Whiteside, M., & Herndon, J. M. (2022). Destruction of Stratospheric Ozone: Role of Aerosolized Coal Fly Ash Iron. European Journal of Applied Sciences, 10(4). 143-153.



Destruction of Stratospheric Ozone: Role of Aerosolized Coal Fly Ash Iron

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ABSTRACT

We have previously provided compelling evidence that aerosolized coal fly ash particles, not chlorofluorocarbons (CFC's), are the primary cause of stratospheric ozone depletion [European Journal of Applied Sciences, 2022, 10(3), 586-603]. Here we turn our attention to iron, one of the most reactive elements among the others in coal fly ash that destroy ozone. Iron in primary and secondary aerosols plays a crucial role in the formation of ice crystals in cirrus clouds and in the polar stratospheric clouds that are involved in ozone hole formation. Iron is associated with reactive oxygen species, like the hydroxyl radical (OH) that destroys ozone in the stratosphere. Iron is known to activate halogens including chlorine, bromine, and iodine. Ozone is destroyed by adsorption onto iron-containing particles and by photochemical reactions with other constituents of coal fly ash. The inability of the scientific community to break out of the CFC paradigm and address the true cause of stratospheric ozone depletion is a potentially fatal mistake. We already face a ghastly future with severely depleted stratospheric ozone levels and devastation from deadly ultraviolet radiation. All sources of coal fly ash aerosols must be reduced or eliminated; first and foremost, the deliberate, covert, and near global jet-spraying of coal fly ash particulates into the upper troposphere.

Keywords: Ozone hole, Geoengineering, Chemtrails, Troposphere, Global warming, Ultraviolet radiation.

WORSENING STRATOSPHERIC OZONE DESTRUCTION

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. 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" [1]. Others have attributed the depletion of lower stratospheric ozone to short-lived substances that contain chlorine or bromine [2]. Two of the largest Antarctic ozone holes on record occurred in 2020 and 2021. Climate change, volcanic activity, and forest fires were suggested as causes of these huge ozone holes [3]. A shift in the polar vortex has been blamed for ongoing stratospheric ozone depletion over the Eurasian continent [4].

The rapidly increasing penetration of ultraviolet B and C radiation to Earth's surface portends a potentially dire depletion of stratospheric ozone. The clearly visible destructive effects of UV on global ecosystems including forests and coral reefs should be a warning sign that stratospheric ozone depletion may be the biosphere's most imminent threat [5]. Recently, not only has a large ozone hole been observed in the Arctic [6], but in the tropics as well [7]. From these indications, as well as from the data shown in Figure 1 [8] and other data [9, 10], one thing is abundantly clear: The Montreal Protocol misdiagnosed the cause of stratospheric ozone depletion, and its sanctions on chlorofluorocarbons have not been the solution.

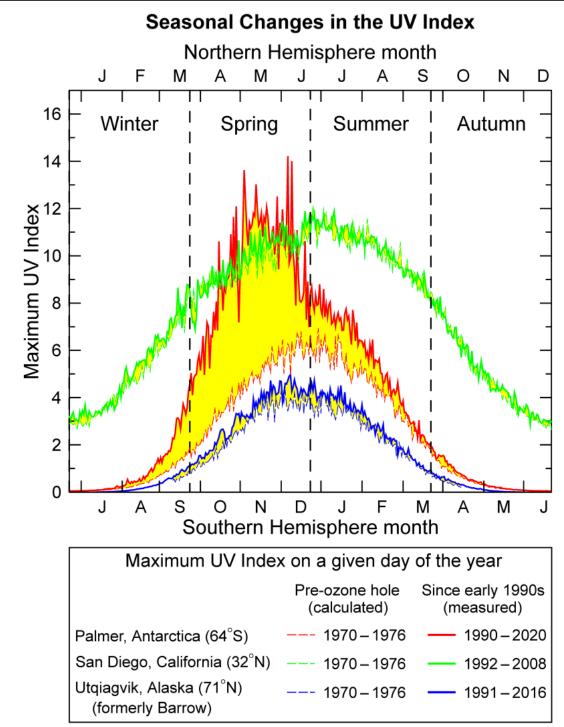


Figure 1. The current and historical status of stratospheric ozone revealed by measurements of UV Index disclosing the worsening of the Antarctic ozone hole. From [8]

We recently published compelling evidence that aerosolized coal fly ash particles, the toxic waste product of burning coal, not chlorofluorocarbons (CFC's), are the primary cause of stratospheric ozone depletion [11] as schematically illustrated in Figure 2.

