



Humic Like Substances (HULIS): Contribution to Global Warming and Stratospheric Ozone Depletion

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ABSTRACT

The authors have previously provided compelling evidence that coal fly ash particles, not chlorofluorocarbons (CFC's), are the primary cause of stratospheric ozone depletion. Coal burning and coal fly ash aerosols utilized in covert tropospheric geoengineering have already severely damaged the stratospheric ozone layer, leading to deadly ultraviolet radiation UV-B and UV-C penetrating to Earth's surface. Coal burning and biomass burning are primary sources of a particular organic aerosol, humic-like substances, referred to collectively as HULIS. HULIS, like coal fly ash, plays a key role in climate change due to its ubiquity in biogenic and anthropogenic aerosols, its ability to absorb solar ultraviolet radiation and to transfer that heat to atmospheric gases, which reduces the temperature difference relative to the near-surface air, which reduces atmospheric convection, and which concomitantly reduces heat loss from the surface, causing regional and global warming. HULIS affects human and environmental health by production of reactive oxygen species and environmentally persistent free radicals. Stratospheric ozone was apparently depleted during the Permian Extinction by coal and biomass combustion aerosols produced by massive volcanic activity. A spike in sea and land temperature during World War II, associated with particulate pollution, also is correlated with a spike in HULIS obtained from Alpine ice cores. Recently, large forest fires have also been shown to deplete stratospheric ozone. Since HULIS is common to both coal and biomass burning, and ozone is taken up by submicron HULIS particles, it follows that HULIS aerosols are another cause of stratospheric ozone depletion. Our time is short to end all geoengineering activities and reduce or eliminate anthropogenic coal fly ash and HULIS-type aerosols.

INTRODUCTION

Stratospheric ozone is Earth's natural sunscreen, blocking most of the Sun's most damaging ultraviolet radiation and protecting all higher forms of life on Earth. The Montreal Protocol, developed by the World Meteorological Organization and United Nations Environment Program, went into force in 1989 [1].

Despite the official narrative of "*gradual ozone recovery*" due to the Montreal Protocol, which led to the phasing out and later banning of chlorofluorocarbons (CFC's), the truth is that stratospheric ozone continues to decline, and atmospheric scientists either do not know or will not say how badly the ozone layer has been damaged [2]. Scientists at the National Aeronautics and Space Administration (NASA) and at the National Oceanic and Atmospheric Administration

(NOAA) in 2018 admitted that there was a decline in lower stratospheric ozone offsetting the overall ozone layer recovery. They claimed they did not know the causes of this depletion and emphasized that “*the causes need to be urgently established*” [3].

A form of air pollution and existential threat to the biosphere is posed by deliberate tropospheric aerosol geoengineering. For decades, several countries and the U.S. military have been co-opted into the aerial spraying of particulate aerosols into areas where clouds form for the purposes of weather modification, climate intervention, communication systems, weather warfare or defense [4].

- There is no truthful public disclosure concerning these operations, despite the obvious particulate trails observed overhead.
- Disinformation claiming the particulate trails represent harmless ice-crystal “contrails” stands in conflict with direct observation and is disputed by scientific evidence [5].
- Forensic scientific investigations have demonstrated that the particulate matter dispersed into the lower atmosphere is consistent with coal fly ash, the fine-grained, light-ash waste product from industrial coal-burning that by regulation must be trapped and sequestered in Western nations due to its toxicity [6].
- Coal fly ash contains aluminum silicates, iron oxides, and numerous toxic trace elements, unconsumed carbon, and even radionuclides. These elements can partially dissolve in water and their concentrations in coal fly ash aerosols are typically higher than those found in Earth’s crust, soil, or even solid coal [7].

We have presented compelling evidence that supports our contention that aerosolized coal fly ash particles are the main agents responsible for stratospheric ozone depletion, not chlorofluorocarbon gases [8-10]. As illustrated in Figure 1, aerosolized coal fly ash particles, uplifted to the stratosphere, not only serve as ice-nucleating particles, but are trapped and concentrated in polar stratospheric clouds. In Springtime, as these polar clouds begin to melt and evaporate, the trapped ozone-consuming coal fly ash particles are released making them available to react with and consume stratospheric ozone.

