpha))^{-1} \quad (4)$$

taken from the acid deposition studies of Schwartz (1986). Here τ is a time constant for transfer from bulk vapor to drop, L is a dimensionless liquid water content (volume/volume), and the back pressure is not included. Equations 1, 2 and 3 can be related to 4 if particle surface to volume ratios are inserted. For purposes here we take the rough average thermal velocity value 3×10^4 cm/s and a mean free path of 0.1 microns, representative of pollutant molecules at standard temperature and pressure. Since the droplet radii are much larger than λ , the tower interior falls in the continuum regime. For accommodation coefficients larger than about 10^{-2} , gradients form in the vapor phase around the particles and transport is diffusion limited and independent of α . The time constant for entry into a particle is 1 to 10 seconds. As the accommodation coefficient drops below the 10^{-2} threshold, gas phase gradients disappear, and transport occurs as in the kinetic regime, but with a high probability of reflection from the droplet surface. Vapor removal time scales rise accordingly.

Accommodation coefficients are only poorly understood for most atmospheric species, but broadly speaking, solubles have $\alpha \gg 0.01$ and insolubles $\alpha \ll 0.01$ (Tang and Lee, 1987; Lee and Tang, 1987; Mozurkewich and Calvert, 1988; Worsnop et al., 1989; Lelieveld and Crutzen, 1991). Table 1 takes Henry's Law constants for some key molecules from Schwartz (1984a and b), supplemented for the hydroxyl radical by a wide range of estimates (Chameides, 1984; Chang, 1985; Hoffmann and Jacob, 1984; Hoffmann, 1986). The value for L within the tower is about 3×10^{-6} , so that species with solubility constants below about 10^5 cannot enter the aqueous phase in large quantities even if they equilibrate. Hydrocarbons and the nitrogen oxides are clearly not affected by the tower droplets. It is currently thought that among organics only large bifunctional decomposition products enter the condensed phase of urban aerosols (Grosjean et al., 1978; Hatakeyama et al., 1985). Although measurements have been

exceedingly difficult, both OH and HO₂ are considered solubles with high accommodation coefficients. Furthermore, they are thought to react rapidly in the aqueous phase so that Henry's Law equilibrium is never attained (Graedel and Weschler, 1981; Graedel and Goldberg, 1983; Chameides, 1984; Graedel et al., 1986; Jacob, 1986; Lelieveld and Crutzen, 1991). Removal of the hydrogen oxide radicals may thus be quite efficient. Some stabilization of organics results downstream from the tower outflow. However, HO_x recovery may be rapid. For a typical midday urban ozone concentration of 100 ppbv, and a photolysis constant J of 10^{-6} at wavelengths near 300 nm, O¹D could reach a number density of about 10^{-3} given quenching by molecular nitrogen and oxygen (Atkinson et al., 1989; Demore et al., 1990). Assuming only moderate relative humidity, hydroxyl could be returned via the water vapor reaction to levels typical of polluted areas (10^6 - 10^7 ; Platt and Perner, 1980; Davis et al., 1984; Hubler et al., 1984; Hewitt and Harrison, 1985; Platt et al., 1988; Perner et al., 1989; Mount, 1992; Mount and Eisele, 1992; Brune, 1992) in minutes to an hour. Loss of hydrogen atoms from degrading hydrocarbon skeletons will amplify the rate (Crutzen, 1988; Lelieveld and Crutzen, 1990 and 1991). At night, the nitrogen oxides undergo significant conversion to N₂O₅, which is hydrolyzed with an α of 0.1 (Mozurkewich and Calvert, 1988; Lelieveld and Crutzen, 1991). There could well be conversion of NO_x to nitric acid after sunset within the towers. The EKMA approach has shown that for typical organic concentrations of about one ppm (Stephens and Burleson, 1969; Finlayson-Pitts and Pitts, 1977; Tuazon et al., 1981; Hanst et al., 1982) reductions in NO_x can either raise or lower midday ozone maxima (Dodge, 1977a and b; Dimitriades and Dodge, 1983; Dunker et al., 1984). The actual direction is impossible to predict without a full photochemical calculation. The general morphology of ozone isopleths from EKMA studies is given in Figure 2.

