

Assessment of the Global and Regional Importance of Missing Atmospheric Oxidants, the Hydro Oxygens; Are they more Important to Earth's Ecosystems' Stability and Economy than currently thought? Introduction of the "Oxygen Earth Protocol"

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Abstract

The emergent discipline of Chemical Meteorology explores the interstices between Meteorology and Atmospheric Chemistry. Not only does Chemical Meteorology investigate in greater depth the mechanics of chemical interactions in the atmosphere, but it can also effectively address political, sociological, economic and industrial issues that are growing in urgency each day. It is our working hypothesis that the system of oxidative interactions in the atmosphere largely explains how homeostasis is attained. Oxidation chemistry permeates the ozone layer, is fundamental to the Chapman Cycle and, below the Tropopause, helps to explain the absorptive capacity of the atmosphere for manmade pollutants down to sea level. Taking six vital points of reference from Chemical Meteorology and oxidation chemistry specifically, the author constructs an experiment to demonstrate that a fairly simple remediation can arrest the seemingly-inexorable process of global warming and climate change. Practical implications are discussed and a working prototype installation is presented.

Keywords: volatile organic compounds (VOC's), particulate matter (PM), infinite solubility, oxidation, photolytic

Introduction

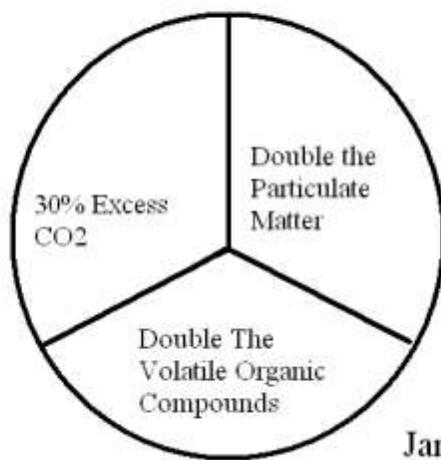
The disconnection between Atmospheric Chemistry and Meteorology results in a failure to understand how the oxidative medium in the atmosphere mediates frontal and weather events. Chemistry and Meteorology are proposed as complementary because they share such concerns as solar bombardment, cycles and events, and pre-existing conditions. They also scrutinize variations such as ocean proximity, landmasses, ice masses, and the effects of these on plant life activity on land and in the oceans.

Both atmospheric chemistry and meteorology also share concerns with the millions of tonnes of emissions and effluents that result from human activities, chiefly the burning of hydrocarbons. This is important because matters of atmospheric pollution will continue to alter both of these disciplines and both disciplines must acknowledge this critical commonality.

Figure 1 (below) is compiled from various sources and depicts the atmospheric effects of carbon-based problems. A cursory inspection suggests that human activity bears the greater

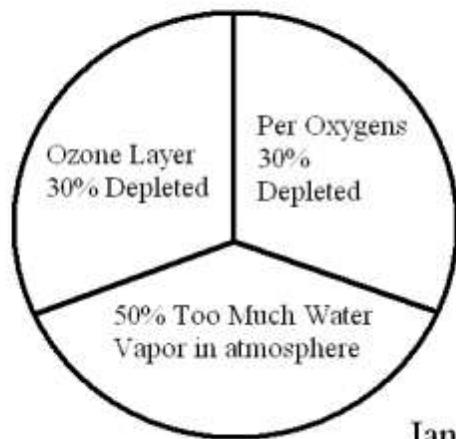
responsibility rather than other natural phenomena such as sunspot activity.

Global Carbon Based Problems



January 2007

Global Solvent & Oxidant Pie



January 2007

Figure 1. Adopted from NASA, BAS, WHO, WMO, UNEP, and Environment Canada data.

The composition of atmospheric pollutants and the effects on gaseous oxidants and solvents affirms the common ground of chemistry and meteorology. Most scientists in these two disciplines will recognize that the primary link between oxidation and hydro-geological cycles lies in the fact that oxidizers such as O^{-2} , OH^{-} , HO_2^{-} and H_2O_2 are infinitely soluble in water and found in all phases of the hydrological system except for oxide. Carbon based problems also loom large.

Yet a third reason for Chemistry and Meteorology to give due importance to their common ground in Chemical Meteorology concerns the consequences, detailed below, of atmospheric pollutants and related phenomena:

General Characteristics of Global Problems

1. 30% Excess CO₂

- Increased ocean acidity (Caldeira et al, 2005).
- Proliferation of inferior plants.
- Calcium based ocean life weakened due to change in pH conditions needed for healthy skeletons.
- Change in radiative and reflective properties of upper atmosphere.
- Increased greenhouse effect interferes with egress of heat from Earth at night; possibly contributing to desertification and drought.

2. Double particulate matter (PM) levels

- Many problems are associated with particulate matter including depletion of per oxygens, causing respiratory problems for all aerobic life forms.
- PM also blocks the venting of heat from the atmosphere.
- PM contains exotic human induced elements and molecules which add to the electrochemical and electrostatic imbalance of air masses that are now missing an electron, thence accepting oxidizers which normally buffer injections of unusual compounds from volcanoes and fires.
- Blocking of sunlight by PM decreases the ability to form both Ozone and Hydroxyl radicals at certain frequencies of sunlight.
- PM also requires oxidation to scrub most of it from the atmosphere effectively either by direct contact or in clouds, so another runaway depletion of cleansers is initiated by excess PM.

3. Double Volatile Organic Compounds (VOC) levels

- VOC's come from fuels and plants; mankind employs many volatile fuels and solvents on a wide scale and this is exacerbated by ignorance about how much is released on every usage occasion.
- Plant life emits solvent like terpenes, particularly climax species evergreen trees. These have also been detected among cattail and when deciduous trees form sticky buds. Terpenes are carbon chain molecules which are normally broken down by oxidation, sun, and water in the correct proportions.
- Volatile compounds block the release of heat from the atmosphere by physically blocking and absorbing thermal heat and converting most of it to mechanical energy; this is known as "steric hindrance".
- VOC's are primarily controlled by robust or even normal amounts of oxidants in the form of OH, HO₂, and H₂O₂.
- Methane is a VOC and is 21 times more potent as a greenhouse gas than carbon dioxide. Moreover, methane requires a great deal of OH and oxygen to eventually break down into CO₂ – and only after 11 years –via a complex chemical pathway tree.

4. Ozone Layer Depletion

- Occurring faster than previously thought prior to 1996 (6 NASA MTPE UARS).
- UVA and UVB radiation can be hazardous to normal plant growth.
- Increased UVA and UVB radiation puts humans at a higher risk for certain cancers.
- Changing the Arctic and Sub Arctic ecosystems by harming slowly metabolizing plants and mobile animal species that relocate.
- A major reservoir of Hydroxyl radicals is the Ozone Layer, and supports general ozone formation due to sunlight. This fully coupled safety net is being eroded by the disappearance of the Ozone reservoir and shielding.

5. 50% excess H₂O

As greenhouse warming increases, the atmosphere's holding capacity for water vapour also increases (Mitchell, 1989). An increase in atmospheric water vapour concentration has numerous detrimental effects, including, but not limited to,

- Alteration and/or exacerbation of periods of precipitation and location of precipitation events.
- Drastic electrochemical and chemical differences in intermixing regional weather fronts as a result of increased pollution pulses (i.e. smoke stacks, large urban area emissions) into the water vapour.

- Violent energy potentials, which result from water vapour's increased specific heat energy.
- Difficulty in weather prediction due to the disturbance of regular meteorology systems.
- An imbalance in the biosphere's overall current deficits and excesses, more specifically a loss of peroxygen compounds in the atmosphere since a 50% increase in H₂O is not necessarily accompanied by a 50% increase in peroxygen compounds.
- A loss of peroxygens. Peroxygens play a key role as electron acceptors since they have a -4C to -20C freezing point. This freezing point is reached inside large cumulus clouds and allows precipitation to fall as rain or snow, thus allowing precipitation to assist in cleaning the atmosphere in colder weather fronts.
- Increased particulates (especially VOC's) in the atmosphere due to the excess water being deprived of oxidants. These oxidants have a direct impact on the atmosphere's oxidizing potential. Slightly oxidized hydrological cycles are very important in maintaining clear air and seasonable weather events.
- More cloud cover, which may deter the formation of ozone, thus diminishing the atmosphere's reservoir of hydroxyl. Peroxygens are able to regulate lower ozone levels, but with the loss of per oxygens, a runaway global air cleanser loss cycle is likely to be created.
- If the continuous production of combustion sponsored carbon monoxide, arguably known as a massive oxidant sink, one can extrapolate that the system is greatly skewed in favour of these depletions.

6. Oxidative layer depleted by 30%

- Depletion is estimated to match that of the upper Ozone Layer in magnitude. Such a relationship is vital as Ozone is a source for monatomic oxygen (of varying energy levels; O-, possibly O⁻²) which pairs with hydrogen split from water to form two hydroxyl radicals.
- The same process occurs lower in the troposphere amongst the more polluted and complex injections of human waste products from industry; here, the ozone-hydroxyl relationship is complicated by the presence of nitrous acid and nitrogen monoxide. The nitrous acid is a reservoir of OH at night while NO is a depletor of OH in sunlight. In net, there is no notable overall gain of oxidants for removal of human generated pollutants.
- There is a sunlight source of hydroxyls via Ozone breakdown as well as water splitting. One might predict that the extra water in the atmosphere is splitting into more OH and the freed hydrogen combines with free oxygen. But since the sun's radiation through to the troposphere is altered, (dimmed), the necessary wavelengths for these events has been altered by PM and VOC absorption and distortion.
- Almost 80% of all human waste is injected into the atmosphere. This includes PCB's and HCFCs which both directly deplete oxidants. In particular, long lasting chlorine and

fluorine blocks the formation of ozone, which is coupled to the reservoir of OH radicals. This is a rupture of a great magnitude with dire consequences for the long-term depletion of stratospheric Ozone

- The solar sponsored formation of OH radicals is not as productive as the Ozone aided reservoir, yet it is being essentially relied upon to generate enough OH to maintain clear air while far too much particulate exists. Mankind becomes increasingly dependent on sunlight alone to remove Methane and VOC's through these pathways. Also anticipating that it helps with precipitation of excess water vapour, buffers an excess of positively electrically charged elements and molecular wastes, and, perform, if possible, some other key biochemical and geochemical-meteorological cycle functions discussed next.

CHAPTER 1: Role of Oxidants in the Atmosphere and Other Natural Processes

Introductory Treatise: for Global Oxidation Events in Consideration of Planetary- Chemical Meteorology and Organic Cycle Regulation in Key Oxidative Processes.

Commonalities between Meteorology and Chemistry of Planet/Atmosphere

Whilst more astute scientists will surely be able to expand on this list, Chemistry and

Meteorology clearly study many of the same phenomena:

- Temperature change
- Pressure change
- Electrochemical potential
- Electrostatic potential
- Stoichiometric phenomena and their properties
- Impurities and stranded or rogue chemical species
- Volcanic eruptions
- Oceanic currents
- Wetland processes
- Trade winds
- Extreme convection
- Urban congestion
- Urban heating

- Van der Waals forces
- Steric hindrance
- Osmotic pressure
- Gas laws
- Diffusion events: heterogeneous and by air, lightning, static and electrochemical energy of atoms and molecules
- Cosmic matter accumulation (often received and handled by oxidants and per-oxidants).
- Chemical polarity
- Deserts, land, poles, oceans and their juxtapositions
- Transpiration from plant life
- Seasonal variations
- Oceanic and water convection
- Rotation of the Earth and Lunar orbit
- And, more indirectly, the underlying causes of concentration or diversity of species

Synoptic meteorology is now validating unusual changes in these and other facets all over the world. Atmospheric Chemistry studies also confirm departures from norms in relation to chemical species changes as well as changes in many of the above aspects of chemical behaviour. This supports the suggestion that Chemical Meteorology may be a valuable lens not only for observing past and current environmental changes, but also for predictive modelling.

Meteorology itself explains the multiple roles of peroxides in global atmospherics. For example, one understands better the rationale for analysis of peroxide concentrations in ice and snow fields. That a global cooling protocol is needed to conserve our ice reservoirs rests on the knowledge that when sunlight sublimates the frozen water in snow, it also manages to cleave a great many water molecules and form massive numbers of hydroxyl radical cleansers. These disperse and keep the surrounding air pristine. This is an overlooked reservoir on a global scale. We now have learned that the best models predicting global warming induced ice loss are inaccurate underestimates by about 66% which may signal the loss of a massive hydroxyl reservoir heretofore unrecognized in ice packs (IPCC, 2007).

Such release of hydroxyls likely also contributes to regional weather over mountains and the snow pack, helping the repeated cycling of precipitation and air cleansing. This is all done with the help of sunlight and the behaviour of per oxygen in super-cooled zones in clouds. Such favourable effects are extended by the intermediate state HO_2 , which has a much longer lifetime of up to six hours and is an excellent reservoir for OH. This means that OH could travel up to 20 miles and even further across land before it reacts with pollution.

Geographically Determined Chemical Composition of Atmosphere is Changing

As a result of unintended and undesirable chemical and meteorological conditions, desert and drought areas have a high tendency to expand and intensify. These changes in chemical and meteorological conditions have an impact on the climate of an area, causing the land to gradually but inexorably lose moisture and plant cover, resulting in extreme desertification and barrenness. This desertification has occurred in sub-Saharan Africa and parts of Asia. It is not likely that releasing oxidants in these areas will have a significant impact on restoring the already oxidized, barren soil. Strategically released per oxygens are more likely to have a positive impact, as they can travel through the atmosphere until they encounter a moisture laden system to dissolve into, thus promoting precipitation that could aid in shrinking these deserts. Field experiments will be needed, however, to prove the validity of this conjecture.

Precipitating Events and Their Dissipation

The lifetime of peroxygens averages one second. This means that an electron from another chemical or molecule is accepted and thus the electron is neutralized very rapidly. This phenomenon is in fact a vital one since peroxygens take on the role of electrochemical buffer by reducing the positive electrical surplus that would otherwise create turbulent contrast when fronts of different total charges collide. The figure below illustrates contrasting scenarios associated with pre-industrial versus industrial age PM effects.