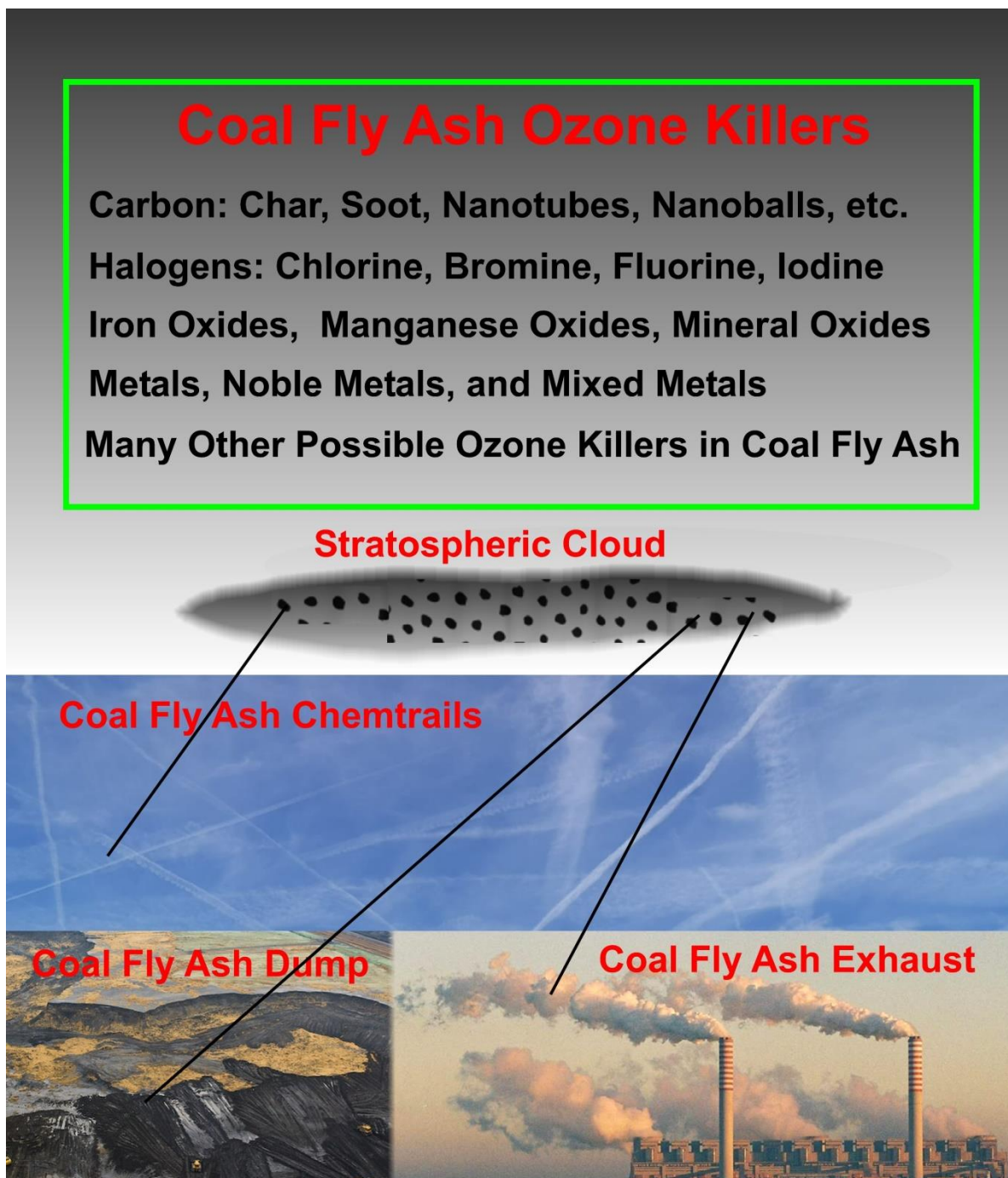


Figure 1. Graphic illustrating the major sources of aerosolized coal fly ash lofted into a particle laden polar stratospheric cloud, and some of the many components of coal fly ash that directly kill ozone [8, 11].

Recently, remarkable changes in the stratospheric abundances of chlorine species and ozone were observed over the Southern Hemisphere mid-latitudes following the massive 2020 Australian wildfires [12]. It is now recognized that large wildfires inject biomass-burning organic particles that contain oxygenated functional groups and water on their surfaces. These same particles also destroy ozone [13]. Humic-like substances (HULIS) are widely distributed

in atmospheric aerosols throughout the world. Primary sources of HULIS are coal combustion and biomass burning. These aerosols are commonly mixed, along with secondary organic aerosols formed from aging organic matter [14]. Since atmospheric humic-like substances are oxidized by ozone [15], it follows that HULIS aerosols, in addition to coal fly ash aerosols, are another cause of stratospheric ozone depletion. In this work we review HULIS aerosols and their contribution to climate change, global warming, and stratospheric ozone depletion.

HULIS REVIEW

HULIS, i.e., humic-like substances, is a category of organic molecules isolated from fog, clouds, and rainwater which resembles the organic material in river/sea water and soils formed by the breakdown of biological material. HULIS has received increasing attention over the past two decades due to its ubiquity and high concentration in both biogenic and anthropogenic aerosols, its participation in many atmospheric reactions, its optical properties, and its effects on clouds and climate [16].

HULIS comprises a significant portion of organic carbon (OC) and water-soluble organic carbon (WSOC), accounting for the majority (60%) of the latter. Due to its surface activity and water solubility, HULIS has an important effect on hygroscopic growth and cloud nucleation, and thus plays a vital role in atmospheric chemistry [17]. HULIS differs from common humic substances (e.g. humic and fulvic acid) in several ways, including its increased surface activity, better droplet activation, less acidity, and a smaller molecular weight with lower aromaticity.

HULIS is thought to most likely form by accretion reactions of smaller molecules or breakdown of larger molecules during combustion, as opposed to the process of biological degradation of humic substances [18]. HULIS has distinct physical and chemical characteristics, including its acidity, ultraviolet and visible light absorbance, fluorescence, and Fourier Transform Infrared Spectroscopy spectra, which show similarity to naturally occurring humic and fulvic acid in atmospheric aerosols. Atmospheric HULIS can be extracted by various laboratory methods including solid-phase extraction, capillary electrophoresis, ion exchange, and reversed-phase chromatography [19].

Humic-like substances (HULIS) are composed of macromolecular organic compounds with a polycyclic ring or carboxyl, carbonyl, and hydroxyl group structure. Recent studies indicate that HULIS originates from both primary emission and secondary formation. Atmospheric chemical processes including condensation, oligomerization, and oxidation are secondary sources of HULIS, while biomass-burning and coal combustion are primary sources of HULIS.

