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Effects of Ozone on Plant Health and Environment: A Mini Review

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ABSTRACT

Ozone, a pale blue gas is an inorganic molecule with the chemical formula O_3 . Tropospheric ozone is a secondary air pollutant and it is formed due to photochemical reaction of hydrocarbons mainly Volatile Organic Compounds (VOC) and Nitrogen Oxides (NO_x) emitted from industrial units and transport services and causes a variety of health problems, damages vegetation and environment. The primary objective of this paper is to review different types of research works undertaken on the effects of tropospheric ozone on different plants, forest, agricultural crops including microflora. This review paper also focuses on the impacts on environment due to ozone pollution. Vegetations are the important sink of tropospheric ozone which enters into the plant through stomata and oxidize plant tissues during respiration producing many oxidizing compounds and affecting various physiological and biochemical processes of plants. Several damages are noticed on plants including accurate signs of damage like necrotic lesions, chlorosis, stunted plant growth, reddening, bronzing, mottling etc. many of which have been analyzed in this review. Tropospheric ozone as a greenhouse gas is one of the factors of global warming, which leads to climate change and it is also a component of photochemical smog. The information and data regarding consequences of ozone emission at ground level on environment and vegetations are compiled as a review paper from various published articles of reputed journals, e-books and internet sources. The current situation of harmful impacts of ozone emission needs urgent remedial measures to protect the environment. At the end of the review paper, emphasis has been laid on the limited number of research data presently available in this field and necessity for carrying out more researches to meet the current need.

Key words: Ozone, Ecosystem, Environment, Plants, Biodiversity

German scientist Christain Friedrich Schonbein discovered ozone in 1840. He named the gas ozone which is derived from a Greek word ozein; meaning “smell”. Swiss chemist J.L. Soret worked out its chemical structure as being a molecule consisting of three bonded oxygen atoms (O_3) [1]. Ozone is categorised as both “good” ozone and “bad” ozone. Good ozone is natural stratospheric ozone and it protects life on Earth by absorbing harmful ultraviolet (UV) radiation from the sun. Bad ozone is tropospheric or ground-level ozone and severely harmful to living systems and environment. It emits from anthropogenic sources and it originates due to the series

of cyclic reactions between Nitrogen (N_2), Oxygen (O_2), Nitrogen dioxide (NO_2) and Nitric oxide (NO). About 90% of the atmospheric ozone resides in the lower to middle stratosphere between about 15 and 35 km altitude (often referred to as the “ozone layer”), while only ~ 10% are found in the troposphere [2].

Dry deposition of ozone is influenced by the weather conditions such as temperature, radiation, and air stagnation and uptake at the surface in particular by vegetation [59]. As per National Ambient Air Quality Index, CPCB (Central Pollution Control Board), India, the permissible limit of O_3 is 100 $\mu g/m^3$ for 8 hours and 180 $\mu g/m^3$ for 1 hour. Warm sunny days are usually favorable condition for increasing the ozone levels in the atmosphere. Global climate change through creating favorable atmospheric conditions aggravate ozone production in the atmosphere and thus ozone level is increasing continuously in many parts of the world [60]. Though O_3 is a short-lived chemical species in the atmosphere, it is a potent greenhouse gas with Global Warming Potential (GWP) between 918 - 1022 and it is also one of the major constituents of photochemical smog. Photochemical smog contains anthropogenic air pollutants, mainly ozone, nitric acid, and organic compounds, which are trapped near the ground by temperature inversion [61]. Elevated exposures to ozone can

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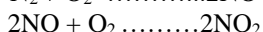
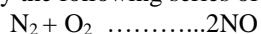
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affect human health, sensitive vegetation, wildlife and the environment. However, as a sink of ground level ozone, vegetations, especially ozone sensitive vegetations are highly affected due to ozone exposure.