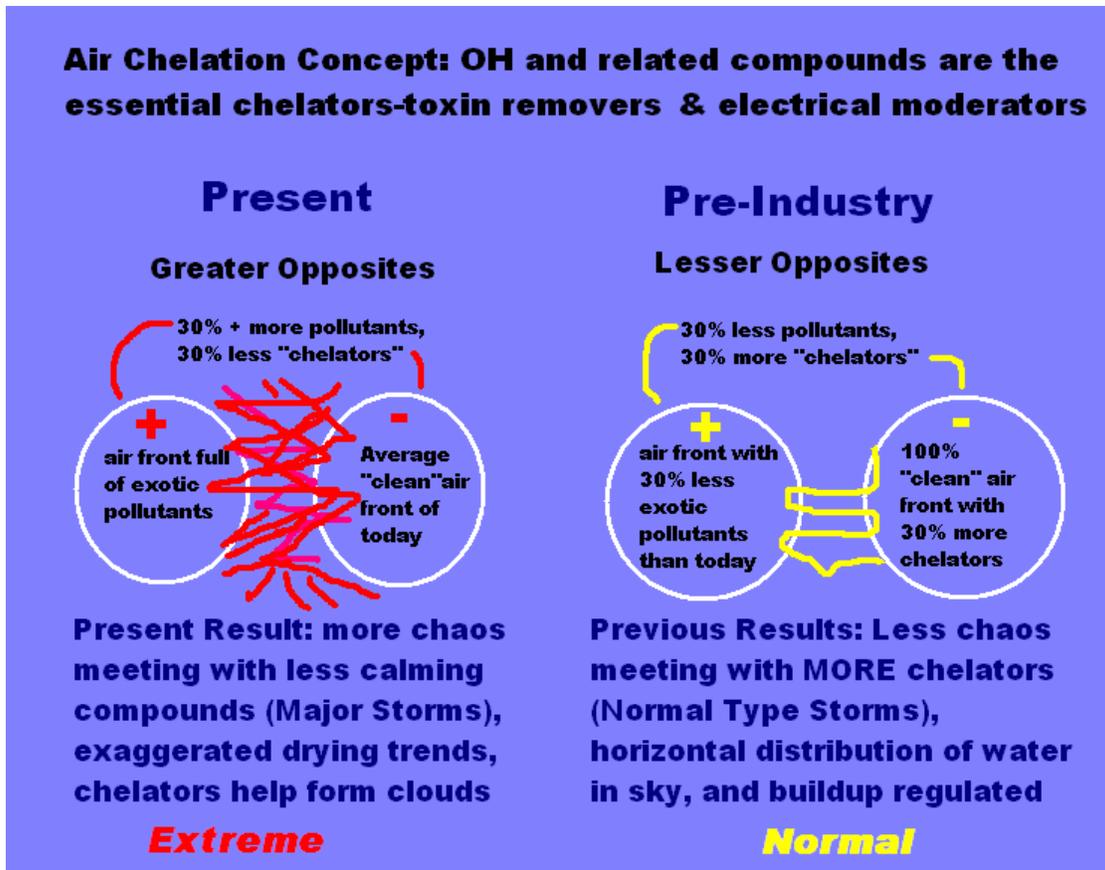


Figure 2.0 This describes the concept of buffering electrical differences in cloud fronts which come into contact. It is suggested that the peroxygen compounds, as electron acceptors, neutralize electrical charges as well as combine with and remove charged particles from the atmosphere both inside and apart from clouds (known as wet and dry deposition). This process is vital to the natural system for removing both common and rarer compounds from the atmosphere to the benefit of respiring life forms. The fate of such peroxygen mechanism has far-reaching impact, given a situation where persistent effluents such as PCB and CFC compounds are found even in such unlikely repositories as the blood of Polar bears.

Global Circulation

Another important fact is the rapid dispersal of particulate matter (PM) in the lower atmosphere, below the Tropopause. Analysis of PM traceable to volcanic effluvia and nuclear events suggests that these take only two weeks to disperse around the globe (this is known as the global circulation model in climate science circles, or GCM). What are the potentially dire

long term implications then of a 1994 finding (see Figure 3.0 below) that over two-thirds of waste from all human activity is released into the atmosphere?

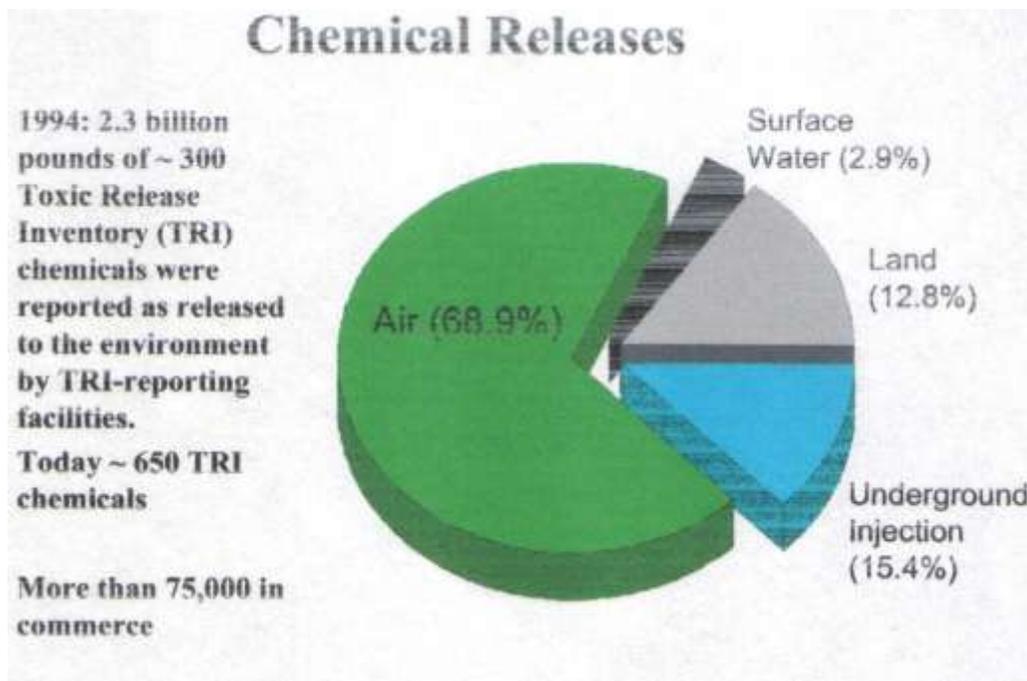


Figure 3.0 The data from 1994 speaks for itself. The situation has likely worsened since then because while a few companies have invested in capping identified persistent compounds, their efforts have far outstripped by industrial growth (as witness China). This is because the halide group – chlorine, bromine, and fluorine in particular – is very potent and persistent as solvents and intermixes all the way to the upper parts of the stratosphere, where they break down ozone because their electrochemical **bonding properties outrank the bonds within other chemical groups** and the ozone molecule itself.

Solar Fluxes: Are They to Blame?

Within the context of the subjects addressed by this paper, the argument that solar activity is responsible for one or more of these changes is not completely sound. While solar action is more likely to have the effect of increasing the number of excited or cleaved oxygen-(yielding ozone) and cleaved water molecules-(producing hydroxyl radicals), hydroxyls and peroxygens

continue to be depleted in the face of excessive moisture in the atmosphere. Solar radiation obviously does not work as expected and cannot therefore be considered as the most important influence. It suggests that depleting chemicals are the cause of the disappearing oxidative layer.

Global Warming

The global warming trend has been observed and measured in a variety of well-publicized ways. Arresting and reversing the trend is a Herculean effort because the antecedents are many. For one, the adverse impact of higher levels of CO₂ and other greenhouse gases is aggravated by the other five global problems outlined in Figure 1.0. Secondly, increased solar activity or the reduced solar shielding that an eroded ozone layer affords seems certain to accelerate the long term rise in global temperatures.

CHAPTER 2: Correcting the Six Major Problems

30% Excess CO₂

Cap CO₂ levels in the atmosphere by separating it from the rest of the smokestack gases and reducing it into recyclable pure and “clean” carbon.

Doubled levels of particulate matter

Initiate reduction strategies through cleaner burning across the board, ranging from vehicle emissions to indoor wood heating systems and mobile sources of carbon based fuels. Using pure carbon based transport fuels and fuel cell technology with no significant emissions is important.

Double VOC levels

Educate the refining, chemicals, metals and petrochemicals industries on the importance of conserving volatile fuels, including CO₂, and preventing them from escaping into the atmosphere. Promoting more complete combustion of fuels will greatly reduce the amount of VOC's in the air and this technology is improving.

Depleted Ozone Layer

We have been reversing the release of CFC's and other halide-based compounds, which displace Ozone. However, we must also recognize the link of ozone to the hydroxyl radical system at all altitudes, given that hydroxyls are formed when free oxygen from ozone is attached to a hydrogen atom coming from water cleaved by specific sunlight wavelengths.

50% excess H₂O

Industry continuously pumps peroxygen-depleted water into the atmosphere in the millions of tonnes each year (cooling towers also add de-sludging chemicals to this gaseous water injection). If the general peroxygen count in the water is brought to normal, 1ppm, precipitation would not be as excessive and this would help in bringing down atmospheric temperatures as well. Our calculations show that if 5MT of Hydro Oxygens was restored to the 1 km above ground environment globally, 1.35×10^5 MW (or mega joules) of energy would be absorbed. In addition, such an "infusion" of Per Oxygens would go a long way toward ensuring that night time heat venting ability of the troposphere be restored. Given such beneficial results hypothesized, it would seem incumbent on the IPCC to model this remediation to check for a reduced incidence of severe climate and weather events and a long-term global cooling effect over 10 to 50 years.

Oxidative gas layer depleted by 30%

The David Suzuki Foundation and others insist that we should now shut industries completely down to address this problem. This seems rather an extremely hard line and alarmist stance, but it could also be prophetic.

Summary

While hydro-geochemicals are not organic, peroxygens react so effectively with organic compounds that they have evolved into the natural atmospheric detergent. They add potency to the cleaning action of water with properties which enhance and regulate the hydrological and organic systems of Earth. They are intermediate "linking" species. We may, by identifying all these enhancements in more depth than this treatise is prepared to go into, adjust our stewardship to include the maintenance of peroxygens through cleaner processes and, in emergencies, restore them directly in order to maintain equilibrium between physical regions.

The technology is readily available. It is suggested that we are in an error phase at this time. Beyond defining the extent of disequilibrium, this paper proposes measures to rebalance the activities of mankind and industry on one hand and do so in alignment with the complex biosphere required and intrinsic to all life.

CHAPTER 3: Weather and Climate Issues: Treatise on Sudden Inclement Weather Forcing

Summary

Many anthropogenic aerosols do not participate in cloud droplet formation. This section will critically investigate the reasons for aerosol build-up, particularly near densely urbanized areas. In addition, peroxygen compound's significant role in healthy cloud models and pH balance will be proposed, and related to sudden rain and hail forcing. This may be due to thermosphere scale and mesoscale peroxygen, as well as pH imbalances in the gas and water phases of two or more interacting air fronts. Gas and water phase changes of interacting air fronts are the changes in the layers or regions of the atmosphere that may contribute to sudden weather events. This discussion will incorporate the recognized one-second rule for the main atmospheric oxidant, HO*, into air front interaction anomalies, and suggest a possible weather-forcing problem relating to the presence of CO₂ at high altitudes. The at-ground value of CO₂ capture will be related to peroxygen radicals in a potentially pivotal manner, reinforcing our need to make use of CO₂ to make peroxygens, rather than allow its dispersal to the air to participate in chaotic atmospheric dynamics at great cost to our overall quality of life.

In 2003-2004, the World Climate Research Program group of 68 scientists published their findings that the global average water vapour concentration has increased 75% over the past 50 years, particularly at altitudes between 3 and 30 miles (Resources News, n.d.). Such water density hampers photolysis of NO₃, acetone, and other VOC's which are reservoirs for OH in the modern atmosphere. At the same time, the decade long time frames build-up of particulate matter at these altitudes may be creating steric hindrance for well-known basic reactions involving Peroxygen compounds. The clean tropospheric reaction of $O_3 + hv \rightarrow O(1)D + O_2$ then $O(1)D + H_2O \rightarrow 2OH$, (Thompson, 1983) is just one example, where the change in anthropogenically induced water content and hydrogen concentration alone can facilitate a liquid phase quenching of this source. This may be so because more UV radiation is reaching lower altitudes because of major CFC caused O₃ depletion. The photoelectric effect of this radiation can enable the reaction $H_2(aq) + 2OH(aq) + 2e^- \rightarrow 2H_2O(aq)$. Photoelectric effects on atmospheric constituents play a role in electrical charge of air masses in the troposphere. Hence, this treatise discusses how human activity has affected the ionic budget and regional

electrodynamics. The radiative dynamics have an infinite combination of possibilities, but in general, science is recording a departure from a relative homeostatic cycling of weather systems to a more chaotic tendency in weather events.

The giants of quantum physics – counting Planck, Einstein, Compton, and Bohr – refer to a one-second unit of energy as a watt or joules/second. E is a photon which can change the orbital state of an electron. An electron's rest mass is 6×10^{-31} kg. For example the work function of the Hydrogen atom-its binding energy of its electron is found at 13.6 eV. The point to remember is that the hydroxyl standard lifetime is considered one second, so it is a timeframe of significance when discussing radiative *and* energy forcing at all atmospheric levels.

It takes 213 photons to excite the electron orbit in a hydrogen atom and 250 photons to make one joule/sec or watt. In terms of the photoelectric effect of the sun, we have therefore quantified a one-second unit of power.

