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Article

Chemical and Biochemical Onslaught of Anthropogenic Airborne Species on the Heritage Monument, the Taj Mahal

Deepankar Banerjee[1] and Sabyasachi Sarkar[2]*

[1] Archaeological Survey of India (ASI), C.G.O. Complex, Salt Lake Sector1, Kolkata, West Bengal, India 700064

[2] Nano Science and Synthetic Leaf Cell, Department of Chemistry , Industrial and Applied Chemistry , Ramakrishna Mission Vidyamandira Belurmath Howrah, West Bengal, India 711022; e-mail: abya@iitk.ac.in

Abstract: The science on the anthropogenic airborne aerosols impacting upon the World Heritage marble monument, the Taj Mahal, at Agra has been studied in the light of modern physico-chemical approaches. The study is an effort to understand yet unrecognized airborne species which were found on the surface of the Taj Mahal monument. These species have been analyzed in the light of current analytical methods to impart characterization features and their possible impacts on the surface of the marble. Chemical constituents of these substrates which were incorporated over the top surface of the monument have been identified. Interestingly, the carbon particulates which were thought in the micro level, popularly called "particulate matters" has now been identified even in the nano domain entity, which are chemically more reactive, have been found on the surface of the monument. Because of their high chemical activity these nano carbons do play newer chemistry in the presence of air and sunlight generating several reactive oxygen species (ROS).These ROS are capable to respond to complicated chemical reactions on the surface of the marble in association with deposited cyanophyceae and other deposits of plant origin causing rapid degradation. This study provides the nature of onslaught borne out by such monument exposed under the prevalent smoggy environmental scenario.

Keywords: Marble black crust; carbon nano particles; soluble dust; blue-green algae (cyanophyceae); humic substances.

1. Introduction:

The world heritage monument, the Taj Mahal at Agra, in the Indian state of Uttar Pradesh has always remained favorite among tourists due to its grandeur and significance. The monument was built in the seventeenth century using Makrana marble, a type of marble found in Makrana marble mines in the adjoining state of Rajasthan. Although Agra has few other notable monuments like the Akbar's tomb at Sikandra (Agra), Fatehpur Sikri-some 36 km away from Agra, Agra Fort and Itmad-ud-Daula, the Taj Mahal due to its immaculate beauty and charm attracts a wider area of aesthetic concern. The environmental concerns with respect to the Taj Mahal came into being in 1974 by setting up of an oil refinery at Mathura some 50 odd km from Agra. The Government of India notified area between Agra and Mathura as an air pollution protected area. Thus a notified area called the Taj Trapezium Zone (TTZ) came into being. In 1999, the Ministry of Environment and Forests, Government of India, notified this area the Taj Trapezium Zone an authority for protection and improvement of the environment of this zone. Many countries have experienced a progressive degradation in air quality as a consequence of rapid development over the last three decades[1]. In the cities of developing countries, the environmental problems are much greater because of the overwhelming scale and speed of unplanned urbanization[2].

Agra is connected with Delhi and Jaipur by National Highways, viz. NH-2, 3 and11. It is also well connected with other major cities by rail, road networks and by air. Recently Yamuna Expressway linked to Agra Inner Ring Road Expressway to directly reach Taj Mahal has been introduced resulting direct heavy traffic flow near to this monument.

There is a pressing concern on the yellowing and soiling of the monument, the Taj Mahal, voiced by many national and international forums where have respective views conserved on the sustainability of the monument and its environment. A detailed study has pointed on the air quality issues[3]. Studies are made on the possible impact of sulfur oxides and associated atmospheric depositions[4], along with the possible impact of dust pollution[5].