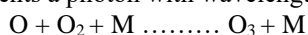
Under favorable meteorological conditions, O₃ may accumulate in troposphere and reach a level that causes significant decrease in growth and yield of O₃ - sensitive plant species [3]. Ground-level ozone causes more damage to plants than all other air pollutants combined [4]. It has been reported that elevated O₃ not only induces visible tissue injury, inhibits photosynthesis, reduces plant biomass and crop yields [5]. Systematic injury surveys demonstrate that foliar injury occurs on sensitive species throughout the globe [1]. However, deleterious impacts on plant carbon, water and nutrient balance can also occur without visible injury [6]. Elevated ozone levels appear to have detrimental effects on soybean plant roots, their relationship with symbiotic microorganisms in the soil and the ways the plants sequester carbon [7]. High proportions of ozone sensitive species were found in the families Myrtaceae, Salicaceae and Onograceae, while low proportions of ozone sensitive species were found in the families Brassicaceae, Boraginaceae and Plantaginaceae [8]. The legume family is widely accepted as containing some of the most ozone-sensitive species like peas and beans are the most sensitive crops to O₃. Horticulture crops like Tomato, Potato and lettuce were recognized to have high sensitivity to O₃-induced oxidative stress [9]. The effects of ozone on the enormous number of herbaceous and shrubby, annual and perennial species that are not deliberately or intensively cultivated have also been reported [10]. All alterations caused by O₃ lead to high losses in both quality and yield of commercial crops, which are already facing the challenge of producing 60% more food by 2050 [11]. To evaluate the risk posed by ozone, it is necessary to quantify the potential effects of O₃ on different plant species and to identify the most sensitive vegetations to O₃. With the aim of understanding how tropospheric ozone affects different vegetations, ecosystem and environment, this review paper has compiled the research studies presently available in this field.

Formation of tropospheric ozone

The most important mechanism for formation of tropospheric ozone is a photochemical cycle, which is driven by sunlight. Two major precursors of this cyclic reaction are Volatile Organic Compounds (VOCs) and the oxides of nitrogen (NO_x), which are produced by natural biological processes, however their contribution is much less important than that from fossil fuel combustion [12]. The photochemical cycle begins with the photolysis of nitrogen dioxide (NO₂) into Nitric oxide (NO) and O. The NO formed then reacts with the O₃ to produce O₂ and NO₂, resulting in series of cyclic reactions between N₂ – NO - NO₂ - O₃ [13]. This photochemical reaction can be illustrated by the following series of equation [81].



Where $h\nu$ represents a photon with wavelength $\lambda < 0.39 \mu\text{m}$.



Where M represents a molecule, whose presence is necessary to absorb excess energy from the reaction. Without M the ozone would have too much energy to be stable, and it would dissociate back to O and O₂.



The diurnal pattern of O₃ concentration in an urban area is not steady. It increases rapidly between 1200 and 1500h during afternoon when the intensity of solar radiation is at a maximum and the NO₂:NO ratio is large. The rate of O₃ formation may then decline, reaching a steady state during the

late afternoon to early evening hours. After that period, O₃ concentrations fall as NO₂ breakdown diminishes and as fresh emissions of NO deplete the O₃ [82].

O₃ concentration levels tend to be higher in rural areas. The transport of pollutants from the urban region over long distances is an observed fact in the North America, Europe [89]. The Indian Ocean Experiment (INDOEX) results have shown a pollution haze over the Arabian Sea and the Indian Ocean as a result of transport of pollutants from the Indian subcontinent [83].

Occurrence of ground level ozone

Atmospheric ozone (O₃) is an integral part of global climate change. Although ozone at the ground level is a “greenhouse gas,” it plays a minor role in regulating our air temperature, contributing only about 7% to the total warming effect as reported by Sagar Krupa *et al.* [19]. There is also a naturally occurring beneficial O₃ layer in the upper atmosphere (between 15 and 50 km above the surface) that strongly absorbs harmful ultraviolet radiation (about 210 to 290 nm: radiation <280 nm is UV-C and 280 to 315 nm is UV-B). In contrast, there are both natural and human made sources of O₃ at ground level. Because of these natural sources, there is a background average O₃ concentration of roughly 20 to 30 nl/liter (ppb) everywhere. There is no place on earth that has not been influenced by human activity, and ozone is found almost everywhere with varying concentrations.