In a study of pollution haze in China, Fourier transform-ion cyclotron resonance mass spectrometry showed CHO/CHNO compounds and lignin-like and protein/amino sugars accounted for a high proportion of HULIS [17]. HULIS-C (HULIS Carbon) is often associated with "crustal," or anthropogenic metals (Al, Fe, As, Se, Sr, Pb), suggesting its formation may arise from mixed sources [20]. Structural characteristics of atmospheric HULIS compared to terrestrial humic and fulvic acids reveal striking similarities in chemical characteristics, except for organo-sulfates, which are unique to atmospheric HULIS [21]. Molecular characterization of humic-like substances in PM_{2.5} atmospheric particles from the offshore East China Sea showed

S-containing formulas (CHOS and CHNOS) represented the dominant components, followed by CHO and CHNO [22].

Fractions of CHO among α -pinene ozonolysis yield S-containing compounds with olefinic structures are abundant in the atmospheric particles, suggesting secondary organic aerosol formation. Biogenic volatile organic compounds (α -pinene or monoterpene) are the dominant precursors in the HULIS samples. Lignin-like species (40-50%) and protein/amino sugars (25-30%) comprise the major species among the substance classes [22].

Figure 2, abstracted from [23], shows examples of size-resolved particulate matter collected in a typical urban site in Greece during the cold and warm periods of the year.

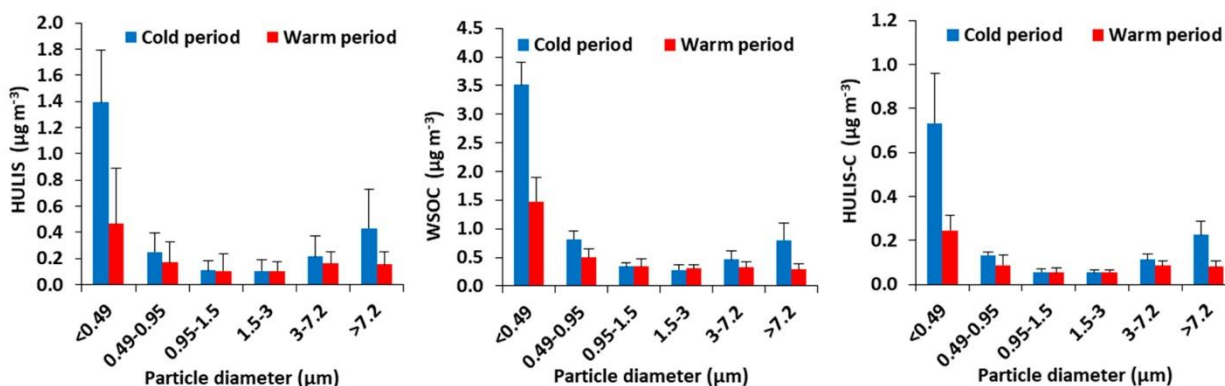


Figure 2. Three graphs from [23] showing mass distributions as function of particle size of HULIS, WSOC, and HULIS-C for two periods differing in temperature.

HULIS from biomass burning contains a high abundance of lignin and polysaccharide derivatives, since biomass is composed mainly of lignocellulosic material. experimental evidence suggests that atmospheric HULIS can be formed either by isoprenoid or terpenoid hydrocarbons in the presence of a sulfuric acid catalyst and/or by a lignin-like precursor that reacts with hydroxyl radicals (OH) in cloud water [24].

Organic compounds including water-soluble HULIS make up a major fraction of atmospheric particles. Water-soluble organic compounds affect cloud and fog droplet activation. HULIS affects cloud droplet activation by the production of surface partitioning and efficiently reducing surface tension. HULIS particles play an important role in cloud formation by serving as condensation nuclei, by their strong surface-active (surfactant) activity, and by their hygroscopic aerosol growth [25].

The efficiency of surfactants coincides with an increase in cloud frequency [26]. Dinar et al. showed that HULIS aerosols create more cloud condensation nuclei than the Suwannee River fulvic acid standard and that the chemical aging of HULIS may improve its cloud condensation ability due to the oxidation of larger molecules into smaller ones [27]. HULIS originating from primary coal and biomass burning sources, and produced from aqueous phase reactions can trigger immersion freezing. HULIS is an important contributor to ice active entities, especially when other ice nucleating particles are low or absent [28].

Isoprene-derived secondary organic particles like those in HULIS have recently been found to nucleate ice in cirrus-level clouds [29]. Not only HULIS but its major components, including lignin and cellulose, effectively nucleate clouds. Lignin acts as an ice-active macromolecule at temperatures relevant for mixed cloud processes. This activity is not susceptible to changes under atmospherically relevant conditions, despite changes observed by ultraviolet and visible light absorbance [30].

Commercial lignin has consistent ice-nucleating activity across product batches, is stable over time, and can even be used as a standard for its immersion freezing ability [31]. A sub-component of lignin, cellulose, can act as an efficient ice nucleating particle in super-cooled clouds of the lower and middle troposphere. Microcrystalline cellulose can nucleate ice in such clouds even in remote and high elevation areas throughout the year [32].

The contribution of light-absorbing organic compounds like HULIS to aerosol absorption and scattering represents one of the greatest uncertainties in understanding the degree of its effect on climate and global warming. In a study of the complex refractive index of atmospheric HULIS retrieved by Cavity Ring Down aerosol spectrometer (CRD-AS), it was found that the refractive index (absorption) of HULIS-containing aerosols greatly increases in the ultraviolet (UV) radiation range and that this absorption was associated with increasing molecular weight and aromaticity. HULIS extracted from pollution and smoke particles absorbed more UV radiation than HULIS from rural aerosols [33]. HULIS and other organic fractions of aerosols including highly polar water-soluble organic matter (HP-WSOM) and water-insoluble organic matter (WISOM) all show increasing radiation absorption of solar radiation (Figure 3) with ultraviolet absorption extending to UV-C levels (100-280 nm) [34].