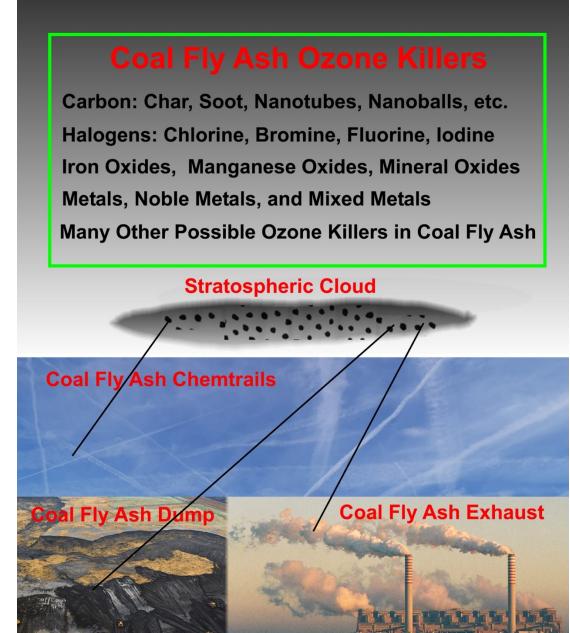


Figure 2. Graphic illustrating the major sources of aerosolized coal fly ash lofted into a particle laden polar stratospheric cloud, and some of the many components of coal fly ash that directly kill ozone [11, 12]

AEROSOLIZED COAL FLY ASH

Aerosolized coal fly ash particles are effective ice-nucleating agents in high altitude clouds. Stratospheric cirrus clouds nucleate around mineral dust and metallic oxides, with important contributions from coal fly ash to both categories [13]. In the troposphere, anthropogenic aerosol particles, especially fly ash, metal, and soot particles, are incorporated into cloud droplets, and subsequently transported long distances to affect global ecosystems, human health, and atmospheric thermal balance [14]. Deep convection and upwelling of cirrus clouds offer a mechanism of troposphere-to-stratosphere transport [15, 16]. The chemical composition, size, and morphology of refractory particles collected inside polar stratospheric

clouds are consistent with those found in coal fly ash. These particles include those containing carbon, silicates, iron, and complex metal mixtures [17]. Evidence suggests that stratospheric clouds capture and concentrate coal fly ash particles [11]. In Springtime, as stratospheric clouds begin to melt/evaporate, these particles are released, and react with and destroy stratospheric ozone [11].

Coal fly ash forms in an unnatural, anhydrous chemical environment in the hot gases above the combustion burner which renders its chemical behavior quite different than similar-sized particles from Earth's crust. At least 39 elements in coal fly ash can be leached or partially extracted by water [18]. Primary elements in coal fly ash include oxides of silicon, aluminum, iron and calcium, with lesser amounts of magnesium, sulfur, sodium, chlorine, and potassium. Carbon is often present in its elemental form as char, soot, nanometer balls, and nanotubes [19, 20]. The many trace elements in coal fly ash include arsenic, barium, chromium, copper, lead, manganese, mercury, nickel, selenium, strontium, thallium, vanadium, and zinc [21].

Coal fly ash itself can destroy ozone [22-27]. Stratospheric ozone can be destroyed by reactive halogens, and chlorine, bromine, fluorine, and iodine are all found in coal fly ash [28]. Ironically, combustion of coal even produces some chlorofluorocarbons that are found in coal fly ash [29]. Experimental data shows that separate components of coal fly ash can absorb or destroy ozone. For example, there is reactive uptake of ozone on mineral oxides including those of aluminum, silicon, and iron, all major components of coal fly ash [30]. The surfaces of coal fly ash carbon are oxidized by ozone [24], and ozone reacts with carbon nanoparticles [25-27]. Submicron carbon and iron aerosol particles are found to destroy ozone efficiently, with the implication that these particles in the stratosphere may represent a significant cause of ozone depletion [31].

AEROSOLIZED COAL FLY ASH IRON

Coal fly ash is a major source of atmospheric iron, with important implications relevant to climate and global biogeochemical cycles. Iron is a primary element in coal fly ash and is contained in both the aluminosilicate glass phase and in oxide mineral phases, including both magnetite (Fe_3O_4) and hematite (Fe_2O_3) [32]. Iron speciation by Mossbauer spectroscopy indicates that ferric iron in the aluminosilicate glass phase is the source of bioavailable iron in coal fly ash: This iron species is associated with combustion particles and not crustal dust derived from soil minerals [33]. Acids formed from anthropogenic gaseous pollutants like sulfur dioxide and nitrous oxides dissolve iron in aerosolized particles, greatly increasing the amount of bioavailable forms of iron to the ocean [34] and, presumably in a similar manner, making iron more available for reaction with stratospheric ozone.