Impacts of tropospheric ozone on environment and ecosystem

Ozone is a potent greenhouse gas with global warming potential GWP 918-1022 and one of the major responsible components for global warming and climate change. Tropospheric O₃ impacts the radiation budget and may cause climate change because it is a greenhouse gas with a strong absorption band centered at 9.6 micro m in the atmospheric window region [62]. An atmospheric window is the portion of the electromagnetic spectrum that can be transmitted through the atmosphere. Tropospheric ozone absorbs solar ultraviolet radiation and infrared radiation emitted by the earth surface and therefore effectively traps heat and cause global warming and climate change. Tropospheric ozone levels have shown significant global or regional responses to meteorological/climatic changes (e.g., changes in the Brewer-Dobson Circulation, the Hadley Circulation, and El Niño–Southern Oscillation) [64].

Ozone, (O₃) is the most abundant photochemical oxidants of photochemical smog [12]. Photochemical smog is a brownish-gray haze caused by the action of solar ultraviolet radiation on atmosphere polluted with hydrocarbons and oxides of nitrogen [63]. O₃ is responsible for many of the undesirable properties of photochemical smog and causes chest constriction, irritation of the mucous membrane, damage to vegetation. The other components of photochemical smog, principally formaldehyde (HCHO), peroxybenzoyl nitrate (PBzN), peroxyacetyl nitrate (PAN) and acrolein (CH₂CHCOH) cause eye irritation [12].

Tropospheric ozone affects the climate beyond increased warming, having impacts on evaporation rates, cloud formation, precipitation levels, and atmospheric circulation. These impacts mainly occur within the regions where tropospheric ozone precursors are emitted, and so disproportionately affect the Northern Hemisphere [61]. These environmental effects impact on the ecosystems and the services provided by these ecosystems.

Tropospheric ozone (O₃) is an important stressor in natural ecosystems, with well documented impacts on soils,

biota and ecological processes [61]. And it continues to be of major concern in the field of air pollution effects on terrestrial ecosystem. The potential effects of elevated ozone (O_3) along with climate variability, increasing CO_2 , and land use change, 4.5% reduction in NPP (Net Primary Production) and 0.9% reduction in total carbon storage net primary productivity (NPP) and carbon storage in China's terrestrial ecosystems for the period 1961–2000 is well documented [67]. O_3 is more sensitive to plants and vegetations and it is responsible for widespread effects on crops, trees and native plant species. Effects of O_3 on vegetation may lead to long-term effects on ecosystem structure and function. It can indirectly affect soil processes and affect water cycling through shifting in plant species composition and its effect on stomata respectively and can alter overall ecosystem productivity [64]. Tropospheric ozone is involved in a complex web of interactions with other atmospheric gases and particles, and through ecosystem interactions with the N-cycle and climate change [65]. O_3 also impose harmful impact on biodiversity. Plants are growing in a highly competitive environment - a slight loss of vitality of a plant species due to ozone can result in a more vigorously growing but less ozone-sensitive species out competing the affected species for light, nutrients and water resulting in a shift in species balance and potential loss of the more sensitive species at a sub-lethal ozone concentration. All of the component species of the plant community would potentially be impacted, including the animals, fungi, bacteria and insects that live in close association with plants or in nearby soils [66]. For example, changes in leaf chemistry will impact on herbivorous insects and plant pathogens, while changes in root exudation will impact on mycorrhizal associations and microbial soil processes. In so doing, ozone induced changes in species diversity or shifts in species balance will impact on many ecological processes, thereby impacting on ecosystem services, flows, goods and values [66].

General effects of tropospheric ozone on plants

United Nations Economic Commission for Europe has defined ozone critical levels for three vegetation categories: crops, forests and semi-natural vegetation [10]. It is critical to measure O_3 concentrations in the air near the leaf, plant, stand or ecosystem of interest. O_3 exposure is used on a qualitative level, both in terms of range and experimental exposure relative to ambient concentrations in the agricultural or unmanaged ecosystem of the investigated species. The terms 'low (roughly 20–70 nl O_3 l⁻¹) 'moderate' (70–150 nl O_3 l⁻¹) and 'high' exposure (>150 nl O_3 l⁻¹) is assumed [14].

A number of experimental studies have been conducted on the effect of ozone on different type of vegetations. Primary producers of all types, in agricultural as well as natural settings, are sensitive to elevated levels of atmospheric ozone, resulting in foliar injury, pigment loss, premature senescence, and decreased photosynthetic/growth rates [27]. Plants act as a sink for ozone, through stomatal and non-stomatal processes [14]. Stomatal conductance to ozone is the inverse of the sum of an array of resistances that ozone meets in specific locations along the path from the outside of the leaf to the reaction site inside the apoplast [15]. Non-stomatal uptake leads to ozone deposition in soil, stems, and cuticles. These sources are considered of minor importance unless in conditions of surface wetness [16].