From 1400 watts/M² at the sun's surface, energy is stepped down through the earth's atmosphere to become 168 watts/M². Accounting for total planetary surface, therefore, the earth receives 13.644×10^{21} photons per M² per second. The Earth's surface re-radiates 66.83×10^{20} photons/M²/second, or, 135 watts/M²/second. The gas and particulates in the atmosphere are therefore subject to both incoming and outgoing radiation.

Both the photoelectric effect and oxidizing capacity are, however, affected and degraded by industrial emissions. It is recommended that further study relating to both how many watts/M²/second there are- just below urban pulse maximums. This also should be verified also at 5, 15, 50, 100, 250, and 500 Km, in order to parameterize the step down of solar power through the atmospheric layers. A campaign to quantify peroxygen compound concentrations and how they are functioning at the mesoscale and urban regional levels correlating with this would be helpful.

Photolysis takes into account energies smaller than this, both in neutrino and other sub atomic energy units. Even then, such energy is sufficient to influence the breaking or creation of atomic bonds.

These energy transfers include collision of atoms and molecules by thermal and photo-bombardment excitation. Under clean conditions, this activity could be considered fundamentally homogenous until it builds to the one-second time frame unit of atmospheric energy dynamics. But when there is large scale anthropogenic introduction of particulate matter, steric hindrance may be a significant factor in slowing down abstractive and oxidative transactions that are assisted by collision, radiative effects, and photolysis.

It would be best to permanently remove CO₂ at the same time that particulates are removed, so that a thermally-balanced recovery is achieved. Since the photoelectric effect unit is 1e or higher generally, intra-cloud or air front E- exchanges might be dramatically enhanced or alternately blocked if the air front is saturated with NO_x, SO₂, PM, and hydrocarbons, which describe a typical emission stream from an urban region. Anthropogenic convection at this scale produces front waves containing these constituents. At high NO_x levels, above 300 ppm, these wave fronts have a major fomenting effect in terms of acidity, where hydrogen abstraction is facilitated and oxidation is suppressed.

Another well-known reaction which may be responding to the enhanced photoelectric effect is: $\text{H}_2\text{O}_2 (\text{aq}) + \text{H}_2 (\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} (\text{aq})$. To remove these constituents, oxidation is generally required.

Figure 4, NASA, GTE, shows an assessment of the atmospheric lifetime of four groups of VOC's, mainly human propagated.

| | τ_{OH} (win) | τ_{OH} (sum) | τ_{O_3} (win) | τ_{O_3} (sum) | | τ_{OH} (win) | τ_{OH} (sum) | τ_{O_3} (win) | τ_{O_3} (sum) |
|---------------------|----------------------|----------------------|-----------------------|-----------------------|---------------------------|----------------------|----------------------|-----------------------|-----------------------|
| <u>Alkanes</u> | | | | | <u>Biogenic HCs</u> | | | | |
| Ethane | 1358 d | 70 d | - | - | Isoprene | 3,5 d | 4,3 h | 1,6 d | 1,1 d |
| Propane | 303 d | 16 d | - | - | a-pinene | 6,5 d | 8,1 h | 5,8 h | 4,1 h |
| 2-methylpropane | 150 d | 7,8 d | - | - | Camphene | 6,6 d | 8,2 h | 23 d | 16 d |
| Butane | 138 d | 7,2 d | - | - | b-pinene/myrcene | 6,5 d | 8,1 h | 1,4 d | 23 h |
| 2-methylbutane | 89 d | 4,6 d | - | - | 3-carene | 4,0 d | 4,9 h | 13 h | 9,4 h |
| Pentane | 88 d | 4,6 d | - | - | <u>Gasoline additives</u> | | | | |
| Cyclohexane | 47 d | 2,4 d | - | - | MTBE* | 119 d | 6,1 d | - | - |
| 2-methylpentane | 62 d | 3,2 d | - | - | TAME | 55 d | 2,9 d | - | - |
| 3-methylpentane | 61 d | 3,2 d | - | - | <u>Halogenated HCs</u> | | | | |
| Hexane* | 62 d | 3,2 d | - | - | CFC-12 | - | - | - | - |
| Mecyclohexane | 34 d | 1,7 d | - | - | Chloromethane* | 18 a | 341 d | - | - |
| Octane | 40 d | 2,1 d | - | - | CFC-11 | - | - | - | - |
| Nonane | 34 d | 1,8 d | - | - | CFC-113 | - | - | - | - |
| Decane | 30 d | 1,6 d | - | - | Chloroform* | 9,3 a | 175 d | - | - |
| <u>Alkenes</u> | | | | | 1,2-dichloroethane* | 362 a | 19 a | - | - |
| Ethene | 41 d | 2,1 d | 14 d | 9,7 d | 1,1,1-TCE* | 88 a | 4,5 a | - | - |
| Propene | 13 d | 16 h | 2,2 d | 1,5 d | CCl ₄ * | 9,8 a | 185 d | - | - |
| Trans-2-butene | 5,5 d | 6,8 h | 2,6 h | 1,9 h | Trichloroethene* | 54 a | 2,8 a | - | - |
| 1-butene | 11 d | 14 h | 2,4 d | 1,6 d | Tetrachloroethene* | 5,5 a | 104 d | - | - |
| 2-methylpropene | 6,8 d | 8,4 h | 1,9 d | 1,3 d | <u>Carbonyls</u> | | | | |
| Cis-2-butene | 6,2 d | 7,7 h | 4,1 h | 2,9 h | Formaldehyde* | 37 d | 1,9 d | 27000 a | 19000 a |
| 1,3-butadiene* | 5,2 d | 6,5 h | 3,3 d | 2,3 d | Acetaldehyde* | 57 d | 2,9 d | 9,5 a | 6,6 a |
| Trans-2-pentene | 5,2 d | 6,5 h | - | - | Acetone | 1591 d | 82 d | - | - |
| Cis-2-pentene | 5,3 d | 6,6 h | - | - | Propanal | 35 d | 1,8 d | - | - |
| <u>Alkynes</u> | | | | | Butanal | 15 d | 18 h | - | - |
| Ethyne | 428 d | 22 d | - | - | Pentanal | 13 d | 16 h | - | - |
| Propyne | 59 d | 3,1 d | - | - | Hexanal | 12 d | 15 h | - | - |
| <u>Aromatic HCs</u> | | | | | Heptanal | 12 d | 15 h | - | - |
| Benzene* | 264 d | 14 d | 333 a | 233 a | Octanal | 12 d | 15 h | - | - |
| Toluene* | 59 d | 3,0 d | 138 a | 97 a | Nonanal | 9,7 d | 12 h | - | - |
| Ethylbenzene | 49 d | 2,5 d | - | - | Decanal | 11 d | 14 h | - | - |
| p/m-xylene* | 18 d | 23 h | 57 a | 40 a | Methacrolein | 13 d | 16 h | 16 d | 11 d |
| Styrene* | 6 d | 7,5 h | - | - | Benzaldehyde | 49 d | 2,5 d | - | - |
| o-xylene* | 25 d | 1,3 d | 33 a | 23 a | m-tolualdehyde | - | - | - | - |
| Propylbenzene | 58 d | 3,0d | - | - | Nopinone | 24 d | 1,3 d | - | - |
| 3-ethyltoluene | 18 d | 23 h | - | - | | | | | |
| 4-ethyltoluene | 29 d | 1,5 d | - | - | | | | | |
| 1,3,5-TMB | 6,1 d | 7,6 h | - | - | | | | | |
| 2-ethyltoluene | 28 d | 1,5 d | - | - | | | | | |
| 1,2,4-TMB | 11 d | 13 h | - | - | | | | | |
| 1,2,3-TMB | 11 d | 13 h | - | - | | | | | |

Mecyclohexane=methylcyclohexane, TMB=trimethylbenzene, MTBE=methyl-*tert*-butylether, TAME=*tert*-amylmethylether, 1,1,1-TCE= 1,1,1-trichloroethane, CCl₄=tetrachloroethane
compounds marked with asterisks () are classified as hazardous air pollutant by U.S. EPA

Figure 4. Average daytime lifetimes of VOCs in reaction with OH radicals (τ_{OH}) and O_3 (τ_{O_3}). Concentrations for OH radicals are daytime averages for winter (Dec-Feb) of $3.3 \cdot 10^4$ molecule cm^{-3} and for summer (Jun-Aug) of $6.4 \cdot 10^5$ molecule cm^{-3} ; for O_3 the monthly average concentrations are for winter $5.6 \cdot 10^{11}$ molecule cm^{-3} and for summer $8 \cdot 10^{11}$ molecule cm^{-3} in Central Finland (adapted from *Hakola et al. (2003)*). Reaction rates at 298 ± 2 K are from *Atkinson (1994)*, except for carbonyls, for which the values from paper V are used and for the TAME reaction rate, which is from *Becker (1996)*.

The grand total atmospheric lifetime of these VOCs when NO_3 is the oxidant is 136.38 years and 143.45 days when OH is the oxidant (NASA GTE). Ozone as an oxidant is the poorest shown

oxidant here, and this may explain why high levels of urban ozone manifest with a haze pooling at the top of urban emission waves. High NO_x and PM levels suppress oxidation, create an anthropogenic inversion phenomenon or consume the oxidant OH* primarily. The anthropogenic urban heat waves and natural convection waves will allow the upward and downwind removal where, a less acidic and more diluted [NO_x], will affect the release of OH via photolysis. This is less sterically hindered than it was in the urban emission zone. This urban event has been well characterized as essentially the convergence of an oxygen-quenched environment, where O⁻, O₂, and OH*, are embedded in S-O, N-O, C-O, and O₂-O⁻ states. Waste heat from combustion, acids and PM all pervade this environment and the introduction of *peroxygen depleted moisture* from all anthropogenic combustion streams provides moisture that will, in each 24-hour cycle, help lift this mass of air as the day closes and re-instate it as the day begins.

General Discussion of OH*

Aerosol and particulate build-up in urban localities and even in the provinces suggests that a removal mechanism is missing, or that the aerosols are refractory to nucleation and dry or wet deposition. The only oxidation number stronger than OH* belongs to fluorine, and O⁻² is stronger still with a nine-fold oxidation power over OH* (Pauling electronegativities). This ozone depleting compound is CFC, and, other F metal compounds, which do accumulate in fossil fuels also reach far across and upward in our systems. The question then becomes: is all the visible particulate attributable to an excess of F compounds? Fortunately the consensus seems to be that visible PM is really varying sizes of soot in combination with different metals that have escaped from combustion systems into the air (Resources News, n.d.).

The oxygen-hydrogen coupling in urban conditions needs a full analysis, as that tree of reactants contains the peroxygen compounds. OH in particular is popularly called the “smog eater”. It is suggested that the oxygen quenched urban setting makes peroxygen compound concentrations an area of uppermost concern. Negative ions and their benefits to human health have a 30 year peer reviewed Psychology literature legacy that is discussed later.

Global determinations of these compounds consistently reveal a downward budgetary trend. That trend is of the same magnitude as stratospheric ozone level depletion, 30% depleted and decreasing (Levy, n.d.; FMC Corporation, 2002; Cundliffe, 2004).

The list below is ordered in descending order by vapour pressures of gases. This suggests their responsiveness to the waste heat generated by combustion and energy production: hydrogen,

helium, oxygen, carbon dioxide, nitrogen; their thermodynamic properties correlate with these layers of gas out to the exosphere (Prentice Hall, 2004). For three of these gases, namely hydrogen, oxygen, and nitrogen – have budgets that are anthropogenically altered.

Hydrogen and It's Atmospheric Effects

SINKS OF ATMOSPHERIC HYDROGEN

- ✚ Uptake at soil surfaces
- ✚ Oxidation by OH
- ✚ $\text{OH} + \text{H}_2 = \text{removal}$

A sophisticated global three-dimensional chemistry transport model is required to determine the rate of hydrogen removal.

THE GLOBAL HYDROGEN BUDGET

| Atmospheric Sources | Tg /yr |
|--|-----------|
| Direct emissions Man-made | 20 |
| Biomass Burning | 20 |
| Photochemical oxidation of CH ₄ | 15 |
| Of C ₅ H ₈ | 11 |
| Of other VOCs | 4 |
| <u>Atmospheric Sinks</u> | |
| Surface uptake | 58 |
| Photochemical oxidation | 17 |

From STOCHEM

ATMOSPHERIC LIFETIME OF HYDROGEN

Global H₂ inventory ----- 172 Tg

Atmospheric sink strength ----- 74 Tg/yr

Atmospheric lifetime ----- 2.3 years

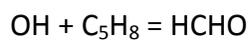
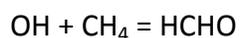
RADIATIVE FORCING CONSEQUENCES OF H₂ PULSES

The emission of a pulse of H₂ into STOCHEM leads to:

- Depletion in tropospheric OH
- Decreased reaction fluxes through OH + CH₄
- Increased build-up in methane in the troposphere
- Increased interconversion of OH into HO₂
- Increased reaction fluxes through HO₂ + NO
- Increased build-up in ozone in the troposphere

Methane and ozone in the troposphere are the 2nd and 3rd most important man-made greenhouse gases after CO₂.

PHOTOCHEMICAL SOURCES OF HYDROGEN

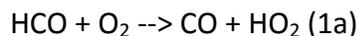
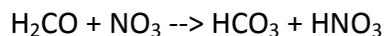
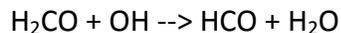
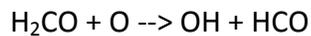
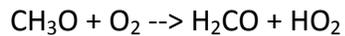


SOURCES OF ATMOSPHERIC HYDROGEN

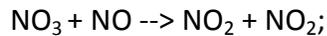
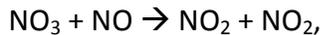
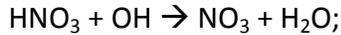
- Motor vehicle exhausts and biomass burning are largest direct emission sources.
- Much of the hydrogen in the atmosphere has come from methane and plant based isoprene oxidation through atmospheric chemistry processes.