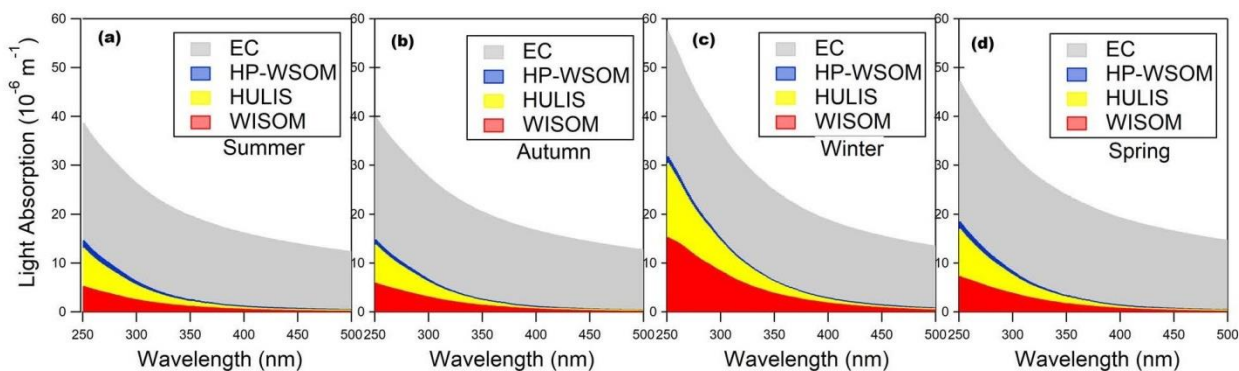


Figure 3. Stacked plots, abstracted from [34], of the seasonal averages of the contributions of the atmospheric organic aerosol (OA) fractions, and elemental carbon (EC), also called black carbon, to the total light absorption.

The mass-specific optical absorption of HULIS aerosol measured by a four-wavelength photoacoustic spectrometer was nearly negligible in the visible light range, but very strong at 266 nm, comparable to black carbon, a major radiation absorbing fraction of ambient aerosols [35]. The light absorption of humic-like substances from simulated biomass burning varies by emission factors, including lignin content [36].

Lignin is a heterogeneous aromatic polymer with a major absorption maximum in the UV-C region, but it lacks significant UV-A and UV-B absorption [37]. Secondary aerosol conversion due to atmospheric aging may cause more aromatic structures in HULIS from biomass burning, resulting in stronger light absorption [38]. Lignin is known to react with and consume ozone [39-43].

Metal ions are important atmospheric components that affect the optical and photochemical reactivity of HULIS. For example, HULIS showed light absorption that increased by 56% for a HULIS-Fe³⁺ system, with fluorescence blue shift and fluorescence quenching demonstrating a dose-effect relationship [44]. The Mass Absorption Efficiency, which describes the efficiency of absorbing solar energy per carbon mass of HULIS, decreases with particle size, suggesting that the finest size fractions contain more light-absorbing chromophores, thus affecting the light-absorbing ability of organic aerosols [45].

A study of light absorption by HULIS aerosols in China showed that the strongest chromophores were produced from anthropogenic precursors. Fossil fuel sources contributed to more secondary than primary HULIS year-round, while the largest contribution to HULIS from biomass burning was found in winter, and the largest contribution to HULIS from biogenic secondary organic compounds was found in the summer [46].

Black carbon particles, originating from combustion sources, are known to absorb sunlight and heat the atmosphere. Black carbon absorbs solar radiation in both the visible and the near-infrared spectra and is a principal cause of atmospheric warming, which results in reduced atmospheric convection, which results in diminished heat removal from Earth's surface. However, emissions from biomass burning and coal burning contain both black (or elemental) carbon and the organic fractions with their short-wave absorption may cause atmospheric heating comparable to black carbon [47].

Types of brown carbon include tar materials from smoldering fires or coal burning, biomass burning, organic compounds emitted from soil, and volatile organic compounds emitted by vegetation and wood decaying fungi. Warming trends in Asia are amplified by brown cloud solar absorption. It is estimated that brown clouds enhance lower atmospheric solar heating by about 50 per cent [48]. Like black carbon, moderate to strong absorption of solar radiation by brown carbon likely exerts a warming effect at the top of the atmosphere [49].

The HULIS fraction of brown carbon contributes to atmospheric warming over the western Pacific [50]. The Arctic is warming at an excessive rate relative to the rest of the planet, and it has been shown that brown carbon (including HULIS) imposes strong circum-Arctic warming [51]. We have provided compelling evidence that particulate aerosols, not CO₂, are the principal cause of global warming [52-55].

Pyrogenic coal fly ash, both from coal burning and from covert tropospheric jet-spraying, for military and/or climate altering purposes, contains black and brown carbon and iron oxides, all of which absorb solar radiation (including ultraviolet wavelengths) and heat the atmosphere. This overheating of the upper portion of the troposphere greatly reduces the

efficiency of atmospheric convection, resulting in diminished heat removal from Earth's surface [52-55].

This new paradigm is supported by multiple lines of evidence including the "Gottschalk Curve," showing a distinct spike in global temperature during World War II (WW2) that shows up in eight independent NOAA temperature databases (Figure 4). This anomalous temperature spike is inconsistent with CO₂-caused global warming as CO₂ persists in the atmosphere for decades [56, 57]. Furthermore, CO₂-caused global warming during WW2 can be ruled out as Antarctic Law Dome Ice core data during the period 1936-1952 show no significant increase in CO₂ during the war years, 1939-1945 [58].