After entering the stomata, ozone reacts with the liquid components of the apoplast to create reactive oxygen species (ROS, mainly H_2O_2 , but also OH radicals) that can oxidize the cell walls to start a cascade of reactions which lead, at the final stage, to cellular death [14]. The most significant direct effects

of O_3 are on plant growth and leaf physiology [17]. There are two modes of action of O_3 within the leaf. At high exposure to O_3 , the flux overwhelms the detoxification capacity and most of the O_3 is not detoxified, causing direct damage to the leaf. At a low exposure of O_3 , it can induce the defense reactions and gene expression in the plants, which require energy to regenerate antioxidants and de novo synthesis (synthesizing complex molecules from simple molecules), ultimately resulting in a decreased carbon assimilation rate for plant growth [18]. In sensitive species O_3 may affect visual attraction traits important for pollination, and spectral reflectance [19]. Non visible effects of ozone exposure include reduced photosynthesis [20] damage to reproductive processes [21], increased dark respiration [22], lowered carbon transport to roots [23], and reduced decomposition of early successional communities [24].



Fig 1 Healthy (top) and ozone-injured (bottom) tulip tree (yellow poplar) foliage [18]

Effects on lower plants

Algae, Fungi, Lichen, Bryophyta are categorised as lower plants and they are non-vascular plants. Algae and bacteria were grown in three different ozone atmospheres (0, 80, and 250 ppb) [25]. Lichens may be considered as rather ozone-tolerant organisms [29]. At sufficiently high ozone concentrations, algae cells are "oxidized to death" and even their by-products may be destroyed [26]. There are differences in the way that certain algae respond to ozone, and different concentrations and exposures times are necessary to eliminate different species [27–28]. In (Table 1) effects of ozone pollution on different lower plants are shown:

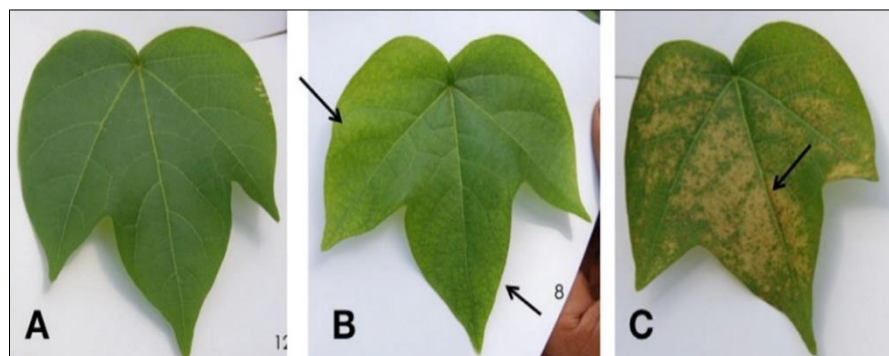


Fig 2 O₃ exposure effects in primary cotton leaves. (A) No exposure; (B) 15-min exposure to 1200 nl O₃.l⁻¹ caused chlorosis (C) 15-min exposure to 2400 nl O₃.l⁻¹ caused necrosis [7].



Fig 3 Changes in color of petals due to O₃ in *Erodium paularense* [19]

Table 1 Effects of ozone pollution on lower plants

Lower plants	Effects of ozone	Reference
Lichens	Precipitous declines in species richness loss of chlorophyll a reduction of photosynthetic rate	[30-32]
Cyanobacteria	Growth and nitrogen fixation severely inhibited heterocyst formation when exposed to ozone concentrations characterized as being “below” ambient” for semi-urban condition	[33]
Sphagnum moss species in boreal and subarctic peatlands and tundra	Significant changes of chlorophyll content, membrane damage leading to leakage, reduction in photosynthesis and growth have been observed	[34]