H₂ is a greenhouse gas by virtue of its tropospheric chemistry and its role in changing the build-up of methane and ozone. The global warming consequences of the global hydrogen economy will depend on the leakage rates for hydrogen manufacture, storage and handling. The IPCC Working Group I report recognized that a future H₂ economy would act as a potential climate perturbation. If a hydrogen economy with a 1% hydrogen leakage rate completely replaced a fossil-fuel economy, then it would produce 0.6% of the climate impact of the fossil-fuel economy.

Methane Oxidation



Notable products are {HO₂, OH} radicals, H₂O, carbonate {HCO₃}, HNO₃ may be helpful oxidant but does not support a net gain of oxidation: HNO₃ + hv → OH + NO₂,



CO and CO₂

CO-reactions are well identified in previous contributions, as the leading precursor to CO₂ via OH* and other peroxygen oxidation.

The atmospheric lifetime of CO₂ is ~500 years, and it has had the following effect according to the British Antarctic Survey:

“The Incredible Shrinking Atmosphere”

While others are looking for evidence of global warming down here at ground level, a British team has found it 180 miles up. For the last 38 years the British Antarctic Survey has been bouncing radio waves off the outer envelope of the upper atmosphere, to map its structure. In September they reported that the thermosphere is now about five miles lower than when they began making the measurements. Our atmosphere, in other words, is shrinking and the British researchers say that the shrinkage is caused by the build-up of Carbon Dioxide. The steps go like this: Sunlight bouncing off Earth’s surface is converted to heat, which is absorbed and then released by carbon dioxide in the atmosphere. The newly released heat is as likely to travel back toward the surface as upward. At lower altitudes, the energy bounces between molecules and warms the atmosphere. In the thermosphere, by contrast, energy that goes upward simply escapes the atmosphere and radiates into space. Researchers have therefore predicted that extra CO₂ should cool the thermosphere rather than warm it, and cooling should make it shrink—which is what the British researchers observed. The observation is a striking demonstration that carbon dioxide is changing our atmosphere; it also shows that the thermosphere may be a good monitor for global climate change.” (Derwent, 2004).

While this is occurring, it may be of concern that CO₂ shrinking in this manner around a sphere such as Earth may be imposing downward pressure on the molecules below this chilling layer and this needs to be studied further. From the lower ionosphere to the stratosphere and thence, to the troposphere, this effect may be understood in the form of its other better-known impact as a greenhouse gas. Below the cooled area, it is trapping and increasing temperature. This suggests that there may be a loss of pre-industrial atmospheric venting of heat, which is

likely entering into the jet stream. Equally affected may be high natural oceanic convection currents that transfer heat, molecular motion and energy to these heights. This may be a major contributor to more drastic weather events based on the well-known general function of temperature in increasing the speed of motion of molecules, and thus deserves further investigation. It is well to remember, after all, that CO₂ has a heat capacity 9 times higher than that of water (Saunders College Publishing, 1987).

| Carbon dioxide in the atmosphere, as parts per million | | | | | | | | | | |
|--|------|----------|------|-------|------|---------|--------------------|------------------|---------|------------------|
| Year | Past | pre-1850 | 1900 | 1970s | 2000 | Present | 2004 | Future estimates | 2100 | 2035 |
| Parts per million of CO ₂ in atmosphere | 170 | 260 | 280 | 295 | 360 | | | Future estimates | 450-900 | |
| Annual increase | | | | | | | + 1.5 ppm per year | Future estimates | | + 6 ppm per year |
| Toxic dose of carbon dioxide for humans: about 700 ppm | | | | | | | | | | |

Figure 5. Source, Abelard, (n.d.)

“Recently scientists studied ice cores taken from a Yukon glacier about a thousand years old. These contained many trapped air bubbles. The research team found that the carbon dioxide level in today’s atmosphere is 27 percent higher than it was before 1850, the beginning of the Industrial Revolution. And over one-third of this alarming increase has been within the last 25 years.” (ourevolvingatmosphere.com, 2004).

In this paper’s conclusion, an important approach to using anthropogenic CO₂ as an asset will be summarized.

NO_x

NO_x are well known in the urban air setting. It is a reactive and variable-state product of combustion which, in cleaner air masses, decreases the oxidizing power of the atmosphere (Saunders, 1999).

Wild, Prather and Akimoto explain an important long term global radiative cooling from NO_x emissions. They discuss the difference between long-lived and short-lived radiative forcing, and that these should be quantified separately. The team also recommended attention to the long-lived CH₄-CO-O₃ coupling and argued for carefully designed high-resolution regional models. In this way, Ozone, OH, and NO_x concentrations, which are all very short lived, compared to CO₂, can be evaluated (Akimoto et al, 2001).

CHAPTER 4: The Peroxygens

Atmospheric Water Content Issues

A recorded 75% global increase in the last 50 years is not fully explained. Here are a few possible factors:

- General Peroxygen compound depletion
- Unchecked waste hot water from boiler systems stacks,-all depleted of Peroxygen compounds
- Greenhouse warming initiating still-unquantified water evaporation and convection
- Cloud scavenging of particulates and compounds known as nucleation processes, are probably suppressed due to peroxygen compound depletion, particularly the hydroperoxyl anion.
- Methane oxidation to CH₂O produces two water molecules per conversion, and the annual methane burden is 4088 Tg/year with an average lifetime of at least 8 years.

Properties of Hydrogen Peroxide Which are Factors in Cloud Cycling

Peroxygen has infinite solubility in water. Its electrochemical properties are as follows:

| Species | Potential, volts |
|--|------------------|
| $\text{HO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}_2$ | 1.5 |
| $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$ | -0.076 |
| $\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^-$ | -0.146 |
| $\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$ | 0.87 |
| O^{2-} oxide created by sunlight | -2.6 |

Table of Electrochemical Properties of Peroxygens

It has a freezing point between -50°C and -40°C at 60% and 70% concentrations with water. In the cold centre of a cloud mass, Peroxygen tends to remain more active and reactive. Peroxygen and, quite possibly, organic peroxides therefore add to the nucleation cycle inside a cloud for a longer time than water droplets do (Cundliffe, 2004).

The peak coupling and binding into CCN (cloud condensation nuclei) of peroxides may be a pivotal preliminary state for the release of precipitation. The dissolution of peroxide into water delivers a negative charge to the cloud water; therefore, in varying cloud formations and fronts that have significant differences in peroxygen content, electrical charges will likely become an issue when such frontal formations interact. This is in addition to chemical, frictional, photoelectric, and relative contributions of atmospheric electrical potentials to cloud charge states (Saunders College Publishing, 1987).

Water Vapour

Excerpt: “Although the higher water-vapour concentrations associated with a warmer climate help offset a certain amount (about 14 to 17% according to this research) of emission-induced reductions in OH concentration, none of the predicted climate changes prevent the predicted reduction in tropospheric OH concentrations and related increases in CO and CH₄ lifetimes. Our research indicates that sustaining OH at current levels will require a cessation or reversal of the predicted trends of increasing emissions of CO and especially CH₄ in the future. Quantitative differences between this work and earlier works exist, due to the more comprehensive approach of including economic and climatic predictions used in this research. Our results indicate that effects on OH of the increase of CH₄ emissions, based on the prediction of the economic development model, are *more substantial* than those caused by the increase of CO emissions. Consequently, lowering the future emissions of CH₄ is more important for limiting future depletion of tropospheric OH than lowering the emissions of CO. Future emissions of CH₄ are thus very important to both climate change and tropospheric chemistry change (represented by the OH concentrations)” (Prinn and Wang, n.d.)

At the Polar Ice sheets

“One key finding has been that Photolysis of snow chromophores initiates the release of a number of important trace gases. Initial modelling suggests that Photolysis of a number of these gases (HCHO, HOOH, CH₃CHO and HONO) results in an enormous production of HOx (i.e., OH and HO₂), which in turn causes a large enhancement of these radicals in the snowpack and in the air just above the snow. Because oxidation by OH is the main sink for many tropospheric gases, including some of those important for climate change and stratospheric O₃ depletion, this enhancement in HOx might significantly perturb tropospheric chemistry. Snowpack chemistry likely also modifies the chemical records of atmospheric composition ultimately preserved in glacial ice” (Miley and Cundliffe, 2004).

Referring to the thermodynamic properties of H₂O₂, (FMC Corporation, 2002), we recall that it can have a much lower freezing/melting point than water depending upon its concentration. The excess penetration of solar radiation to the ice surface and any warming trends within the ice sheets may release much more peroxygen compound vapour than first considered. In general, the melting of land glaciers may have provided a supplemental reservoir of oxidant power to our troposphere and the same mechanism may be working on our remaining ice. H₂O₂ -and its variants- from ice may be lost due to particulate matter dimming of albedo which stops H₂O photolysis at the ice surface area. Pollutants darken the snow and absorb solar energy, increasing the temperature of the ice and melt rate. Often it will be the generated OH that brings down the particulate, so the particulate must be controlled at point source if possible.

Mesoscale Implications Using a Simple Box Model Analogy

If a large urban region, such as a highly industrialized Mid-Eastern US states, is sending peroxygen depleted heat and waste water from stacks, fuel exhausts, VOC's and PM aloft, its charge state and balances will be quite different from that of a moist front convected from the ocean. The oceanic front will likely have a higher electrical and pollution scavenging power, and different temperature. One should become positive relative to the other, in electrical and chemical interaction. However, the important situation here is that 79% of all human global wastes, and an anthropogenic layer of water ~1.87 cm in thickness at ground level, is now added to tropospheric ecology. **A simple analogy is that 75% more balls have been added to the billiard table, which are all moving in any of six directions according to meteorological and other principles as yet not understood but governing them nonetheless. One fifth of the table is randomly covered by haze at the end of each day, which accounts for industry, fossil fuels, volcanoes, forest fires and biomass burning. Seventy-five percent more water fog pervades this

haze. The natural oxidants from peroxide are absent around some of the balls and 70% of the normal balls (i.e., pre-industrial) have peroxygens around them. Light effects on the table surface fluctuate owing to annual anthropogenic injections amounting to an estimated 10 million metric tons, catastrophic but random events (in 1999, the Mt. Pinatubo eruption alone was estimated to have ejected sulphur amounting to 22 million tons, see “Supplemental” below). Owing to decreased insulation, sunlight has scorched formerly green table surfaces. Sudden ball interactions have unleashed unprecedented amounts of water onto the table surface, causing erosion and land sloughing; ice sheets at both ends of the table are deteriorating, and terrestrial ice sheets near each end are evaporating. Retaining the analogy, there is a layer of CO₂ 12 feet above the table, potentially shrinking downward and gradually decreasing the space for this meteorological billiard ball model.

A scientist, who encounters this “box model”, with the miniature human race functioning in it, has the ability to make alterations to the model. What measures would the scientist start with?

Supplemental

The 1999 Mt. Pinatubo eruption brought heat, gas, fire, lightning and cold eventually in the form of a ¼ degree temperature reduction on a global scale. Because the effluvia diffused or was borne on air currents all over the earth, we deal with the consequences today, compounded by solar radiation and atmospheric turnover. The atmosphere is indeed a thin haven from outer space and we would do well to inventory its dwindling assets.

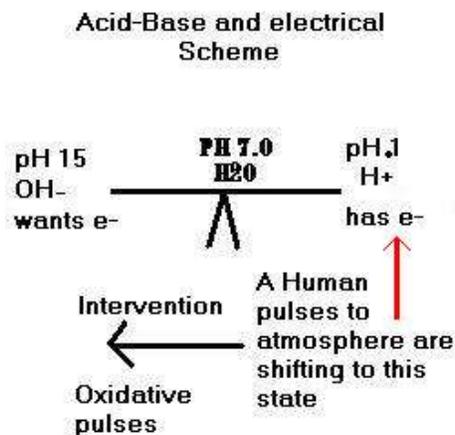


Figure 6: The general electrochemical imbalance trend of the atmosphere.

This suggests a potentially stormier interaction with more pH neutral air fronts in the unusual horizontal plane rather than the normal vertical plane. It is significant that oxides with a few exceptions are heavier in weight, making a more substantive contribution to cloud Condensation Nuclei as well; oxides are generally less electro conductive, or less excitable than hydrogen abstracted compounds.

Oxygen is the most abundant element on our planet, mostly combined with other elements as oxides. However, this gas that makes up 21% of the atmosphere is being rapidly combusted into CO₂, and NO_x.

It reacts with all elements, except group 18 noble gases

Oxides are acidic if oxygen combines with a non-metal (example NO₂)

Oxides are basic if oxygen combines with an electropositive metal (example Na₂O)

Oxides are amphoteric (can act as either acid or base) when combined with a weak electropositive metal; (examples are BeO, Al₂O₃, ZnO).

Oxides are neutral if the compound does not react with water, aqueous acids or bases

- across a Period, the oxides begin as basic compounds (Gp 1&2) and become **amphoteric** (with transition metals) then acidic (with non-metals).