The atmospheric processing of coal fly ash aerosols increases iron solubility due to changes in the morphology of aluminosilicate glass. Consequently, iron is continuously released into the aqueous solution as coal fly ash particles break up into smaller fragments [35]. Recent studies suggest the atmospheric burden of iron from anthropogenic (fossil fuel) combustion is much greater than previously calculated, and it exceeds that of dust and biomass burning sources. Iron plays a key role in atmospheric aerosols, including surface heat retention [36], ocean biogeochemistry [37], global carbon cycle, and snow/ice and albedo effects [38]. Reactive iron

contained in coal fly ash aerosols in the upper atmosphere has the potential to deplete stratospheric ozone by several different mechanisms which are addressed here.

Previously. the origin of metal ions in the upper/lower ionosphere was ascribed to the evaporation of small micro-meteors crossing the Earth's orbit, not coal fly ash [39]. Polar mesospheric clouds, also known as noctilucent clouds, are thin layers of ice particles that occur between 82 and 87 km in the high-latitude summer mesosphere. Lidar measurements, using iron spectral wavelengths of 372 and 374 nm, show that these clouds overlap in altitude with a layer of iron, which they take up [40]. These results confirm our suggestion that coal fly ash particles (not just iron metal), lofted into the stratosphere, not only serve as ice-nucleating agents, but are trapped by clouds, including polar stratospheric clouds. In Springtime, the icy stratospheric clouds melt/evaporate releasing their trapped coal fly ash particles, and making those ozone-consuming coal fly ash particles readily available for destruction-reaction with ambient stratospheric ozone [11].

Insoluble refractory material, in the form of primary and secondary aerosols, is thought to play a crucial catalytic role in the activation of ice crystals in cirrus clouds in the troposphere and in polar stratospheric clouds, the latter associated with ozone destruction [41]. Analogues of refractory "meteoric" particles, containing iron, silicon, and magnesium, have been shown to be able to nucleate ice and the nitric acid hydrates in polar stratospheric clouds [41, 42]. Meteoric metals, to some extent a metaphor for coal fly ash particles, are recognized as important aerosol components in the mesospheric, tropospheric, and lower stratospheric zones. These aerosols are usually derived from anthropogenic, terrestrial, and marine sources [43]. Transport of air from the troposphere to the stratosphere occurs primarily in the tropics, and it is associated with the ascending branch of the Brewer-Dobson circulation. Deep atmospheric convection [44], including the monsoon circulation, provides an effective pathway for coal fly ash pollution from the Asian continent to enter the global stratosphere [45].

Iron oxide in aerosols can chemisorb sulfur dioxide, converting it to sulfate at the gas-solid interface. Surface coating of insoluble aerosol particles with soluble materials enhances their cloud nucleating capacity [46]. An increase in secondary species through cloud processing increases aerosol iron bioavailability, and by implication increases its destructibility of stratospheric ozone.

In a study of secondary species in cloud residue (dried cloud droplets) at a mountaintop in China, iron-rich particles from combustion sources, as opposed to dust particles, contributed the majority of the iron-containing cloud residues. Over 90% of the particles already contained sulfates before the cloud events. Cloud processing led to an enhanced fraction of nitrate, chloride, and oxalate in the iron-containing cloud residues [47]. Iron is mobilized in acidic atmospheric environments, both before and during aerosol deposition. Coal fly ash interacts with the highly acidic, deliquescent layer formed around its particles by the uptake of water and acidic (pH<4) atmospheric gases. Atmospheric processing dissolves iron in aerosols by proton-mediated mechanisms and chelation processes. In hydrochloric acid suspensions at low pH, significant fractions of aqueous-phase iron (Fe2+) are released from coal fly ash. In nitric acid suspensions, a surface redox reaction suppresses the mobility of Fe2+, leading to the formation of nitrites. In the presence of solar radiation, atmospheric

processes enhance the formation of Fe2+ and nitrous acid from combustion particles [48]. Unprocessed coal fly ash shows strong heterogeneous ice nucleation activity at temperatures below 235° K in the deposition and/or pore condensation and freezing mode. In contrast to atmospheric organic aerosols, coal fly ash shows a decrease in ice nucleation activity after processing in mixed and cirrus-type clouds [49].