Effects on agricultural and horticultural species

The productivity, product quality and competitive ability of important agricultural and horticultural plants in many regions of the world may be adversely affected by current and anticipated concentrations of ground level ozone (O₃) [38]. Ozone sensitive crop and horticultural species include alfalfa, bean, clover and other forages, cotton, grape (*Vitis vinifera* L.), lettuce, oat (*Avena sativa* L.), peanut, potato (*Solanum tuberosum* L.), rape (*Brassica napus* L.), rice, soybean, spinach (*Spinacia oleracea* L.), tobacco, tomato, watermelon (*Citrullus lanatus* (Thunb.) Matsum. & Nakai) and wheat [35-41]. A detailed account of the effects of ozone in different agricultural and horticultural crops is discussed below from various research papers:

Rice

- Reduction in dry mass and grain yield [42].
- Rice grain, protein and iron yield tended to decrease in plants exposed to high ozone [43].
- O₃ caused generation of polymorphic DNA bands affecting genome template stability. O₃ reductions in yield and change in the quality of grains [50].
- Ozone exposure affected the nitrogen distribution in rice, as indicated by altered foliar activity of the enzymes involved in nitrogen metabolism, such as glutamine synthetase and glutamine -2-oxoglutarate aminotransferase [51].

Wheat

- Chlorophyll (a + b) and carotenoid loss, and membrane leakage [44]
- Lipids were immediately oxidized by ozone (12 ppm) [45]
- Visible leaf injury on seedling plants (three-leaf stage) was observed after fumigation with 160 or 240 (g m⁻³ O₃) [46].

- O₃ can potentially promote oxidation and/or degradation of the chemical constituents of grains [47].
- There was a strong negative effect on grain weight, volume weight and on starch concentration [48].
- Elevated O₃ decreased wheat grain yield by 29%, and above ground biomass by 18%. O₃ range was between 31 and 59 ppb (average 43 ppb), there was a significant decrease in the grain yield (18%) and biomass (16%). Elevated O₃ significantly decreased the grain protein yield (-18%), photosynthetic rates (-20%), stomatal conductance (-22%), and chlorophyll content (-40%). For the whole plant, rising O₃ induced a larger decrease in below ground (-27%) biomass than in above ground (-18%) biomass [49].

Vegetables and fruit crops

- Ozone concentrations affected both the photosynthetic and respiratory processes in blueberry, broccoli, carrot [56]
- Greatest impacts in fruit and vegetable crops may occur from changes in carbon transport, which causes lower quality in such important crops as potatoes, sweet potatoes, carrots, onions and garlic [53].
- Elevated concentrations of atmospheric ozone can induce external and internal disorders, which can lower the post-harvest quality of fruit and by causing such symptoms as yellowing (chlorosis) in leafy vegetables, alterations in starch and sugars contents of fruits and in underground organs [54].
- Elevated levels of ozone can induce visual injury and physiological disorders in different species, as well as significant changes in dry matter, reducing sugars, citric and malic acid, among other important quality parameters [54].
- Elevated atmospheric ozone can result in the decline of the photosynthetic rate, growth, biomass accumulation and

potential reduction in volatile ester emissions in strawberries [55].

Ornamental plants

- i) Reductions of photosynthetic activity were observed in all the species; they were associated to stomatal closure and/or mesophyll limitations [56].
- ii) Increased tropospheric ozone effects on photo physiological mechanism in urban ornamental plants [57].
- iii) The exposure of the seedlings of *Pinus armandi* Franch to O₃ caused the reductions in dry weight, root dry weight relative to the whole plant dry weight, net photosynthetic rate, transpiration rate in light, water-use efficiency and root respiration activity, and increases in shoot/root ratio, and leaf dry weight [58].

Effects on forest tree

- i) Vegetation exposure to ozone decreases photosynthesis, growth, and other plant functions [70].
- ii) Reduced carbon sequestration of temperate forests [70].
- iii) Noticeable injury symptoms like chlorophyll degradation, chlorotic molting and untimely ageing [67-68].
- iv) It also effects physiology as well as photosynthesis and can quicken leaf ageing and foliar loss that effects the whole tree growth and productivity [67-68].
- v) Ozone can raise forest susceptibility to drought, wind in addition with insect and pest attack (e.g., bark beetle, wood borer, fungal infection) [67], [69].
- vi) It can reduce root: shoot ratio, leaf area, Rubisco and chlorophyll content, transpiration rates, tree height and stem diameter [67], [70-71].