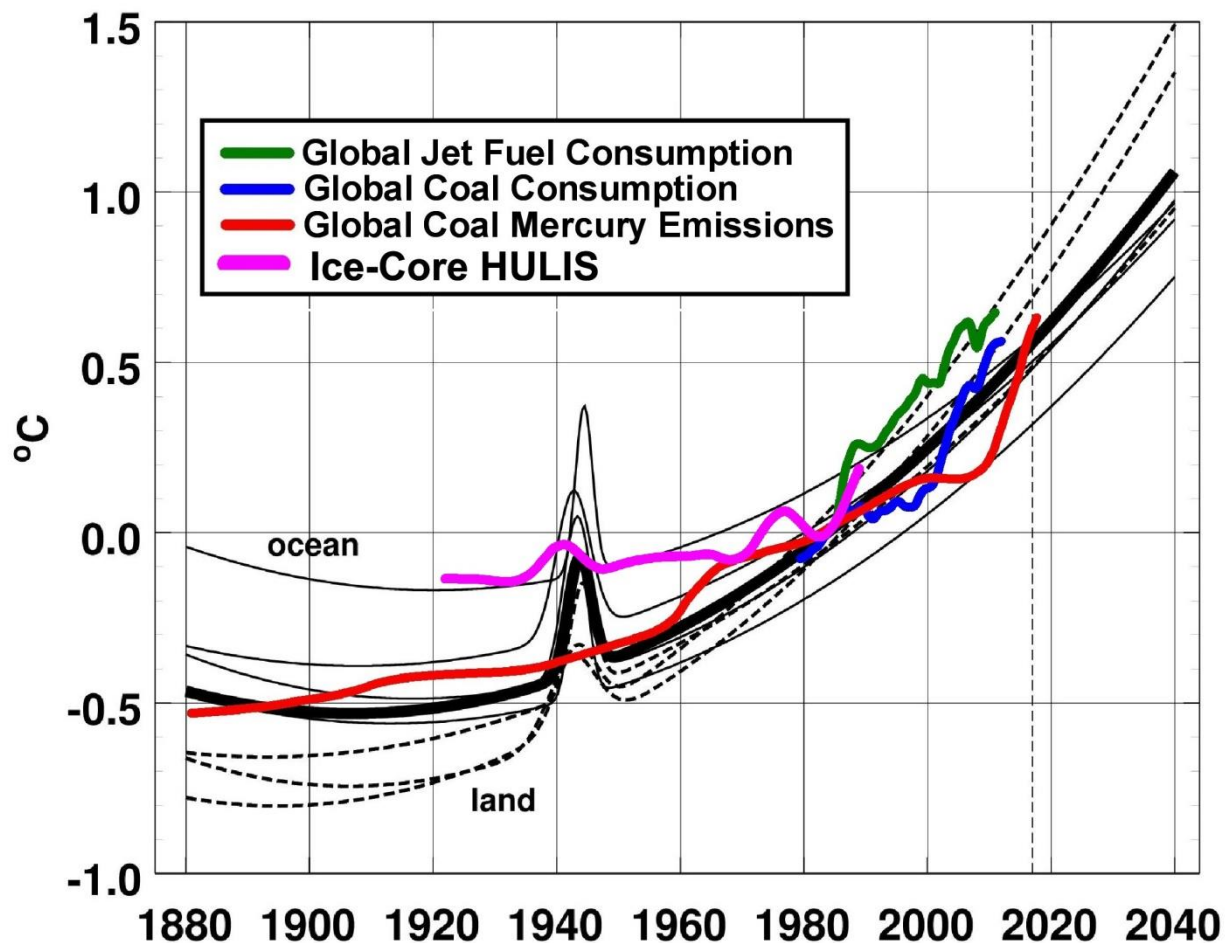


Figure 4. From [53, 59]. Copy of Gottschalk's fitted curves for eight NOAA data sets showing relative temperature profiles over time [59] to which are added proxies for particulate pollution. Dashed line: land; light line: ocean; bold line: weighted average.

World War II activities injected massive amounts of particulate matter into the troposphere from extensive military industrialization and vast munition detonations, which included demolition of entire cities, and their resulting debris and smoke [52-55]. The implication is that the aerosolized pollution particles trapped heat that otherwise should have been returned to space, and thus caused global warming at Earth's surface [53] which would have subsided

rapidly after hostilities ceased. Rapid cessation of WW2 global warming is understandable as tropospheric pollution-particulates typically fall to ground in days to weeks [60-64].

Figure 4, from [53, 59], shows relative-value, particulate-pollution proxies added to Gottschalk's figure: Global coal production [65, 66]; global crude oil production [66, 67]; and, global aviation fuel consumption [66]. Each proxy dataset was normalized to its value at the date 1986, and anchored at 1986 to Gottschalk's boldface, weighted average, relative global warming curve. The particulate-proxies track well with the eight NOAA global datasets used by Gottschalk [53].

To Figure 4 we have also added summer values of water soluble HULIS from Col du Dôme ice-core data [68], normalized to its 1986 value and anchored to that date. Clearly, this is a World War II peak, but the reason is not known why the peak value is shifted somewhat to the earlier war years, perhaps an artifact of ice-core dynamics [69]. This spike in temperature during World War II as reflected by the Gottschalk curve could be at least partly influenced by HULIS aerosols produced by massive coal and biomass burning during WW2.

At the present time, Earth's global environment is threatened, not only by coal burning and global forest fires, but first and foremost by the undisclosed jet-spraying of coal fly ash and other particulates into the atmosphere. Evidence indicates the main motive is to melt polar ice, presumably to get at underlying natural resources [70].