Ozone, the chief smog oxidant, is not itself soluble. Acid rain studies have demonstrated that its reaction with SO₂ in the aqueous phase is a step in the production of sulfuric acid rain and fog (Richards et al., 1983; Munger et al., 1983; Maahs, 1983). Sulfur dioxide may in fact be present in sufficient quantities to titrate ozone in some cities

(Bennet et al., 1985). The high pH of seawater would favor rapid removal of any O₃ inside of droplets (Maahs, 1983; Schwartz et al., 1983). However, the accommodation coefficient is on the order of 10^{-3} (Tang and Lee, 1987), and it seems likely that in the tower configuration sketched here, aqueous uptake would limit removal. If ozone were removed from tower air, the urban photochemical system could probably regenerate it within an hour or two. Observationally, oxidants appear in Los Angeles in a few hours during the daytime (Finlayson-Pitts and Pitts, 1977; Tuazon et al., 1978 and 1981). It is a simple matter to connect the production directly with hydrocarbon oxidation. Imagine a typical multi carbon organic present at a ppm or so. Its oxidation may be initiated through reaction with the hydroxyl at 10^{-12} cm³ molecule s⁻¹ (Atkinson et al., 1989; Demore et al., 1990), and ozone should build up at 10^7 - 10^8 molecules cm³. The timing of tower processing thus becomes critical. If all air in a polluted city basin is processed in on the order of one day, as envisioned in the original Los Alamos documents, only the portion moving through the towers just before and during oxidant generation began would be cleansed effectively. Night and morning cycling would not be beneficial. The diurnal patterns of Los Angeles type smog chemistry may require that an ozone filtration device see air below the boundary layer over the restricted time scale during which ozone production occurs. The number of reverse convection towers would have to be multiplied several times to achieve such turnover rates, sacrificing some of the feasibility of the project.

A microphysical sidelight is worthy of some discussion here as well. Droplet evaporation which cools tower air must also raise the relative humidity. Condenser attachments to reduce RH again may or may not prove practical. It has been demonstrated many times that as the water concentration rises in a smoggy city, visibility suffers (Groblicki et al., 1981; Waggoner et al., 1983; Charlson et al., 1974a and b). One of the major causes is swelling of ammonium nitrate and sulfate aerosol particles (Pilinis et al., 1987 and 1989; Pilinis and Seinfeld, 1987 and 1988; Wexler and Seinfeld, 1990, 1991 and 1992). The convection towers might be removing the inorganic salt particles, but in a polluted city organic oxidation can lead to regeneration of nuclei

as condensables form (Husar and Whitby, 1973). It is conceivable that addition of water vapor to processed air parcels could counteract the visibility enhancements expected from scavenging within the towers.

The chemistry taking place in atmospheric aqueous phases remains very uncertain, and the uncertainties extend naturally to the tower concept. It is thought that the gas phase acts as a source of reactive radicals to droplets, either directly as the OH and HO₂, or indirectly to form the superoxide radical O₂⁻ (Graedel and Weschler, 1981; Graedel and Goldberg, 1983; Chameides and Davis, 1982; Chameides, 1984; Graedel et al., 1986; Jacob, 1986; Lelieveld and Crutzen, 1991). Lelieveld and Crutzen (1991) argue that because formaldehyde forms the stable diol methylene glycol (Finlayson-Pitts and Pitts, 1986), and because clouds can remain in contact with the vapor phase for relatively long periods of time, aqueous phase CH₂O removal disrupts the usual HO_x release along the methane oxidation sequence. Methylene glycol formation and reaction are relevant to the convection tower situation as well because there is sufficient time for removal of solubles. Diol equilibria for other organics are less favorable, however, and most hydrocarbons partition mainly into the gas. Cloud chemistry studies have usually shown that OH and HO₂ entering drops react away rapidly, but their main role appears to be oxidation of soluble inorganics concentrated into the condensed phase (Graedel and Weschler, 1981; Richards et al., 1983; Maahs, 1983; Jacob, 1986). We therefore suspect that water within the reverse convection towers will leave smog hydrocarbons unaffected. This logic should apply to seawater droplets as well despite their high concentrations of metals, particularly in the transition series (Graedel and Weschler, 1981; Graedel et al., 1986). Transition metal complexes may facilitate charge transfer in atmospheric solutions (Taube, 1957; Treinen, 1970; Graedel et al., 1986; Weschler et al., 1986). Investigations into the chemistry of sea spray appear to be rare and so analogies for natural droplets are difficult to come by. The photochemistry of surface seawater, however, is consistent with the notions presented here (Thompson and Zafiriou, 1983; Zafiriou, 1983; Zafiriou and True, 1979a and b, Zafiriou et al., 1984; Zika, 1981).