Impacts on plant community and biodiversity

Several plant species are known to exhibit foliar injury to ambient O₃ exposure. Plants like white ash (*Fraxinus americana* L.), jack pine (*Pinus banksiana* Lamb.), big-leaf aster (*Aster macrophyllus* L.), and spreading dogbane (*Apocynum cannabinum* L.) have been found to be very sensitive. Similarly, widespread O₃ induced foliar injury was reported in native black cherry and tall milkweed (*Asclepias exaltata* L.). How these foliar responses translate to other issues such as competitive sustainability of a given species within the native plant communities are yet to be fully understood. Nevertheless, tests conducted to determine the effects of O₃ on the competitive relationships between native plants showed, that the rate of blackberry: broom-sedge (*Andropogon virginicus* L.) litter decomposition was reduced with increasing O₃ concentrations, with implications for altering nutrient cycling and biological diversity. Remarkable reductions in flowering and fruiting were observed when species fitness or reproductive capacity was used as a parameter for assessing biological diversity. Experimental O₃ exposures reduced growth and flowering of the butterfly bush (*Buddleja* spp.) [9]. Similarly, exposures to O₃ reduced flowers and fruits in spreading dogbane. Another very important finding was that foliar injury was not necessarily associated with negative effects on sexual reproduction and thus changes in biological diversity as reported by Sagar Krupa [19].

Effects of tropospheric ozone on microflora

Bacteria and microscopic algae and fungi, especially those living in a particular site or habitat are microflora. The effect of ozone gas is particularly noticeable on microflora also. They include mesophilic bacteria, lactic acid bacteria, coliforms, yeasts and moulds [72]. Changes in the ratio of fungal to bacterial biomass induced by plant's exposure to ozone effect on the biomass of fungi and bacteria have been reported in *Pinus ponderosa* Douglas ex C. Lawson [73]. A shift in the overall community structure of microbes in response to ozone has been found in beech trees (*Fagus sylvatica* L.) [74]. The quality of litter from *Fagus sylvatica* L. and *Picea abies* L. was changed due to elevated ozone, which influenced the structure of litter-colonizing microbial communities [75]. Several studies described effects on mycorrhizal abundance for tree species when exposed to ozone [76]. There are several studies on ozone-induced reduction in carbon allocation in fungal symbiont in a mycorrhizal association [77], impacting on mycorrhizal species composition in *Betula pendula* Roth [78] and *Fagus sylvatica* L. [79]. A three years experiment conducted in meadow soil, provided evidence that elevated ozone is able to modify the structure of the microbial community and decreased the biomass of bacteria and fungi [80]. Thus, it is clear that microbial communities are influenced due to elevated ozone in terms of both the dynamic of nutrient cycling processes and the community composition.

Ozone and disease incidence

Ozone is reported to influence the development of plant diseases. But the factors affecting the underlying processes are not well understood. O₃ is reported to decrease the incidence of diseases caused by obligate parasites, while increasing the problems associated with facultative parasites. However, Ozone is unlikely to have direct effects on fungal pathogens; rather, the effects are believed to be host plant mediated. Conversely, altered foliar responses to O₃ have been reported due to occurrence of diseases. Much of this knowledge is based on empirical field observations and experimental studies conducted in controlled environment, greenhouse, or field exposure chambers. There is no information on the combined effects of O₃ and disease on plant growth and yield under field conditions.

CONCLUSION

Ozone is a "criteria air pollutant." and is well known to have documented adverse effects on people, plants, or materials at high concentrations, or approaching those, found in polluted air. A number of experimental studies have been conducted on the effect of ozone on different type of vegetations. All types of vegetations have been found to be sensitive to elevated levels of atmospheric ozone, resulting in foliar injury, pigment loss, premature senescence, and decreased photosynthetic growth rates. Overall, it has been concluded that tropospheric ozone impacts on whole life system including the environment. However, researches on impacts of ozone have been mainly carried out on plants grown in controlled environments and field chambers and not in open fields. Thus, more researches on the impact of ozone pollution on plants in field grown conditions and on other living objects with long-term observations are necessary to understand the effects of ozone on biodiversity, ecosystems and environment fully.

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