Whole scale altering of Earth's natural environment by deliberately polluting the troposphere with particulate matter, especially coal fly ash, is destroying life on Earth. Undisclosed tropospheric aerosol geoengineering will lead to unimaginably large increases in heating and demise of stratospheric ozone, with associated increases in deadly ultraviolet UV-B and UV-C within just a few years [70].

Earth's great extinctions correlate with epic volcanic phenomena called Large Igneous Province [71]. The Permian Extinction ("The Great Dying") 250 million years ago coincided with the Siberian Traps LIP, a massive outpouring of lava and intrusion of underground magma which mixed with thick coal seams and organic rich material. This mixture produced plumes of pyroclastic fly ash, soot, sulfate, and basaltic dust which ascended to the upper atmosphere [72]. These aerosols dispersed globally, and certain resulting char deposits in Permian-aged rock are known to be nearly identical to modern coal fly ash [73]. The Permian was characterized by high levels of carbon dioxide, methane gas, and rapid global warming to levels lethal to most living organisms [74]. A period of deadly ultraviolet radiation stress during the Permian Extinction almost certainly resulted from ozone depletion by the coal fly ash and organic aerosols uplifted to the stratosphere [75]. We recently provided strong evidence that coal fly ash aerosols, not chlorofluorocarbons, are the primary cause of stratospheric ozone depletion [8-10].

During the Permian Extinction, lethal aerosols were produced from a mixture of coal and biomass burning, which are the two primary sources of HULIS in the atmosphere. The chemical make-up of HULIS and its components produced from the co-combustion of coal and biomass is a major challenge due to its complexity. However, recent sampling and analysis of these

aerosols indicate that the most abundant compounds are aromatics, that ultraviolet-absorbing chromophores are prevalent, and that ultrafine fractions are the most reactive [76].

Both coal and biomass combustion produce an abundance of fine ($\leq 2.5 \mu\text{m}$) and ultrafine ($\leq 0.1 \mu\text{m}$) particles. Atmospheric aerosols including HULIS are comprised of material from different sources which are reflected in their composition. The primary particles may be siliceous or carbonaceous from combustion, or salts from seawater, or of biological origin. Secondary growth of these particles occurs by adsorbed water, salts, and organics. Due to their small size, these particles can remain suspended in the atmosphere for long periods [77].

In combustion processes, vaporization is favored by high temperatures and a reducing (oxygen starved) environment. With coals (especially lignite) and biomass, metals are often present as salts at surface carboxylic and phenolic groups [78].

Submicron and ultrafine coal fly ash particles are usually spherical and contain large numbers of alkaline earth metals (Na, K, Mg, Ca) and transition metals (Ti, Mn, Fe, Co, Ni, Zn, Cr, and Cu). Ultrafine particles usually contain carbon, and the increased toxicity of ultrafine particles is thought to result from the presence of carbon which mediates transition metal (e.g., Fe) complexes that in turn promote reactive oxygen species, oxidation-reduction cycling, and oxidative stress [79, 80].

In ambient aerosols at a rural site in China, particles in the range of $0.32\text{-}1.8 \mu\text{m}$, the abundance of HULIS was 40-90% of the combined abundance of sulfate and ammonium, suggesting that HULIS should be considered when quantifying the amount of sulfate aerosols serving as cloud condensation nuclei [81].

Emissions from biomass burning and coal combustion both contribute to pollution aerosols. Gas condensation on existing inorganic particles leads to the formation of secondary inorganic aerosols. Transmission electron microscopy show that refractory aerosols (soot, fly ash, and organic particles) adhere to the surface of secondary inorganic aerosols particle due to coagulation. The organic coating and soot on the surface of aged particles affect their optical and hygroscopic properties [82].

In urban aerosols, water-soluble organic carbon (WSOC) and HULIS dominate water-soluble particulate matter and they usually occur in submicron size. There is a significant positive correlation between oxidative potential and the WSOC-HULIS fraction of atmospheric aerosols [23].

The ubiquitous ultrafine particle emissions from combustion sources affect the lifetime of water molecules in the atmosphere which presumably plays an important role in the rapidly increasing global warming observed within the last two decades [83]. The effect of ultrafine particles on meteorological processes and the hydrological cycle may ultimately have more devastating effects on human health than their direct toxic effects [84].

Ambient fine particulate matter is well-known to cause adverse health effects from the generation of reactive oxygen species like OH and H_2O_2 which are known to cause oxidative

stress in living tissue. Humic-like substances (HULIS) are the major contributors to reactive oxygen species in organic aerosols [85]. Environmentally persistent free radicals (EPFRs) are defined as organic free radicals stabilized on or inside particles. They were first discovered in coal and humic substances. Two types of EPFRs have been described; a transition metal mediated EPFR, and a carbon centered EPFR (CCR) produced inside organic matrices, like the ones formed during biomass pyrolysis or humification [86].

Environmentally persistent free radicals (EPFRs) are primarily emitted from combustion and thermal processing of organic materials, in which the organic combustion by-products interact with transition metal-containing particles to form a free radical-particle pollutant. While the existence of EPFRs in combustion have been known for over 50 years, only recently have their true importance to the environment and human health been studied [87]. EPFRs are found in elevated concentrations in atmospheric particulate matter, iron ore, clay, microplastic particles, and combustion by-products derived from wood, coal, and biochar. Many epidemiological studies show such particles can be inhaled and contribute to chronic respiratory and cardiovascular diseases [88].