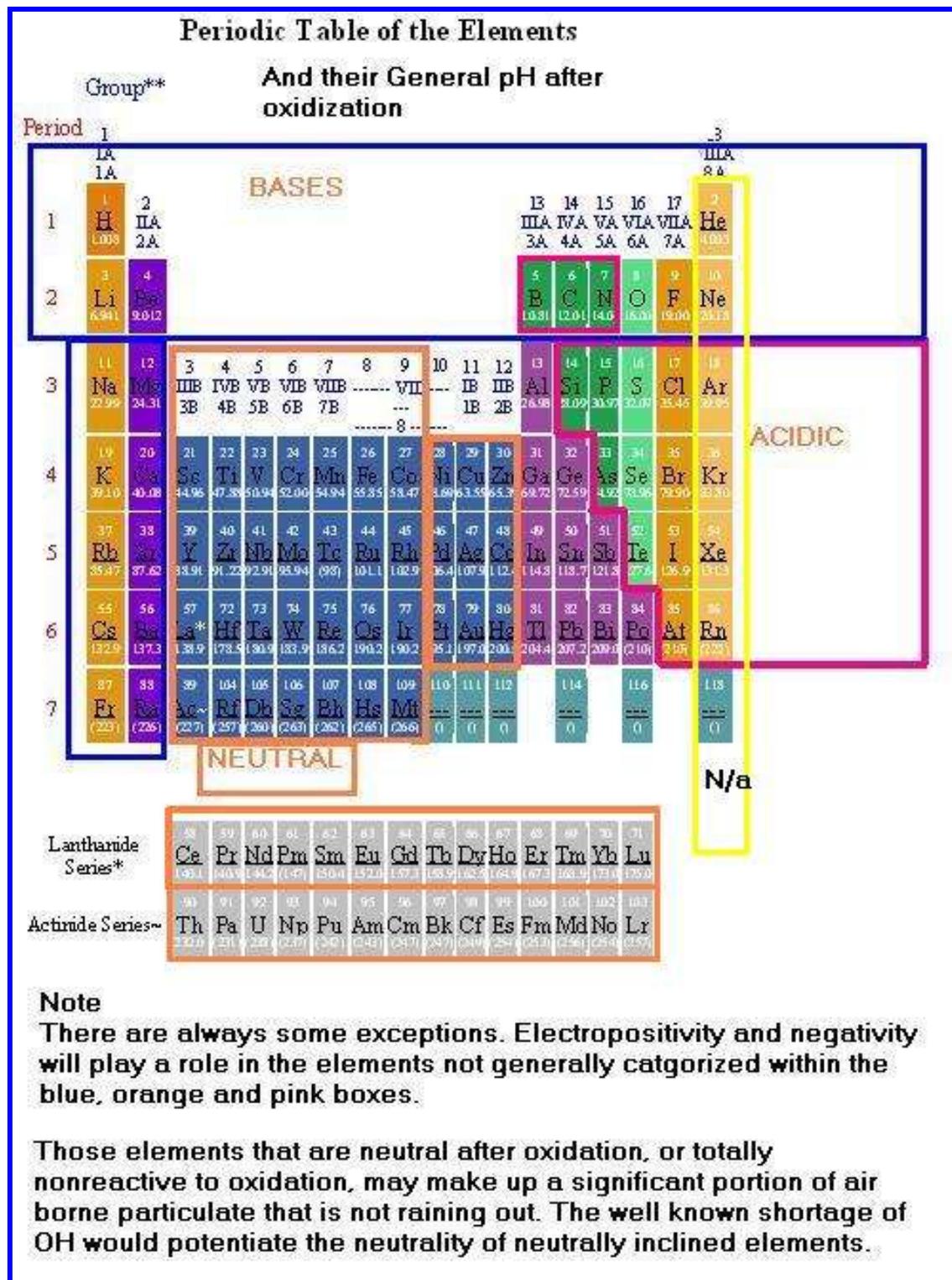


Figure 7: Water insoluble compounds are likely a major component of haze. Original table courtesy of LANL, 2004

General Balance Sheet Of Compounds And Processes

Liabilities

- ✚ 30% decrease in stratospheric Ozone
- ✚ 30% decrease in global hydroperoxyl compounds
- ✚ 75% increase in water vapour, which best cools when it is cycling in cloud precipitation
- ✚ 1,000,000 metric tons of injected human waste annually since 1950
- ✚ Particulate aerosol causing regional warming and cooling deviations, hence Steric hindrance
- ✚ 30% increase in global CO₂ levels

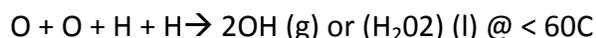
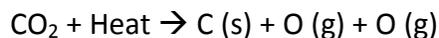
Assets

- ✚ Natural photochemistry, which recycles oxidants in water, cloud, and ice surfaces and NO_x
- ✚ Homogenous chemistry, which recycles oxidants
- ✚ A functioning biome, which is a carbon sink and oxygen supply
- ✚ Oceanic plants and convection cycles-not as depleted of peroxygen
- ✚ Lithosphere, which is a hydrogen sink
- ✚ Water vapour, which appears to be serving as a growing reservoir for wastes

Summary

Oxygen, oxidants, and consequent electrochemical balance are likely the key components to increase. Carbon dioxide, water vapour, and amphoteric metal species are likely the components to decrease. If one integrated technology process could break down carbon

dioxide, the most stable and highest simple oxidation state of oxygen (because oxygen makes up 72.6% of its atoms), this would unleash a vast reservoir of oxygen and abruptly reverse CO₂ build-up. Water is also 75% oxygen by weight, a rapid chemistry oxidant, and CCN protagonism by peroxygen compounds can also be reinstated in an available technology process (Halliday and Wiley, 1974).



CO₂ as the highest carbon simple oxidation state and also the most rapidly growing liability may be the key to atmospheric remediation and stabilization. Rather than leaving CO₂ to break down naturally (it has a 100 year lifetime), science and technology would better serve humanity by unlocking the oxygen and subsequent oxidant products which can perform their cleaning services in less than one second in many cases; in bulk plumes the lifetime is up to six hours. It is postulated that earth needs the “one-second wonders” at normalized capacity via our solar, atomic and molecular drivers of the greenhouse ecology. Mankind, not just science, must be convinced of the security and correctness of emissions capture technology, particularly in the case of CO₂, since dealing with this CO₂ may be a pivotal source of peroxygens.

CHAPTER 5: Hydro-Geological Actions of Hydro-Oxygens

Treatise

Composite Theory Describing Peroxygen activities in the Global Hydro Geological Cycle of Earth

The field study of peroxygen activity has been a very difficult area to pursue by scientific investigation as the compounds are short lived before they combine with another compound and release a single oxygen atom or oxidize a chemical partner. The three per oxygens, OH, HO₂, and H₂O₂ are the subject of this theoretical treatise and it is important to note that other peroxide compounds do exist, (including oxide) where an OH will wholly attach to a carbon or inorganic molecule and become a “secondary” free radical. In order to maintain some clarity in this introductory treatise, the basic peroxygens will be the main subject of discussion.

These per oxygens likely play several pivotal roles in the dynamic stability of hydrological events. Here presented are a group of synoptic descriptions of these roles based upon the pre industrial and post-industrial presence and concentration of per oxygens.

The properties of peroxygens are very interesting because due to the water based meteorology of our planet, peroxygens are beneficial in several ways. Peroxygens are made up of the same elements as water: hydrogen and oxygen. This species closeness and compatibility is a vital chemistry lesson applicable to better managing the Earth's systems. It should also alert scientists to consider that in other planetary systems, minority compounds which are soluble in the majority of meteorological compounds may be playing roles of major concern (Akimoto et al, 2001; Derwent, 2004; EPA, 1998; Jacobs, 2000; Kuhlmann, 2001; Prinn and Wang, n.d.; Saunders, 1999).

For example, negative peroxygens adsorb excess electro positivity –as a powerful proton acceptor geochemically produced by sunlight cleaving water and leaving an OH, and often abstracting to a nascent oxygen during daylight wherever 190-330nm sunlight makes contact with the water-- the process has enormous distribution capabilities. This reaction occurs through all strata of the atmosphere, on all water bodies both ice and liquid (Hernandez et al, n.d.).

This ubiquitous but minor presence may be a reason that it is not widely known how active as a group of energy and stress buffering agents hydro oxygens can be, partially because it coexists with water infinitely and is still technologically hard to measure. It is postulated that more study will support its key importance.

A Brief History of Hydrogen Peroxide

Hydrogen peroxide has been with us for three billion years. As sunlight hits water molecules, a hydrogen atom is split off, forming an OH radical, making it free to pair up to form H₂O₂ (hydrogen peroxide) in the air. In water, it is known as HO₂, a negative ion, and this group forms the hydro oxygens, which have been found to act as the most important atmospheric cleansers in this system.

Louis Jacque Thenard discovered hydrogen peroxide (H₂O₂) in 1818 by reacting barium peroxide with nitric acid.

In the environment, hydrogen peroxide can be found in very low concentrations (ppm). Gaseous hydrogen peroxide is produced by photochemical (sunlight) reactions in the atmosphere surrounding the earth. It can also be found naturally in water in small quantities.

In the 1950's it was first implicated as an atmospheric compound of importance when Dr. Witherspoon modelled urban smog. At first it was thought that single oxygen atoms were removing smog, but further study of sunlight action in 1969 showed that carbon monoxide was rapidly removed and something faster than oxygen atoms was involved. In 1971, Dr. Levy showed a model with high concentrations of OH in unpolluted air that came from the sunlight breakdown of ozone. This suggested that OH was the main oxidizer of carbon monoxide because it is a radical, which reacts faster than ordinary atoms and molecules. Studies of the oxide ion need to be added to this area of work.

Further work by McConnell *et al.*, Weinstock and Niki, Heicklen, Kerr *et al.*, Demerrjian *et al.* in 1970-1974 confirmed that oxidation by OH of hydrocarbons in urban air was the main removal agent:

“Considerable evidence over the past three decades supports the view that tropospheric OH is the main oxidant for non-radical compounds in the atmosphere” Dr. Daniel J. Jacob, Harvard University, January 2000.

Unlike other chemical substances, hydrogen peroxide does not produce residues or gases. Safety depends on the applied concentration, because hydrogen peroxide is completely water-soluble.

Oceanic Peroxide Activities

Hydrogen peroxide is a reactive oxygen intermediate that can play a role in a variety of redox cycles. In the ocean, it is generally considered to be dominantly photolytically produced with negligible concentrations in deep waters (Heikes et al, 2000).

Peroxides and Glaciers

Hydrogen peroxide can be deposited on ice by diffusional contact. This deposition rate is limited by the lifetime of H₂O₂ against photolysis in the atmosphere (≈6 h), equivalent to a travelling distance of <1 km for a diffusion coefficient of $2 \times 10^5 \text{ cm}^2 \cdot \text{s}^{-1}$. The diffusional deposition of H₂O₂ is also sensitive to the H₂/O₂ ratio. Enhancing the hydrological cycle will always enhance the rainout rate of H₂O₂ as well as the concentration of H₂O₂ in H₂O ice, analogous with evaporation processes in H₂O₂-H₂O solution, which enhance the concentration of H₂O₂ in the solution. The total production rate of H₂O₂ by gas-phase chemistry is $\approx 10^{11} \text{ molecules cm}^{-2} \cdot \text{s}^{-1}$, which provides an upper limit to the rate of H₂O₂ deposition by diffusion and precipitation.

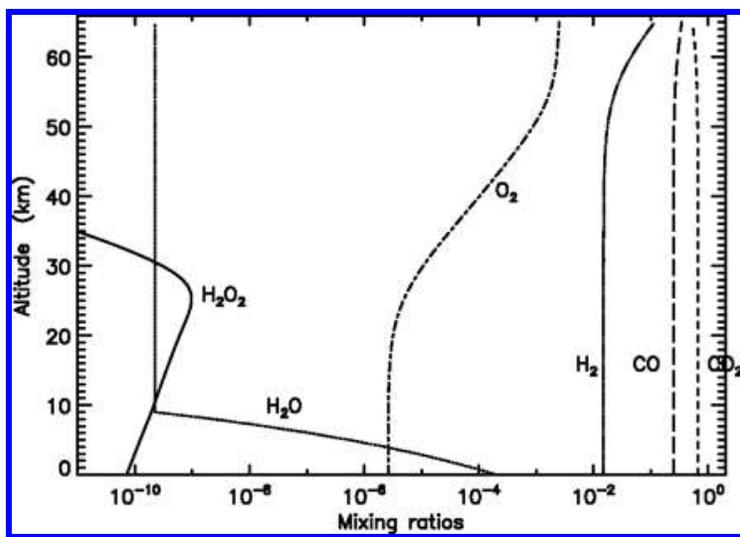


Figure 8: Profiles of H₂O (dotted line), H₂O₂ (solid line), O₂ (dash-dotted line), H₂ (triple dot-dashed line), CO (long-dashed line), and CO₂ (dashed line) calculated with the reference model, in which surface temperature is 240 K, temperature gradient is -10 K

Pollution of the tropospheric environment by the introduction of new chemical compounds or by changing the abundance of existing ones affects the natural chemistry of the region. Much of this chemistry involves the OH radical: it acts as a detergent, reacting rapidly with hydrocarbons, both natural and anthropogenic, and decreasingly preventing their build-up. Since many hydrocarbons are radiatively active gases, OH may be considered to play a role, albeit indirect, in determining the climate (Levy, n.d.). OH also reacts rapidly with oxides of sulfur and nitrogen with the ensuing production of soluble species that are rained out or lost from the atmosphere by dry deposition. As well, OH plays a major role in the production and loss of tropospheric ozone, an important radiatively active gas whose concentration may have been changing over the last century. Although the Earth's atmosphere has been studied by satellite experiments for many years, it has only recently become possible to monitor the composition of the troposphere from space: the main technical challenges are the variable surface of the planet and the presence of clouds.

This is the number one atmospheric cleanser, hence commonly referred to as our natural smog eater. However, OH is much more. It interacts with well over 165 other compounds in the atmosphere, including methane, sulphur-containing compounds, and volatile organic compounds, which are caused by incomplete combustion processes. Of serious note is the trend found, that where the OH* radical is missing, Ozone tends to become an oxidizer in its place and can be lost most importantly in the stratosphere and at the poles where we currently want stable ozone. (Madronich, S. 1993, Vol. 18, NATO-ASI Series, 437-61). Loss of OH in mid latitudes is of primary concern as well.

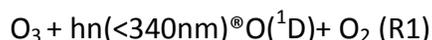
The OH* molecule is now being depleted substantially on a global scale, particularly in the Northern Hemisphere. At ground level, it is true, the OH* radical has had a replenishment cycle involving nitrogen oxides. But as Dr. Ronald Prinn of MIT points out, this system has been seriously compromised, and only recently identified.

Respected estimates of an aggregate 50% loss of OH* by 2060 compared to pre-industrial times have been presented (Wang & Prinn, "Interactions Among Emissions, Atmospheric Chemistry, and Climate Change: Implications for Future Trends). This underlines the seriousness of halting the deterioration.