Summary and Discussion

Engineered remediation schemes have been proposed for pollution dilemmas in all corners of the atmosphere, from the ozone hole (Elliott et al., 1994) to the modern cityscape (Cupitt, 1981). The present study addresses photochemical ramifications of a newcomer to urban pollution engineering. It has been suggested that the reverse convection tower, originally intended as a means for generating electric power (Carlson, 1975), be altered slightly to serve as a cleansing and filtration apparatus for Los Angeles and areas with similar smog phenomena (Krakowski and Miller, 1992; Prueitt et al., 1993). Evaporation of an injected mist drives a down draft sufficient to supply energy for lifting water to the tower top, and mist droplets can be made effective scavengers for most urban particulates through electrostatic charging. Several lines of reasoning indicate that interactions between gases and tower droplets might also reduce oxidant levels somewhat. The hydroxyl and hydroperoxy radicals are likely removed from the vapor phase rapidly into the mist droplets even on the limited timescales available during descent through the towers, and react rapidly in the aqueous phase (Jacob, 1986; Lelieveld and Crutzen, 1991). Oxidation of gaseous hydrocarbons will therefore be inhibited after air parcels exit the convection structures.

Hydrolysis probably removes a significant fraction of N_2O_5 from air processed during the night (Mozurkewich and Calvert, 1988), leading to lower nitrogen oxide levels over the next photolytic period. At the elevated pH of droplets composed of seawater, ozone is likely to react rapidly with sulfur IV in the form of SO_2 (Schwartz et al., 1983). However, other factors point in the opposite direction. Relaxation times for the return of HOx would be in the minute range so that suppression of oxidation cannot last for long. Nitrogen oxide loss could in fact lead to an increase in ozone production under some photochemical conditions (Dodge, 1977a and b). Entry of ozone into the tower mist may be limited by reflection at the particle surfaces.

To sort out the opposing influences of tower engineering on urban photochemistry would require an ambitious modelling effort. The convection structures are essentially point processors on the scale of a

large city, and since both the chemistry and the microphysics involved are highly non-linear, three dimensional simulations would be needed. Chemistry/aerosol models of urban airsheds are expensive to develop and run (Jacobson and Turco, 1993). Other aspects of the convection tower problem would require similar levels of analysis. Local meteorology could in fact be altered. A cool, moist air source in the lower boundary layer could form a density current propagating radially away from bases of the structures. The development of fogs and of low stratus clouds are distinct possibilities (Prueitt et al., 1993). The challenge of waste management has not been dealt with. A solution of smog gases in brine is likely to accumulate at the bottoms of the towers as they are currently designed, and could be costly to dispose of. Models of all these factors would have to be constructed and run prior to any implementation, and perhaps before testing could commence. Even if such a collection of calculations were to be commissioned, experience with other atmospheric engineering notions teaches us that their results may not be trustworthy (Cicerone et al., 1991 and 1992; Elliott et al., 1994).

Like all large scale engineering fixes for pollution problems, the tower proposal faces a set of fundamental obstacles. The effects of a system of a hundred reverse convection towers on Los Angeles type smog may be too complex to simulate with confidence at present. Unfortunately, confidence in model results would be demanded by residents of any city contemplating a filtration technique. Total costs for the project would likely be on the order of the building of dozens of new skyscrapers simultaneously, and may well be too vast for the pocketbooks of those it is supposed to benefit. Expense is the rule in atmospheric engineering, and is simply a manifestation of entropy principles; it will often be easier to make messes than to clean them up.

Our analysis here might seem to indicate that time and resources could be saved by simply ignoring environmental engineering schemes as they come before the atmospheric community. We do not view this as a viable option. Engineering concepts will necessarily continue to arise as we enter the era of global change, driven if nothing else by anticipation. The chance that one of them might move into the realm

of testing and implementation will motivate scientists, technologists and inventors alike. Technological solutions to environmental problems have after all been the hallmark of our species for thousands of years. If trained, mainstream professionals do not accept responsibility for evaluating new propositions, initiative will pass to the fringes of the atmospheric community. This situation could prove wasteful or dangerous. We feel strongly that atmospheric engineering ideas should be debated in the open scientific literature, however controversial they may be.

Acknowledgments

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Appendix

A simple point balance thermodynamic model may be helpful in elucidating the operation of the convection towers. The equations below refer to the attached Figure A-1. Air of humidity H_o (kg H_2O /kg air) enters the top of a tower of height l (m) at a temperature T_o (K) and mass flow rate G_g (kg/s) to be humidified to H_l (kg H_2O /kg air) and temperature $T_l < T_o$ by water injected at a mass flow rate G_l (kg/s). Mass balance at the top humidifier section gives

$$H_l - H_o = \frac{G_l}{G_g} . \quad (A-1)$$

If Δh_v (J/kg) is the heat of vaporization of water and the heat capacity is c_p (J/kg K), an energy balance across the top-side humidifier section results in the following relationship between temperatures and humidities:

$$T_o - \frac{H_l + 1}{H_o + 1} T_l = \frac{H_l - H_o}{H_o + 1} \frac{\Delta h_v}{c_p} \quad (A-2)$$