Biomass and coal combustion are both important sources for EPFR's [89]. Correlation of EPFRs with SO₂, NO₂, O₃, and 12 kinds of polycyclic aromatic hydrocarbons indicate that both fuel (coal and biomass) combustion and photoreactions in the atmosphere influence the concentrations of EPFRs [90]. Long-lived surface-bound radicals like EPFR's form on combustion-borne particulates such as fly ash [91]. We have shown that coal fly ash aerosols like those utilized by ongoing tropospheric aerosol geoengineering contribute to COPD and respiratory disease [92], cardiovascular disease [93], neurodegenerative disease [94], and lung cancer [95].

Myriad ultrafine magnetic pollution particles from combustion sources have been found in human brains [96] and in human hearts [97]. These same aerosols have resulted in universal human exposure to iron oxide nano-particulates and other ultrafine pollution particles [93]. In viscous, organic-rich aerosol particles containing iron, sunlight can induce anoxic conditions that stabilize reactive oxygen species and carbon-centered radicals. Studies show oxygen does not penetrate these particles due to the combined effects of fast reaction and slow diffusion near the particle surface, allowing photochemically produced radicals to be trapped in an anoxic organic matrix. These radicals can attain high concentrations, which alter aerosol chemistry and magnifies health risks [98]. Studies of the quantification of EPFRs and reactive oxygen species in atmospheric aerosol particles suggest that they are formed by decomposition of organic hydroperoxides interacting with transition metals and quinones contained in atmospheric humic-like substances (HULIS) [99].

There is accumulating evidence that HULIS aerosols, which are often mixed with coal fly ash aerosols, also play a key role in stratospheric ozone depletion. Chemical interactions of fulvic acids (or HULIS) represent a driving force for the uptake of ozone on liquid organic aerosols [100]. Experimental work shows photo-enhanced ozone uptake on both humic acid films and submicron HULIS-type aerosols [101].

Concentrations of organic carbon, water-soluble organic carbon, HULIS, and HULIS functional groups (carboxylic acids, aromatic carboxylic acids, and organo-sulfates) overlap with Arctic haze with elevated concentrations during winter to late spring [102].

During haze periods in the winter North China Plain, it has been shown that particle phase photoreactions of HULIS and transition metals like iron create a strong source of H₂O₂ and particulate sulfate [103]. Most of the stratospheric aerosol mass is liquid sulfuric acid and associated water, but a large fraction of particles contains either metals or organic material. These solid phases may act as freezing nuclei for polar stratospheric clouds.

Organic-sulfate type particles in the stratosphere can also contain bromine, iodine, and mercury [104]. Organic particles are found in significant concentration in both tropospheric and stratospheric samples during periods of Arctic haze [105]. Record-breaking stratospheric ozone loss observed over the Arctic and Antarctic in 2020 been linked to wildfire smoke. The direct impact of this smoke below the polar stratospheric clouds simulates well-known volcanic sulfate aerosol effects, and at the polar stratospheric clouds height the smoke was able to increase the particle number and surface area concentration [106].

Previous laboratory studies indicate that a photo-induced heterogeneous reaction of ozone on the surface of aerosol containing humic substances (HULIS) has the potential to affect the ozone budget in biomass burning plumes [107]. Due to its reactivity with aromatic and unsaturated compounds, ozone is used as a chemical pretreatment of lignocellulosic biomass. Ozone has direct and selective reactions with lignin [39-43], a major component of HULIS, although it does not have the same effects on cellulose [108].

Iron-catalyzed oxidation in biotic and abiotic systems can convert organic matter in nature to organo-halogens [109]. Halogens can react with secondary organic aerosols and organic aerosols derived from combustion sources [110]. Brown carbon species including HULIS can contain carbonyls, di-carbonyls, or aromatic carbonyls like imidazole-2-carboxaldehyde, which can act as photosensitizers because they form excited triplet states upon ultraviolet and visible light absorption. These excited triplet states are strong oxidants and initiate radical reaction cycles at the surface of atmospheric particles. The triplets can also react with halides, generating halogen radicals and molecular halogen compounds which destroy stratospheric ozone [111].

Humic-like substance (HULIS) is a unique material that can account for warming of land, sea, and air. We have previously documented increasingly deadly amounts of ultraviolet radiation UV-B and UV-C penetrating to Earth's surface [112]. Higher air temperatures and incoming solar short-wave radiation is heating lakes, rivers, and oceans. Temperature differences between surface and deep waters are increasing, with this thermal stratification causing barriers to upward mixing of nutrients necessary for photosynthesis. In lakes and coastal oceans, dissolved organic matter, including its UV-absorbing HULIS fraction, is accelerating and it is associated with greater runoff, decaying biota and atmospheric deposition. Solar ultraviolet radiation breaks down dissolved organic matter, making it available for microbial processing [113].

Armstrong and Boalch showed that the ultraviolet absorption of seawater is about twice that of solutions containing the same concentration of inorganic salts and they attributed this difference to the presence of organic, humic-like material found in seawater. They also recognized that nitrate was important in absorbing ultraviolet radiation in deeper water [114]. The absorption of ultraviolet light between 210 and 230 nm can be accounted for almost entirely by dissolved organic material (HULIS), nitrate, and bromide [115].

Browning of lakes and coastal waters around the world has been attributed to increasing concentrations of dissolved organic matter of terrestrial origin. Increasing iron concentrations also contribute to this color change [116]. There is a strong positive linear relationship between humic substances and dissolved iron concentration in browning surface waters [117]. Pyrogenic iron-containing aerosols from coal and biomass burning represent primary sources of soluble iron to the open oceans [118]. A missing source of this soluble, bioavailable iron to oceans is amply supplied by ongoing, near-global tropospheric aerosol geoengineering operations that utilize coal fly ash aerosols [119, 120].