As identified by Rowland, Crutzen, and Molinas, (1995), the Stratospheric Ozone Layer is substantially depleted, and hydrogen radical depletion *in combination* with this signals potential danger. Dr. Rowland describes the chemical link between O₃ and OH* as follows: "The chain reaction of OH with O₃ to form HO₂ + O₂, followed by HO₂ + O₃ to form OH again forms a chain which converts two O₃ into three O₂ molecules", thus it may be suggested that via OH, O₃ is a recirculating reservoir for O₂, from which emerges the Chapman Cycle, and OH cleansing activities. Therefore, this suggests that hydro oxygen depletion is directly linked to ozone depletion. This is also essentially true for urban situations. The release can be regionalized to account for the short lifetime of OH*, estimated at up to 6 hours in clean air, but the longer-term effects of the HO₂ ion in water is vital (Ronald Prinn, Chien Wang, 1997).

Ozone: A Reservoir for Hydroxyls

Ozone depletion clearly leads to per oxygen depletion, as it is the main source by photolysis everywhere in the atmosphere.



Since we have found a depleted ozone layer, we also find a depleted flux or population of hydroxyls, which in turn will depress HO₂, and H₂O₂ populations over a long-term injection of pollution that is consuming oxidants. The following figure shows how closely the atomic O¹D can be the pathway of depletion by the associated pathway of OH consumption.

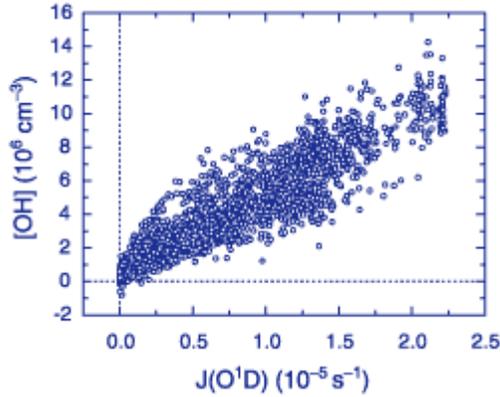


Figure 9: Correlation plot of all LIF OH data versus the photolysis frequency of ozone, $J(O^1D)$. (Adapted from Holland et al., 1998)

During the cycling between OH and HO_2 , ozone (O_3) is produced. Ozone production occurs when HO_2 and RO_2 react with NO to form OH (or RO) and NO_2 . The NO_2 is rapidly destroyed by sunlight into $NO+O$, and the O atom rapidly reacts with O_2 to make O_3 . On the other hand, the production of HO_x can destroy O_3 , as can the reactions of OH and HO_2 with O_3 . Thus the net ozone production is dictated by the expression:

$$d[O_3]/dt = \{k_{HO_2+NO}[HO_2] + k_{RO_2+NO}[RO_2]\}[NO] - \{J_{O^1D}f[H_2O] + k_{OH+O_3}[OH] + k_{HO_2+O_3}[HO_2]\}[O_3]$$

where $[OH]$ is the OH concentration, k_{X+Y} is the reaction rate coefficient for $X+Y$ products, and $J_{O^1D}f[H_2O]$ is the production rate of $O(^1D)$ times the fraction that react with H_2O . The level at which NO becomes more important than O_3 depends on the $[NO]$ and $[O_3]$ [Crutzen, 1979]. For typical $[O_3]$ values, it occurs when the NO mixing ratio exceeds a few tens of pptv.

The second most crucial depletory of ozone over time may be the depletion of hydroxyls by a steady injection of hydroxyl consuming compounds as a result of industrial activities. The worst direct interference in the above equation about O_3 has been identified as Chlorine CFC's. However, the second depletion mechanism, massive hydroxyl depletion, may over time have comparable catastrophic results on ozone abundance in the troposphere (where it is most useful) as well as elsewhere.

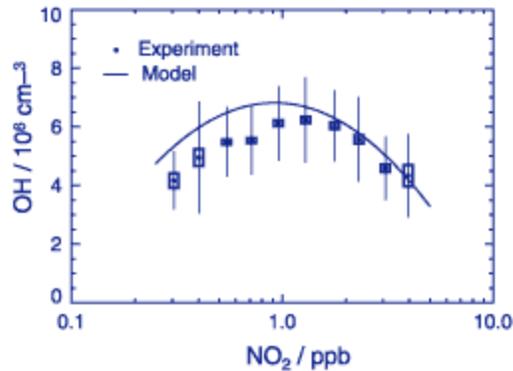


Figure 10: Dependence of the measured OH concentration on NO₂ during the POPCORN field campaign. To make this behavior visible, the OH data were first normalized with respect to J (O1D) and then plotted versus equal log (NO₂)-intervals of 0.1.

In summary, the above figure shows that a natural secondary OH source system is in place via NO₂. The task to preserve this system is less difficult as NO₂ and HONO are ubiquitous para-regionally and functional in urban areas diurnally. Cleaner combustion processes will improve both the highlighted OH reservoir systems discussed here. This means that there will be less NO and more NO₂ for this reservoir system.

Plant and Animal Stress Signals Involve Hydrogen Peroxide

Hydrogen peroxide helps organisms respond to changing climatic events and perturbations.

H₂O₂ is not simply a cytotoxin in living cells, it is a key signal chain member and when a defence mechanism relies upon a signal chain, this is a critical survival component. In other words, in the right amounts and locations, H₂O₂ is vital in maintaining homeostasis.

H₂O₂ is also now well characterized as a cold stress tolerance agonist in plants, something that renders a plant adaptable to different latitudes and a variety of isolated climatic events (10). The increase in H₂O₂ level triggered by cooling and subsequent changes in the GSH/GSSG ratio during chilling seem to be involved in redox signalling, which activates specific transcription factors and antioxidative enzymes. Indeed, it has been shown that pre-treatment of seedlings with H₂O₂ induces chilling tolerance (Brune, 2000).

Desikan et al. (2001a) provided further evidence of H₂O₂ as a central signalling mediator. Their study showed that the expression of some genes is up-regulated by H₂O₂ (Wennberg, 1999).

Disturbance of cellular red-ox homeostasis may activate transcription factors and gene expression of those involved in the protection of plants against damage during chilling and cold acclimation (Brune, n.d.). This may be explained by the fact that the stress-induced oxidized state of the cell may lead to the disulfide bridge formation in proteins, including transcription factors. The modification of proteins may lead to conformational change and consequently activate transcription factors, which will in turn control the expression and accumulation of certain antioxidants (Wennberg, 1999).

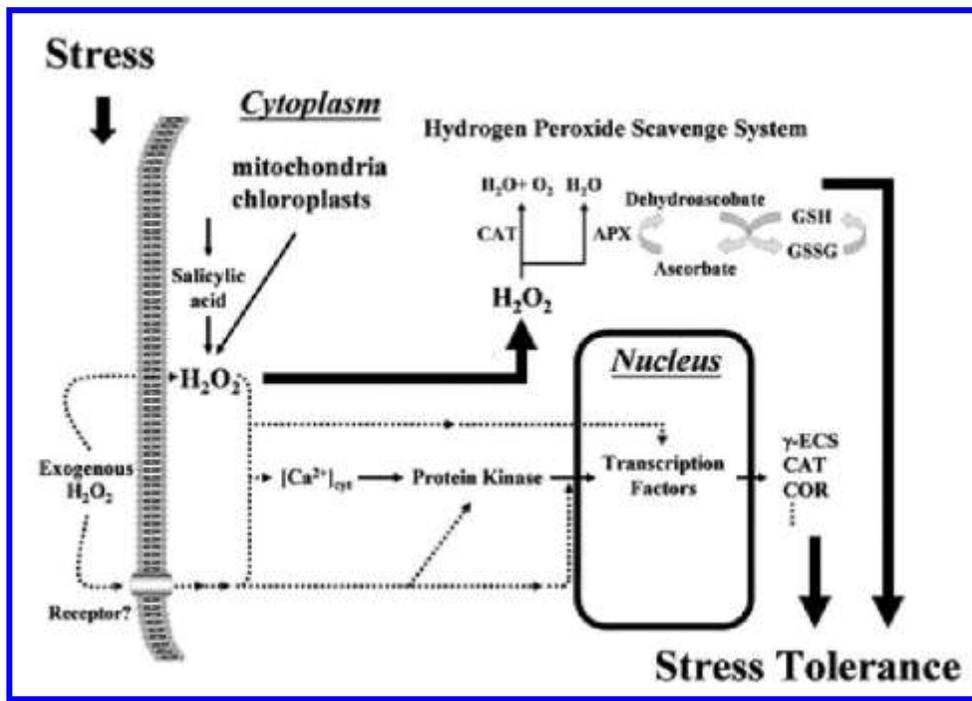


Figure 11. Stress signal model for the H_2O_2 -induced signaling cascade. Abbreviations: APX, ascorbate peroxidase; CAT, catalase; COR, cold regulated gene; γ -ECS, gamma-glutamylcysteine synthetase; GSH, glutathione; GSSG, glutathione disulfide; H_2O_2 , hydrogen peroxide

Lowered atmospheric OH could cause a lowering of stress signals in plants, lowering their immune response abilities.

Peroxide and Soils

Peroxides break down on coming in contact with soils. It is widely used as a soil reclamation compound as it reacts with many toxic substances and hydrocarbons. Commercial potting soils

are sterilized with peroxide to remove unwanted bacteria and fungi populations. Dry and wet deposition from the air generally leads to rapid decomposition of the peroxygens.

Mean pH is 6.0 and a biologically neutral level is 7.4. As pH is the negative log of the hydrogen ion concentration, it then is also the positive log of the OH⁻ ion concentration. It is generally understood that soil and air acidity has become a problem due to the required oxidation of sulphurs and nitrous oxides from manmade injection of many compounds into the defence layer of oxidants where the acids are then formed so that they can be removed by wet and dry deposition. The result is accumulation of acids in soils and water bodies which are shifting aquatic environments into lower pH ranges and affecting plant and animal life.

Conclusion

In conclusion, the peroxygens, OH, HO₂, and H₂O₂, are very important electron acceptors and oxidizers of many harmful compounds which interfere with radiative and hydrological systems. In short, they are energy sponges whose net effect is to reduce potential energy and very likely mediate electrical potential differences horizontally across weather fronts, providing a calming or damping mechanism that reduces the impact of storm perturbations which normally have cloud charge differences in a vertical dynamic.

The hydroxyl radical is a very important source of O¹D oxygen for ozone formation, and should be more seriously considered as a species which, if conserved, will assist in the regeneration of the ozone layer of the stratosphere.

While we do not yet have a carbon neutral source of peroxide which could be reintroduced into the atmosphere, the prospect of improving air quality and restoring the chemical dynamics of the troposphere to a more vertical and “normal” state is highly desirable. Unlike the hydro geological cycles of the past, it has now been found by Liang *et al.* (2006) that a peroxide “burp” has very likely led to at least one cycle of global cooling. This strongly suggests that science needs to further consider that global warming is not only caused by greenhouse gas excesses by human activity, but also the 5 MT per year depletion of hydroxyls and hydro oxygens. This loss is most likely affecting both global climate forcing and reducing the recovery rate of the ozone layer. In light of the propensity of per oxygen compounds for interacting with natural and manmade emissions, society may greatly benefit from taking a very serious look at initiating a carbon neutral peroxide or oxide (111.111 ppb v) injection plan to manage global temperature and climate stability.

CHAPTER 6 Global Oxidant Remediation: Future Opportunities for Experiments

Part 1

Introduction: Peroxygen Compound Restoration Plan to Advance Global Cooling

The following environmental information is for a project which is global. The author is working to ensure that more individuals will hear about this project, which was invented in Canada in 1996, because it has a major benefit for global health and temperatures, cutting across industrialised and developing countries.

This is how NASA and the UNEP Executive Director responded in June of 2003.

“Dear Ms. Cundliffe--The proposal sounds interesting and appears to be well thought-out and with practical application.”

V E Delnore, NASA Global Tropospheric Experiment Official:

“It is an interesting proposal and as an Engineer, one I can appreciate”

Mark Radka, Energy Programme Coordinator, United Nations Environment Program;

“I wish you all the luck in your search for funds for this great initiative.”

Luiz Ros , Director, New Ventures, Sustainable Enterprise Program, World Resources Institute.

Technical Statement and Overview

This is an Atmospheric Contingency Plan to restore the hydrogen radical concentration to the atmosphere through a reservoir species, HO_2 which is the negative ion of hydrogen peroxide in water. This ion can last up to six hours in the atmosphere, far longer than the OH^* radical and is itself a source of OH radicals. When HO_2 self-reacts to form H_2O_2 , it then can separate into the radicals far away from its release point. Over 165 reactions with OH^* are involved in the global atmosphere.

The author would only propose the reinstatement of the OH radical back to its 100% natural background level, not enough to disturb natural background ozone levels (Alex Keiko and Russian Atmospheric Modelling Group, Russian Academy of Sciences, personal communication). Successfully installing one facility and verifying the plume from it will validate the subsequent facility installations. A region-by-region or air shed treatment approach may be the most practical approach. The key to the viability of this restoration is by utilizing the reservoir species, HO₂, to bring about the dispersal and formation of OH* radicals.

Background of Environmental Adaptation and Remediation

This proposed global background adaptation facility where H₂O₂ is formed into gas or atomized and released into the troposphere, might deserve to be replicated in a number of suitable regions. In a recent communication, Dr. Ronald Prinn of MIT's Department of Atmospheric Science saw merit in the proposal. Since 1996 the author has studied and proposed the controlled release of Hydrogen Peroxide to restore the oxidizing power of the atmosphere. Along with findings that the OH radical aids in the natural regulation of Ozone (Keiko, personal communication, 2003), and removes particles from the atmosphere (POP's and VOC's), there is corroboration that the OH* radical concentration does affect climate events (Levy, n.d.).

It is now lower by 30% from pre-industrial times globally and especially deficient near active polluting operations (Prinn and Wang, 2002; Jockel, Brenninkmeijer, and Crutzen, 2002). Therefore, the author suggests this deficit is developing climate consequences; (1.0 x 10⁶ molecules per cm³ presently, and 1.41 x 10⁶ pre-industrial) (ref. Geneva Convention Public Statement, 1999). We can deplete these compounds; therefore, we should replace them until Preindustrial levels are achieved on a regional or locality basis.