The hydroxyl radical (OH) is the most important oxidant in the troposphere, oxidizing natural and anthropogenic hydrocarbons and producing pollutant-type ozone. However, in the stratosphere and mesosphere, OH is a key catalyst for ozone destruction [50]. Ambient and laboratory-generated secondary organic aerosols form significant amounts of OH in cloud water, which can be explained by the decomposition of organic hydroperoxides. Chemical reactivity and aging of secondary organic aerosol particles (including those in coal fly ash) is greatly enhanced by iron, which produces OH by Fenton chemistry between ferrous iron (Fe2+) and hydrogen peroxide (H_2O_2) [51], presumably produced by ozone, O_3 [52]. Atmospheric iron, as the dominant species of transition metals in the atmosphere, is associated with radical OH generation in ambient particle extracts, especially those from anthropogenic sources. [53]. Coal fly ash aerosols are an important source of OH in the presence of an added electron donor (ozone) or H₂O₂ [54]. In cloud droplets, the "photo-Fenton" reaction occurs by the rapid photoreduction of Fe3+ to Fe2+, which in turn supports the classical Fenton reaction, that is, \hat{Fe} (II) + H_2O_2 (presumably produced by ozone) yields Fe (III), OH, and OH- [55]. It has been discovered recently that during the first few minutes following cloud droplet formation, the material in aerosols produces a near-UV, light dependent "burst" of hydroxyl radicals, ranging up to five times larger than previously known. The source of this burst is previously unrecognized chemistry between ferrous iron and peracids [56].

Chlorine atoms consume volatile organic compounds and influence the cycles of ozone (O_3) and nitrogen oxides (NO_x) . In addition to heterogeneous reactions, photochemical reactions involving the aqueous HNO_3 and H_2O_2 on and within the surface of polar stratospheric clouds might be another important coal fly ash halogen activation pathway for ozone destruction [57]. The release of reactive iron particles with associated activation of halogens from thawing polar ice clouds in Springtime may explain yet another mechanism whereby coal fly ash constituents destroy ozone, producing ozone holes during this period.

Recent detection of iodine in the stratosphere was assumed to arise from oceanic emissions [58]. We dispute the alleged source being solely oceanic emissions. Aerosolized coal fly ash from polluting industrial sources and jet-emplaced into the upper troposphere, which is further lofted into the stratosphere, contaminates the atmosphere with iodine, other halogens, and other elements, including mercury [59-61]. Restrictions on the production and disposal of mercury have not diminished its presence in the atmosphere [59]. Not surprisingly, like many of the other components of coal fly ash, mercury reacts with and consumes ozone [62-64].

Coal fly ash aerosols, especially those emplaced high in the atmosphere, not only explain the chemical composition of a large portion of stratospheric particles, but provide numerous, experimentally verified reaction paths to kill stratospheric ozone, including but not limited to the complex halogen reactions that contribute to stratospheric ozone depletion. In many

instances iron metal and iron compounds not only kill ozone directly but facilitate other ozone-killing reactions, further supporting our evidenced-based assertion that aerosolized coal fly ash is the primary material responsible for stratospheric ozone destruction [11].

CONCLUSIONS

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. This international agreement was based on what could be called "consensus science," blaming chlorofluorocarbons (CFC's) for stratospheric ozone depletion. Since this time, the Montreal Protocol has been hailed as a great success, not only preventing further damage to the ozone layer, but ameliorating climate change. However, the reality is that the world supposedly avoided by the Montreal Protocol is already here, with steadily worsening ozone depletion and deadly ultraviolet B and C already penetrating to Earth's surface. All it takes is to go outside and feel the sun burn your skin and see the signs of UV destruction on all the trees. We have provided additional evidence that coal fly ash, not CFC's, is the most important cause of stratospheric ozone depletion. Coal fly ash itself and the multiple elements and compounds contained in coal fly ash can absorb or destroy ozone. Here we focused on iron, an abundant element in coal fly ash which can both destroy ozone and interact with multiple other elements, including all of the halogens, to deplete ozone in the stratosphere. The inability (or unwillingness) of the scientific community to break out of the CFC-ozone depletion paradigm and address the true cause of stratospheric ozone depletion will be a fatal mistake for humanity. All sources of aerosolized coal fly ash must be reduced or eliminated, most importantly the deliberate, covert, near-global, jet-sprayed material into the upper atmosphere evidenced as containing coal fly ash. Until the population "wakes up" to the unimaginable damage to our planet brought to bear by this kind of technological manipulation, the current anthropogenic "Sixth Great Extinction" will continue to unfold at blinding speed.

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