The density difference $\Delta\rho/\rho_o = T_o/T_l - 1$ drives a buoyant force that creates a down draft with velocity v_1 at the base of the column given by

$$\Delta p = g\Delta\rho l = \rho_o v_1^2/2 \quad (A-3)$$

The flow power per unit cross-sectional area of the column, $A_g = \pi R^2$ is

$$\frac{P_F}{A_g} (W/m^2) = \sqrt{2} \left[g l \frac{\Delta\rho}{\rho_o} \right]^{3/2} \rho_o . \quad (A-4)$$

With the power needed to pump water to the top of the tower being $P_l = gl G_l$, the efficiency of the pump being η_{pump} , and the efficiency with which P_F is converted to electrical power P_{ET} being η_T , the recirculating power fraction is defined by

$$\varepsilon = \frac{P_l / \eta_{\text{pump}}}{\eta_T P_F} = \frac{H_i - H_o}{\eta_{\text{pump}} \eta_T} \quad (\text{A-5})$$

With v^* defined at $\sqrt{gl}$, the following expressions give the driving density difference, the specific flow power, the mass flow rate, and the flow velocity, respectively:

$$\frac{\Delta \rho}{\rho_o} = (H_i - H_o) \frac{\Delta h_v}{c_p T_i} \quad (\text{A-6})$$

$$\frac{P_F \left(\frac{W}{m^2} \right)}{A_g} = \sqrt{2} \rho_o v^{*3} \left[(H_i - H_o) \frac{\Delta h_v}{c_p T_i} \right]^{3/2} \quad (\text{A-7})$$

$$\frac{G_g \text{ (kg/m}^2\text{s)}}{A_g} = \sqrt{2} v^* \rho_o \left[(H_i - H_o) \frac{\Delta h_v}{c_p T_i} \right]^{1/2} \quad (\text{A-8})$$

$$v \text{ (m/s)} = \sqrt{2} v^* \left[(H_i - H_o) \frac{\Delta h_v}{c_p T_i} \right]^{1/2} \quad (\text{A-9})$$

In addition to the efficiency with which the flow power, P_F , is converted to net-electric power, $\eta_p = \eta_T(1 - \varepsilon) = P_E/P_F$, the following two expressions give the efficiency η_F with which latent heat is converted to flow energy, and the ideal Carnot efficiency η_c :

$$\eta_F = \frac{P_F}{G_l \Delta h_v} = \frac{gl \Delta h_v}{H_i - H_o} \quad (\text{A-10})$$

$$\eta_c = \frac{T_o T_i}{T_o} = 1 - \frac{H_o - 1}{H_i + 1} + \frac{H_i - H_o}{H_o - 1} \frac{\Delta h_v}{c_p T_o} \cong (H_i - H_o) \frac{\Delta h_v}{c_p T_o} \quad (\text{A-11})$$

Lastly, the efficiency η_T with which the flow power, P_F , is converted to electricity, P_{ET} , is estimated using the ducted-propeller geometry depicted on Fig. A-1. Under the assumption of incompressible, inviscid flow, and with v_i and p_i the velocity and pressure at the i^{th} station indicated on Fig. A-1, the force on the slug of fluid bounded by entrance surface #1, exit surface #2, and the horizontally flared streamlines is equal to $\sim \rho_o Q (v_1 - v_4)$, where $Q (m^3/s) = v_i A_i$. Since the only retarding force is that across the propeller, $A_2(p_2 - p_3)$, where $A_2 = A_3$, it follows that

$$p_2 - p_3 = \rho_o v_2 (v_1 - v_4), \quad (\text{A-12})$$

where the assumption of incompressibility and $A_2 = A_3$ results in no velocity change across the propeller. Application of Bernoulli's equation between surfaces #1-2 and #3-4 gives, respectively

$$p_1 - \rho_o v_1^2/2 = p_2 + \rho_o v_2^2/2 \quad (\text{A-13})$$

$$p_3 + \rho_o v_3^2/2 = p_4 + \rho_o v_4^2/2 \quad (\text{A-14})$$

where upon adding leads to

$$p_1 - p_4 + \rho_o v_1^2/2 = (p_2 - p_3) + \rho_o v_4^2/2 = g \Delta p l \quad (\text{A-15})$$

Multiplying by $Q = v_i A_i$ to express equation (15) in terms of power, recalling that $P_T = Q(p_2 - p_3)$, using equation (12), and defining $\eta_T = P_T/P_F$ gives the following expression for the turbine efficiency:

$$\frac{1}{\eta_T} = 1 + \frac{(A_2/A_1)(1 - \eta_D)^2}{2 \eta_D} \quad (\text{A-16})$$

where $\eta_D = 1 - A_1/A_4$ is a measure of diffuser efficiency; for $A_1 = A_2$ and $\eta_D = 0.5$, the turbine efficiency is $\eta_T = 0.80$, which is the value used for the following numerical example.