Our future is at stake in terms of the health of the atmosphere, and human health which is improved by negative ions (extensively published in the field of Psychiatry) and this is one leading answer to a significant group of atmospheric problems. The author suggests there is enough evidence to demonstrate that much talk about capturing exhaust gases at source has not been acted upon due to the heavy industrialization of the world and this restoration is very likely necessary. A short term (30 year) restoration to the atmosphere in order to gain a long-term balance of the OH* radical in the environment is important to consider because the earlier this remediation is effected, the greater the likelihood that more global biodiversity will be preserved. The author strongly recommends the long-term balance of such an important component in our atmosphere. The less the atmosphere oxidizes, the greater the long-term build-up of atmospheric pollution, which greatly worsens global warming. This measure may offer relief for this situation and may greatly benefit localities and regions with unacceptable weather and climatic changes.

Excerpt:

"University of Saskatchewan
Department of Physics and Engineering Physics

Professor G.R. Davis (quoted)" Measurements of Pollution in the Troposphere

Scientific Objectives

"The troposphere is the region of the Earth's atmosphere from the ground to the temperature minimum, which occurs at an altitude of 10-15 km. It is the region in which we live and in which weather occurs.

Pollution of the tropospheric environment by the introduction of new chemical compounds or by changing the abundances of existing ones affects the natural chemistry of the region. Much of this chemistry involves the OH radical: it acts as a detergent, reacting rapidly with hydrocarbons, both natural and anthropogenic, and preventing their build-up. **Since many hydrocarbons are radiatively active gases, OH may be considered to play a role, albeit indirect, in determining the climate.** OH reacts rapidly with oxides of sulphur and nitrogen with the ensuing production of soluble species that are rained out or lost from the atmosphere by dry deposition. It also plays a major role in the production and loss of tropospheric ozone, an important radiatively active gas whose concentration may have been changing over the last century. Although the Earth's atmosphere has been studied by satellite experiments for many years, it has only recently become possible to monitor the composition of the troposphere from space: the main technical challenges are the variable surface of the planet and the presence of clouds."

Included is an expanded description of the merits and consequences of this proposed procedure. We can expect the OH* produced to couple with in situ pollution and acid deposits in the atmosphere for this is one of the detergent actions of the species. The author recommends a remote or strategically located, moderate-pollution, moderate-humidity area for these facilities - desert or prairie backcountry, or slightly more lush. Since the 1999 Geneva Convention scientists publicly identified pollution as a barrier to the natural repair of the Ozone layer and tests are ongoing of the hypothesis that urban pollution is being studied for its climate-forcing properties, locality programs should counteract this problem.

OH* is reported widely to be losing its ability to replenish itself (Prinn & Wang, 2002). This is a key and very serious development. Also of concern is that scientists might refute the long-term gains of an OH* release by focusing on the shorter-term consequences such as a moderate

short-term purge of acids from the cloud system. Vibrationally excited OH* transported with water will travel upwards, generally, and H₂O₂ and its intermediates are infinitely soluble in water, so the release of acids should be accompanied by ample amounts of water. The HO₂ molecule is considered an important component of clouds, both gaseous and aqueous phases, and may be involved in normal nucleation activities, and therefore its depletion may contribute to droughty or deserting effects. (Skubnevskaya and Dultseva, 2003 personal communication)

Strategic Atmospheric Repair Stations

These proposed facilities are quite simple and capable of flexible release rates. This facility's purpose is to restore a very important atmospheric stabilizer and detergent to the atmosphere, from more than one semi remote location, over a period of five to ten years. Scientific concern for the OH* molecule or radical is rapidly increasing, with recently developed instrumentation coming on line in North America to measure it directly. Photolysis of H₂O₂ is in the 230-240 Nm range and the formula is $H_2O_2 + hv \rightarrow OH^* + OH^*$. (Madronich, 1993.)

It is a source of H₂O₂ further along, in the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, which assures proxy distribution of H₂O₂ and the OH radical via water which is a key carrier on a permanent basis (Williams, Dentener, Vanden Berg, 2001). The presence of oxide, O⁻² needs to be studied as well as sunlight may generate this species from O^{1D}.

While the problem of OH depletion is very serious, human aided replenishment is a valid proposition that is quite affordable for a global or region-by-region project. In the latter case, directly-affected human populations can take action using "Clean Air Factories" once a sampling of their air is performed to determine how much OH, is missing, a calculation of how much H₂O₂ would effectively produce a 100% normal oxidizing atmosphere can be performed. This is also essentially true for urban situations. The release can be regionalized to account for the short lifetime of OH*, but the longer-term effects of the HO₂ ion in water is vital.

Depleted Peroxygen Compounds

All the forms of the peroxygens- OH, HO₂, and H₂O₂- can be reintroduced via dispersal through water fogging with concentrations of hydrogen peroxide ranging from 3ppm to 1 to 10% in remote areas; 3ppm is a reasonable amount near populated areas. Higher steady concentrations in dry remote areas should improve the global count of per oxygens.

This may be directly sourced from the successful capture and reformation of CO₂ into pure carbon fuel and a new method to make peroxide from the oxygens in CO₂. A human induced peroxide "burp" may become a necessity within a few years. According to calculations, one

tonne of coal will generate 15 tonnes of 100% H₂O₂. A 5 MT release of H₂O₂ would cost the equivalent of 335,000 tonnes of coal every year, as the flux of H₂O₂ that industry and cars use is about 5MT annually.

It is suggested, therefore, that this contingency plan be considered. It is true that CO₂ removal technology may arrive too late to stop a full global ice melt but the cooling accommodation actions of a peroxide dispersal may very well resolve a tipping point problem for the global climate. The author was the first scientist to recommend a peroxide release protocol in 1996 and a remote and regional based protocol remains a meritable option to buy time and remediate a pressing set of atmospheric problems – human-induced lowering of atmospheric oxidation and high particulate levels, methane, each causing climate forcing – for an acceptable energy and CO₂ cost. The technology is progressing in the Kamloops, British Columbia District.

Conclusion: Replacement Plans Can Vary By Air Shed

The proposed release of hydrogen peroxide is made up of a simple facility, a tank, a pump system, and a stack with piping in it from the pump, and a special widely-available nozzle at the top of the stack. This release can be executed at one or several locations over a recommended period of ten years. It is known that total troposphere-stratosphere mixing takes an average of six years, but the troposphere takes the brunt of almost all pollution, and circulation within the troposphere takes three weeks. Fogging H₂O₂ into the atmosphere at ground level gasifies the hydrogen peroxide and it is broken into the OH* radical by sunlight, and vibrationally excited by sunlight; it is also effective to fog at night, where the formation of HONO (and HO₂) would build up and become a source for OH* in the early morning after NO + OH* forms HONO at night, then it photolyses: $\text{HONO} + \text{NO}_2^- + h\nu (h+) \rightarrow \text{NO} + \text{OH}^*$ (Williams, Dentener, Van Den Berg, 2001). The HO₂ ion then migrates upward and disperses with the water cloud, and in remote settings should have an opportunity to disperse ($\text{HO}_2 + \text{NO} \rightarrow \text{OH}^* + \text{NO}_2$ Yuhan Wang, 2000). It is the number one atmospheric detergent of the atmosphere, and therefore it merits being gradually dispersed at from 1ppm to 100 ppm rates, till replacement to its 100% “normal level, particularly around population centres, is achieved. This normal level is $(1.41 \times 10^6 \text{ molecules/cm}^3)$, whereas communities generally have less than $1.0 \times 10^6 \text{ molecule/cm}^3$ ” (Prinn, 2002). Some of this molecule will couple with in situ pollution, which will return to the ground in a variety of forms, including acids; however, this is temporary and a true long term view of regional restoration is recommended because bringing this defence mechanism back to 100% will serve to remove those compounds which we know threaten air-breathing life (with respect to biodiversity and global temperature) as robustly as it used to three hundred years ago.



Figure 2: Regional Background Atmospheric Replenishment Station gasifies from 600-4500 Litres per day

Outdoor Facility

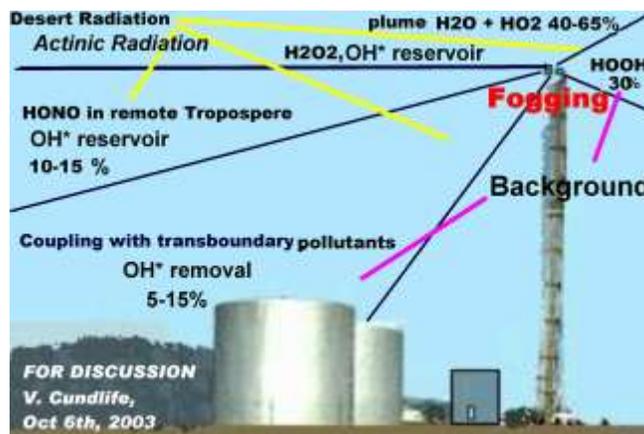


Figure 12: *Suggested* plume partition of species in fogged H₂O₂ in water into its components with average day-night estimates for visualization purposes

This is a small facility and can be scaled down. Preliminary checking shows that it is competitive cost-wise with at-source pollution capture technologies.

An enhancement of OH* has merit since ~ 30% is currently missing globally which is about 5 megatonnes. As a vibrationally excited molecule, the OH* will tend to travel upwards quite readily after the photolytic (sunlight) splitting of the H₂O₂ gas has formed it. Night time release is also productive. One goal is to gasify 600-10,000 litres a day until a calculated replacement is achieved. The average 24 hour period of fogging would yield a 1 Km x 1 Km x .1 Km cube of gas, which is mostly water.

The effects of this release would likely be seen in a matter of 2-3 weeks regionally but would take 8-15 years to have a total global effect. Even then, hundreds of dispersal units would have to be in operation. Adjustments in the amount of the release would be in keeping with

amounts measured at various locations using ground based sniffing, aircraft, balloon, and other methods such as satellites with the necessary detection capability, already in place as of 2004.

Supplemental Rationale

It is becoming increasingly clear that the OH* molecule cannot indefinitely replenish itself, particularly in industrial “hot spots” or high intensity zones; therefore, these simple installations are recommended. Where ozone forms at ground level, OH has been aggressively abstracted and O is left to form O₃. Oxide may be involved as well but has not been studied in situ. Stratospheric O₃ depletion suggests that OH has been oxidized and abstracted (reacted with) in large pulses of particulates. Particulates use up O_x in being oxidized firstly by OH, and then the O₃ is decreased in acting as an oxidant. OH, as the main oxidant, is the known first order reactant in both cases, and is lost very rapidly. O₃ is the OH molecule’s reservoir of O¹D oxygen.

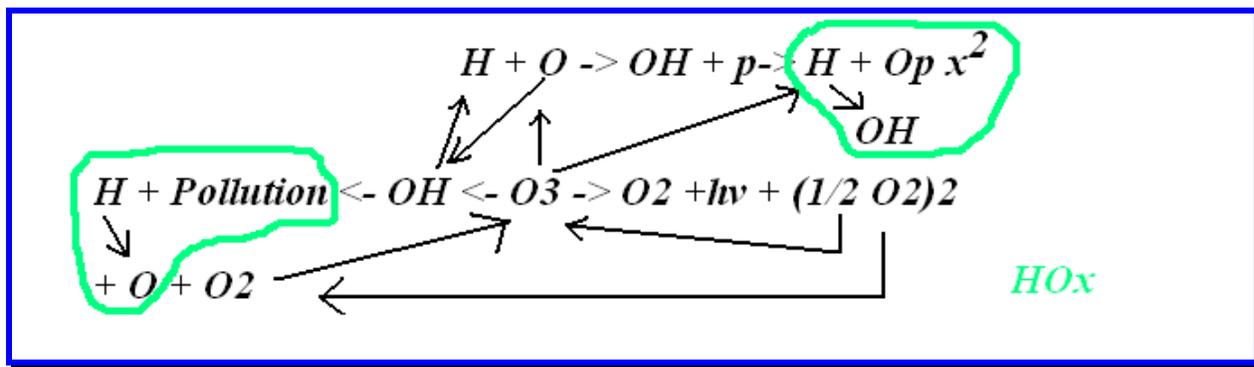


Figure 13. The Close Coupling of the Chapman Cycle in Summary Showing the Need to Address Ozone and Hydroxyls status as *one problem* in the Stratosphere (Cundliffe, 2007.).

OH is an O₃ depletor due to acidic sources of H which flood the O₃ layer and rapidly forms OH. If we look we will find lots of HOx, but we need free OH, not combined OH. The HOx also scavenge particulates and then fall to the ground or become PM 2.5 or larger and persist as POP’s. The key is to add free perhydroxyls which will additionally and supplementally create removable PM or directly remove PM. This can be shown and measured in a smog chamber system or tested in a small pilot facility. The HO₂ lifetime at up to six hours positions a proposed release as a viable remediation procedure with achievable regional and para regional reach.

It is suggested that just sitting back and watching the continued reduction of this atmospheric cleanser would have much more serious consequences to the environment and air breathing life forms than effecting a restoration of it. This is the justification for performing this procedure.

Conclusions

This proposed facility could be run as a singular pilot project, evaluated, and if effective increase of the OH radical occurs, it could be adapted as an ongoing contingency plan supported by government and industry. Hydrogen peroxide is an ancient component of the atmosphere. It is an approximately 3-billion-year-old mechanism, and its irreversible depletion may be at hand. High methane, carbon, and carbon monoxide concentrations as well as the presence of particulate matter and volatile organic compounds are the major sources of hydroxyl radical depletion. Introducing the hydroxyl radical at ground level would also counteract the already released tropospheric chlorine compounds, bromine compounds, and methane before they reach the stratosphere.

All in all, the dispersal of hydrogen peroxide into its components has the distinct potential for atmospheric restoration and rebalancing as well as aiding to cool the global atmosphere.