Resulting atmospheric deposition of nutrients, including soluble iron, has tilted the global plankton population away from the “good phytoplankton” responsible for primary production, and toward the harmful blooms of algae and cyanobacteria now plaguing much of the world [121]. Water soluble organic carbon including HULIS comprise the dominant fraction of submicron aerosol particles in marine aerosols. Phytoplankton blooms effectively transfer organic matter into this fine-aerosol fraction [122].

Light-absorbing organic carbon, ubiquitous in the atmosphere, along with black carbon reduces snow albedo and accelerates glacier melting [123]. Cryoconite granules are mixtures of mineral particles, organic substances, and organisms that decrease ice albedo and produce water-filled holes. Chemical analysis of the organic matter in cryoconites reveal their light absorbency depends on the concentration of humic substances they contain [124]. The geochemistry of cryoconite holes reveals a complex structure that reflect local sediment sources along with long-range transport of a host of elements that are found in anthropogenic aerosols, including coal fly ash [125]. Evidence from an accidental air drop suggests that coal fly ash/organic mixtures have been used to deliberately melt glacial ice [126].

CONCLUSIONS

HULIS is increasingly recognized as playing a key role in climate change due to its ubiquity in biogenic and anthropogenic aerosols, its ability to absorb short-wave solar radiation, and reducing atmospheric convection and concomitant surface heat loss. Coal combustion and biomass burning are primary sources of HULIS, while atmospheric processes like condensation, oligomerization, and oxidation are secondary sources of HULIS. Organic particles including water-soluble HULIS make up a major fraction of atmospheric particles and affect cloud and fog droplet activation. Not only HULIS but its major components of lignin and cellulose effectively nucleate clouds at both cirrus and mixed cloud layers. The contribution of light-absorbing organic compounds like HULIS to aerosol absorption and scattering represents on the greatest uncertainties in climate change and global warming. The mass specific optical absorption of HULIS aerosol is very strong at short wave ultraviolet radiation into the range of UV-C. Metal ions like iron in HULIS aerosols significantly increase this short-wave radiation absorption and

reactivity. It has been shown that HULIS-containing brown clouds account for warming over Asia, the western Pacific, and the Arctic. Like black carbon, strong absorption of solar radiation by brown clouds heats the top of the atmosphere, diminishing the temperature difference relative to ground-level air, thus reducing atmospheric convection and concomitantly reducing heat loss from the surface. HULIS is found in all terrestrial, aquatic, and atmospheric systems. It is the one material that can account for warming of land, sea, and air.

Ambient fine particulate matter is well-known to cause adverse health effects from the generation of reactive oxygen species. Humic-like substances (HULIS) are major contributors to reactive oxygen species in organic aerosols. Environmentally persistent free radicals (EPFRs), first discovered in coal and humic substances are organic free radicals stabilized on or inside of particles. They are primarily emitted by combustion and thermal processing of organic materials. Only recently has the critical importance of EPFRs to human and environmental health been recognized. Biomass and coal burning are both important sources for these EPFR's. There is now abundant evidence that air pollution from coal and biomass combustion is a major contributor to such chronic diseases as COPD and respiratory disease, cardiovascular disease, neurodegenerative disease, even lung cancer. There is irrefutable evidence from electron microscopy and tissue analysis that the majority of Earth's biota including humans have been contaminated with ultrafine particles, including carbon and iron oxide, from these combustion sources.

Earth's great extinctions correlate with widespread volcanic activity, or Large Igneous Province (LIP). It has established that the greatest extinction, the Permian (250 million years ago) coincided with the Siberian Trap LIP, a massive outpouring of lava and intrusion into vast coal seams mixed organic material. This mixture produced plumes of coal fly ash, soot, sulfate, and basaltic dust which ascended to the upper atmosphere and was dispersed globally. The period of extreme ultraviolet stress during the Permian almost certainly resulted from the ozone depletion by coal fly ash and organic aerosols uplifted to the stratosphere. These lethal aerosols were produced from a mixture of coal and biomass burning, the two primary sources of HULIS in the atmosphere. We have recently provided strong evidence that coal fly ash aerosols, not chlorofluorocarbons (CFC's), are the primary cause of stratospheric ozone depletion. Photo-enhanced uptake of ozone occurs on humic acid films and submicron HULIS particles. This work suggests that HULIS aerosols, often mixed with coal fly ash aerosols, are an additional cause of stratospheric ozone depletion.

The Gottschalk curve shows a distinct spike in global temperatures during World War II which is not explained by carbon dioxide, but rather a massive increase in wartime particulate pollution including coal and biomass burning. Alpine ice cores show a remarkable spike in water soluble HULIS during this same time frame. Both the temperature spike and HULIS spike during World War II came down after the war, but both have risen rapidly in recent decades. We propose that not only coal and biomass burning, but most importantly, the near daily, near global jet-spraying of coal fly ash and other, possibly organic, particles into the atmosphere by tropospheric aerosol geoengineering, will lead to exponential global warming within this decade.

Contrary to the prevailing narrative, the stratospheric ozone layer is already badly damaged, and there are signs all around us that increasingly deadly ultraviolet radiation UV-B and UV-C is penetrating to Earth's surface. Our time is very short to operationalize the new paradigm we have presented and end all geoengineering operations and reduce or eliminate sources of coal and biomass emissions, both primary sources of atmospheric HULIS. The good news is that reducing atmospheric particulates will reduce global warming in a matter of weeks or months and allow Earth's vital life support systems like the stratospheric ozone layer to begin to recover.

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