A convection tower of height $l = 200$ m and radius $R = 100$ m is used to evaluate the scaling relationships developed above. The ideal case of a bone-dry ambient air ($H_o = 0.0$) is chosen to maximize power and air throughput for a given tower size, although the optimism of the scenario should be kept in mind. Furthermore, saturation conditions at the humidifier exit are assumed, which for $T_l = 300$ K (70°F) corresponds to $H_l = 0.022$ kg H_2O /kg air; this is also optimistic, since water droplets (rain) in the tower, although possibly desirable for particulate scrubbing, will add to the recirculating power required by the water pumps. Also, heat loss through the tower walls to the hotter ambient is ignored. Other physical parameters are listed in Table A-1. Evaluation of Eqs. (A-1)-(A-16) gives the parameters in Table A-2 for $l = 200$ m and $R = 100$ m.

If a 1-km height of atmosphere is to be cycled through this tower once every week and the convection tower operated at full capacity 75% of the time, each tower would service an area of 360 km^2 (19×19 km). Using the same capacity factor and expressing the once-through water usage per unit area of land served results in 1.37 m/yr . If such a tower reduced the particulate concentration from $100 \mu\text{g/m}^3$ to $50 \mu\text{g/m}^3$ a total of 943 tonne/yr of particulate material would be removed.

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Table 1. Rough values for Henry's Law constants for several atmospheric species, in units of Molar(liquid phase)/Molar(gas phase). In the third column a minus sign indicates that the species would not be partitioned into the liquid phase in reverse convection towers, a plus sign that it would.

O ₂	10 ⁻²	-
O ₃	10 ⁻¹	-
NO	10 ⁻¹	-
NO ₂	10 ⁻¹	-
HNO ₃	10 ⁷	+
HO ₂	10 ⁵	+
OH	10 ³ -10 ⁶	+
H ₂ O ₂	10 ⁷	+
PAN	10 ²	-
C ₂ H ₄	10 ⁻¹	-

Table A-1. Some physical parameters for a generic tower operation calculation.

- $\Delta h_v = 580 \text{ cal/g} = 2.43 \times 10^6 \text{ J/kg}$
- $c_p = 0.25 \text{ cal/g K} = 1,040 \text{ J/kg K}$
- $\rho_o = 1.18 \text{ kg/m}^3$
- $\Delta h_v / c_p T_i = 7.5$

Table A-2. Results from a generic tower operation model. Values in brackets [] correspond to 50% ambient relative to H_t .

- $G_g/A_g = 30. \text{kg/m}^2 \text{ s} [21.27]$
- $P_F/A_g = 9,617. \text{ W/m}^2 [3,400.]$
- $v = 25.3 \text{ m/s} (91 \text{ km/hr, } 57 \text{ mph}) [17.9]$
- $A_g = \pi R^2 = 3.14 \times 10^4 \text{ m}^2$
- $G_g = 9.4 \times 10^5 \text{ kg/s} (2.87 \text{ km}^3/\text{hr}) [6.6 \times 10^5]$
- $G_l = 2.07 \times 10^4 \text{ kg/s} (20. \text{ Mgal/hr}) [7.3 \times 10^3]$
- $P_F = 30.2 \text{ MW} [10.7]$
- $P_{ET} = 24.2 \text{ MWe} [8.5]$
- $\epsilon = 0.034 (\eta_T = 0.8, \eta_{\text{pump}} = 0.8)$
- $P_E = 23.3 \text{ MWe} [8.2]$
- $\eta_F = 0.037$
- $\eta_c = 0.165 [0.083]$

Figure Captions

Figure 1. A schematic of ozone and oxidant production after irradiation of organic mixtures in smog chamber experiments. The acronym PAN signifies peroxyacetylnitrate.

Figure 2. Daily ozone maximum contours from empirical kinetic model investigations with varying nitrogen oxide (NO_x) and nonmethane hydrocarbon (NMHC) levels.

Figure A-1. Rendering of the convection tower model adopted in the Appendix equations.

Figure 1

Figure 2

Figure A-1