PART 2: Proposed Experiments

A) Testing of Varied Concentrations of Dilute H_2O_2 into Controlled Living Ecosystems to Determine Safety of Long Term Environmental Remediation of the Tropospheric Ecosystem's Oxidative Layer. (Mao-Chang Liang et al, 2006)

Equipment:

1) Small Terrarium Biosphere with small animals that will be treated with low doses of atomized H_2O_2 and a control biosphere. Both systems require sunlight, and closely simulate outdoor conditions. The soil, water, sediment and humus populations are counted evaluated and compared to the control populations. The animals are monitored using basic health parameters. Residual air samples taken by vacuum & analyzed compared to control. Plant cuticle layers, root systems & associated bacteria are studied counted and compared.

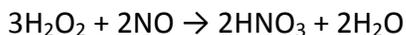
2) A smoke residual box modeller with control box. Both boxes subjected to wood and other smoke injections and the experimental box dosed with mild H_2O_2 and other

peroxygens and oxide in water. The residues from both boxes after equal time periods are sampled and analyzed to compare chemical evolution and evaluate the effect of H₂O₂ and others on pollution disturbances.

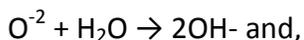
3) A hydroxide ion distribution system to correct oceanic water and fresh water lowered pH. The pH of water bodies could be remediated if a large supply of hydroxide or oxide such as the route of synthesis related to this proposal were utilized. A small scale titration and premixing system for a boat/barge platform could be investigated and verified.

B) Indoor testing of hydro oxygens using Petri dishes at varied distance from per oxygen source for several days and weeks to demonstrate that compared to controls, the compounds create clean indoor air. The air of these test areas can be tested for all related species including $\frac{1}{2}O_2$, O^{-2} , O_2 , OH^* , OH^- , H_2O_2 , HO_2^- , H_2O , VOC's, particulates, CO, NO_x, SO_x, and any other trace contaminants of interest.

C) There are two routes to treat NO_x at the stack. Recycling HNO₃ by electrolytically splitting it while 50% dilute in water and recovering H and O while releasing NO₂ safely: Cheap clean peroxide via a new commercial route can provide power to achieve this.



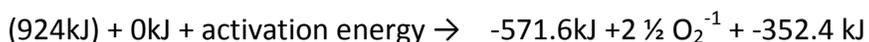
Both can be reduced to NO₂, H, O by electrolysis but the rates for a larger system need to be studied in a small scrubber bench unit using pure NO (g) as the feedstock. Other research is looking into oxide added to water and whether hydrated oxide is a scrubbing compound for flue gas. NO₂ may also be reduced back to N₂ and O₂ in a proposed new technology which is not available to elaborate here. Heats of reaction, MS and stoichiometric analysis are necessary. The in-situ source for these agents needs a bench test as well:



O⁻² can likely be made by heating O₂ with quartz heaters in an aquarium-housed thermal chamber and passed through a zirconia membrane, which is being studied (MS can verify this on the CO₂ splitting chamber oxygen if a good flow obtained). OH⁻, which can be synthesized on site where needed is of active interest. These could give in-situ ultra high purity sources thus avoiding the current anthraquinone source route which has a high carbon footprint and transport hazard issues. Industry should find in situ hydro oxygen sourcing and recycling attractive from safety and economic standpoints if validated by testing.

D) Checking for Fuel Value and Testing OH⁻ as a fuel which produces environmentally remedial exhaust to the environment, using bomb calorimetry tests and MS species characterization of expected species. The OH would have an oxygenic source on a large scale (a source with a *negative* carbon footprint).

Enthalpy of combustion of H₂O₂ is 136.3kJ/mole. Bond Enthalpy of OH is 462 kJ/mole. To write a charge-balanced combustion reaction, this is how it would look:



(Combustion)

Some energy has been used to form the $\frac{1}{2} \text{O}_2^{-2}$ or oxide radicals as they are not ground state. This is where further investigation with a combustion chemist/physicist is needed as the activation energy or flame energy needs to be determined to balance this.

The rearrangement of oxygen and hydrogen from H₂O₂ to 2OH⁻ without H₂O on the left side would need to be validated. If both species on the left are liquid, this may have potential as at this point the 2OH⁻ + O₂ is potentially 3.36 times more energy dense than H₂O₂'s combustion enthalpy. Hydrogen peroxide clearly is already a known and well understood fuel and its exhaust's oxygen production would be a *built in route to increasing the oxidizing capacity of the atmosphere*. In summary, using aviation exhaust such as from hydroxide to deliver a remediation compound to the environment would be highly cost effective, since the aircraft would conduct normal operation such as it

already does while giving off a non-hydrocarbon based remedial fuel. This may effect a direct repair of the Ozone layer if needed.

PART 3 Regional Costs for Regional Test Release of Hydrogen Peroxide
Project Pristine ESTIMATES for A PILOT OPEN AIR TREATMENT SITE DISPERSING HYDROGEN PEROXIDE IN WATER.

| | | | |
|---|--|--------------------|--------------------------|
| Accuro Draeger tube pump kit | | | \$592.00 |
| Pump and tube training CD | | | \$36.00 |
| 10- H ₂ O ₂ tubes, 0.1-3ppm | | | \$111.00 |
| Pac 3 mobile sensor, 1-20ppm | | | \$500.00 |
| Mini Fogging System | | Atomizers & Tubing | \$450.00 |
| Volunteers, administration, documentation | | | \$200.00 |
| Preparation | | Communications | \$50.00 |
| Pumper system and locating | | Safety equipment | \$1500.00 |
| Total | | | <u>\$3,500.00</u> |

Table 3. Small Scale Test Line Items Cost

| | | | |
|--|--|------------------------|-------------|
| 2 Metal lined Garages with Doors | | | \$10,000.00 |
| 2 facility Fences with gates | | With barbed wire | \$4,500.00 |
| Concrete rated 2500MPA @ 14 M ³ | | Rated for inside tanks | \$2,500.00 |
| Concrete Forms | | In kind if possible | \$3,000.00 |
| Power Supply and Telemetry | | Remote if desired | \$9,000.00 |
| Tanks-2 x 4,000 Gallons | | | \$16,000.00 |

| | | |
|--|----------------------|----------------------------|
| 2-Guy supported Towers, 125 Feet Tall | | \$60,000.00 |
| 2 x Pumps & piping | | \$10,000.00 |
| 2 x 4 Gpm Fogger-atomizers | | \$3,000.00 |
| Safety Equipment-Scott air, radios | | \$7,000.00 |
| Earthen Burms around buildings | Contractor donations | \$700.00 |
| Community in kind labor-erections | Incl. Safety meets | \$20,000.00 |
| Permits and Quality Control | | \$4,000.00 |
| 700 barrels of 35% Grade H ₂ O ₂ | With 2 static mixers | 70,000.00 |
| <u>Sub Total for two facilities</u> | | <u>\$219,700.00</u> |
| Coordination, Community Education | One year | \$5,000.00 |
| Honorarium | One year | \$10,000.00 |
| Grand Total | | \$235,000.00 |
| Science Coordination & Documentation | | 25,000.00 |
| Composite Grand Total | | \$260,000.00 |

Table 4. Small Scale Test Line Items Cost

A brief look at the global cost is given below.

Summary for a global placement that delivers 5MT annually of H₂O₂:

Need 250T/yr. of H₂O₂ for each facility. This would require 20,000 facilities or the equivalent in gross production. The equivalent cost is US\$5,000,000,000 US. This cost in terms of this quote,

“The *Stern Review*, a 2006 report by the former Chief Economist and Senior Vice-President of the World Bank Nicholas Stern, predicts that climate change will have a serious impact on economic growth without mitigation. The report suggests that an investment of one percent of global GDP is required to mitigate the effects of climate change, with failure to do so risking a

recession worth up to twenty percent of global GDP. The *Stern Review* has been criticized by some economists, saying that Stern did not consider costs past 2200, that he used an incorrect discount rate in his calculations, and that stopping or significantly slowing climate change will require deep emission cuts everywhere. Other economists have supported Stern's approach ^[12] ^[13], or argued that Stern's estimates are reasonable, even if the method by which he reached them is open to criticism. " (Stern, 2006).

http://en.wikipedia.org/wiki/Economics_of_global_warming

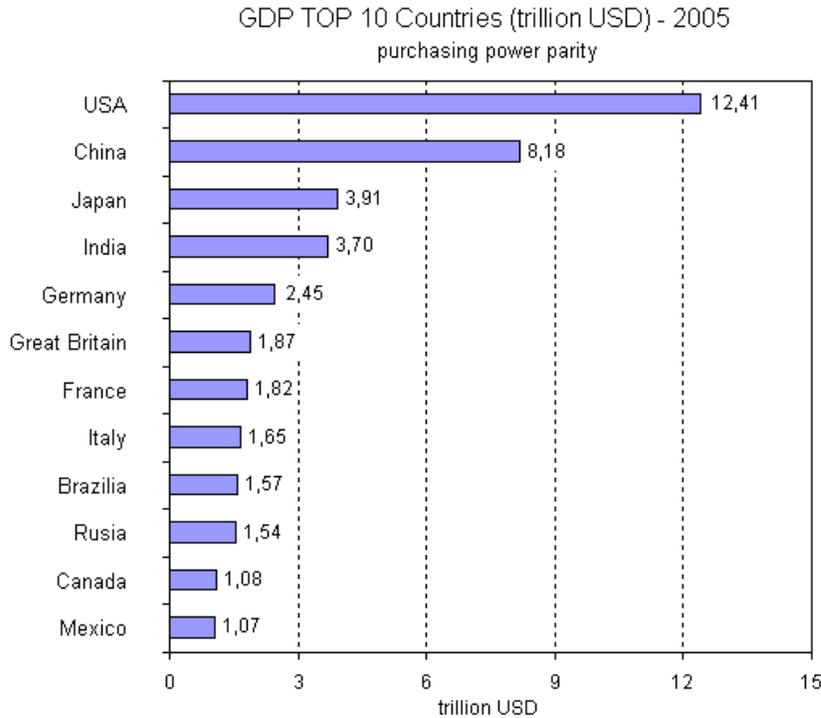


Figure 14. The Weak GDP and Climate Change Cost Argument.

<http://euroekonom.com/graphs-html/gdp-top10-2005.html>

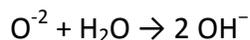
This equals USD 41.25 Trillion for 2005, compared to which \$5,000,000,000 is .001212% or an infinitesimal amount. If 1% of 2005 GDP were applied once as a budget for this release program, *it would pay for 825 years of operations*. Further discussed is the cost of oxide dispersal in relation to the Global GDP and it offers a compelling and greater affordability.

This makes a very strong case for remediation of the oxidizing capacity of the atmosphere and this release is estimated to provide a 50% reduction in warming of the atmosphere if performed over one year.

It is recommended that serious consideration of a release procedure be performed due to the overwhelming cost-benefits.

PART 4: Lowering Global Atmospheric Chemical and Meteorological Energy through Negative Ion Restoration: General Introduction to Emergency “Oxygen and Intermediates” Protocol.

The several decades of research available about the oxidizing capacity and medium of the atmosphere over the past twenty years is utilized. It is a badly depleted atmospheric component. It is also directly coupled to the ozone layer in the stratosphere. Many scientists attribute climate forcing to particulate congestion, methane, and VOC's. Because the polar ice sheets are melting at triple the rate all of the IPCC model predictions, action is necessary now. This option of releasing (energy –electron) receptors of hydro oxygens would absorb about 2.7 GW per 100 T of peroxide. Multiply this by 3.36 if OH- ions are utilized; multiply this by 8.15 for the oxide anion which would absorb 22 GW of energy per 94 T of oxide. The oxide ion, O_2^- , is the conjugate base of the hydroxide ion, OH^- , and is encountered in ionic solid such as calcium oxide. O^{2-} is unstable in aqueous solution – its affinity for H^+ is so great ($pK_b \sim -22$) that it *abstracts* a proton from a solvent H_2O molecule and forms the following:



Globally, if 576,690 T of O^{2-} was scientifically restored to the environment, 1.35 GW (or Giga Joules) of energy would be absorbed. This would cost about \$35 a tonne and \$350 million including operating costs (0.000085% of Global annual GDP for one year). This potent action is in addition to ensuring that night time heat venting ability of the troposphere would also be significantly restored especially around urban air sheds. It would be very interesting to have this remediation modelled to look for the severity reduction of climate and weather events and determine the global cooling effect over 10-50+ years. There is a 30 year body of evidence regarding negative ions in the Psychiatry field, outlining their positive effects on human health. Peer reviewed data can easily be found on this subject online or in the public domain.

Air sheds have been modelled well where there is human population. Cloud charge and cloud physics can be identified in each air shed with some good scientific observation as the general dynamics of these in enough air sheds has become well understood in Meteorology and Atmospheric Chemistry expertise can easily couple to this and produce reliable predictions on how the moderation of horizontal cloud charge difference over time in a negatively ionized air shed would reduce the excessive energy and unstable precipitation events in frontal systems in those regions.

Summary

There are both valid reasons and affordable means to use the hydro oxygen and oxide to remediate and nucleate critical levels of atmospheric overloading of water, problematic aerosol pollutants, and urban ozone. Because of the speedy reaction rates of hydro oxygens, and the very affordable oxide ion, the benefits of dispersions would yield measurable and timely results to fight the spectre of a looming “tipping point of the Earth’s temperature”. We may need to proactively allow the venting of heat by reducing and oxidizing off of our excess pollution. According to scientific study this would improve human health at the very least. It is left up to the educated reader to extrapolate the numerous other benefits.

Full or normal homeostasis of our dynamic global and regional environments may pivotally rest upon addressing this aspect of our planetary Geochemistry and Chemical Meteorology. Testing of the proposed measures has potentially vital global importance and can be done a variety of ways to ensure confident predictability on larger scales. The Author places this short treatise on record in the event that these measures are determined by further climatic and air quality problems, to be necessary for survival of our present systems which support life. The term Oxygen Earth Protocol refers to the herein detailed actions, which are available, affordable, can be modelled and may be profoundly important in the future.

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