Apart from these, studies on the effect of dry deposition on foliage surfaces at Agra[6], on the rates of dry deposition of sulfur on natural surfaces(marble), and dry deposition velocity of particulate sulfate on marble were calculated[7], the nature of water soluble fraction of the aerosols at Agra , the associations of the aerosols, the ionic balances were also studied.[8] In a recent work it was highlighted that black carbon ,brown carbon and airborne dust which were from biomass combustion, trash/refuse burning, mobile sources were responsible for the discoloration of the Taj Mahal monument (**Figure 1**).[9]

Perhaps the first concrete literature on the scientific concerns and conservation issues of the Taj -Mahal was provided in 1997 by the ICCROM-UNESCO Report[10] of the mission to Agra, Satdhara and Sanchi by M.L.Tabasso. This report provided a precise but thorough study on the interdisciplinary approach to the aspects of conservation of the Taj Mahal monument. The report pointed on the presence of pigeons, bees with hives which cause conservation problems. The major conservation problem of the Taj marble, it stated was the frequent presence of fractures and sporadic exfoliation layers. The study also stated that the color of the monument is a concern for specialists and the general public, and noted that newspapers occasionally raised the alarm that the monument was turning grey or yellow due to air pollution or lack of maintenance. In this regard it also mentioned that the human eye though sensitive had a very poor memory of colors, slight variations could hardly be demonstrated unless objective data were available. Last but not the least the report said, a major conservation issue has been the presence of blue green algae which grow on different parts of the monument.

The literature in the international scenario is well equipped with researches on air quality data, air quality trends, findings on the acidic gases, monitoring on the concentrations of daily, monthly, yearly study trends on the concepts of acidic gas inputs and their possible effects on the stone surfaces. In India such air trend reports, yearly data can be witnessed by the national air quality studies done through the Central Pollution Control Board, the main nodal agency under the Ministry of Environment and Forests, Government of India. Although no reports of the study of aerosols on the monument surfaces in India from such agencies can be seen.

To have a concise, research data based, pragmatic yet sighting an overall impact of atmospheric species on the Taj Mahal monument, a study was recently reported[11]. This study pointed out that the pollution load on the Taj monument could be from natural as well as anthropogenic inputs.

In aerosol science it is generally believed that particles with aerodynamic diameter > 50μm do not usually remain air borne very long as they have a terminal velocity > 7cm/second. Dust particles are mostly found with dimensions around < 1μm and for these settling due to gravity is negligible for practical purposes. In this regard, it can be considered that dusts are made up of solid particles with size range from below 1μm to nearly 100μm. These can become airborne depending upon their physical characteristics, ambient conditions and origin. Mineral dust has free crystalline silica as quartz, coal, metallic dusts like lead, cadmium, nickel etc. other chemical dusts such as bulk chemicals, pesticides, bio hazards like potential viable particles such as moulds and spores. Airborne dusts are particles based airborne species, they are also considered as Particulate Matter (PM), composed of solid particles and liquid droplets that can float in the air. Dust phenomena occur due to construction, mining, changes in agricultural patterns, industrial activities, dust storms due to wind erosions. Dust particles can be composed of different mineral profiles. Mineral profiles affect

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their physical and chemical properties. An understanding of the chemical nature of the dust requires the determination of the soil mineral profile since soils become airborne by the action of wind.

Dust fall is a measure of all air pollutants containing smoke, soot or other potentially active particles that settle along with or without the rain due to their own weight. It can be considered as a total depositional profile in a particular study area. Dust fall, though a simple non-specific test method, can be very useful in study of long term trends as actual input of organic, inorganic and biological inputs. Dust fall can be scientifically studied by way of its soluble and insoluble fractions. Water soluble organic compounds can be determined from the soluble dust fall.

Buildings have been subject to the impact of micro flora like cyanobacteria (blue green algae) and chlorophyta (green algae) which can be considered as basic inhabitants in the colonization of stones. Due to their photoautotrophic nature of cellular metabolism these microorganisms grow on stone surfaces and form colored patinas and incrustations. These organisms form a body in which airborne pollutants, particulates, organisms get entrapped in the form of a potentially live area which can be referred as a bio film. Such bio films are found in areas protected from rainfall.The main inhabitants found in the bio films are the blue green algae (cyanophyceae).

The external surface of any building in urban polluted environment is inevitably destined to be covered with gray or black layers generally called, black crusts.[12] (**Figure 2**)Sulfur dioxide and nitrogen oxides are the most harmful air pollutants for stone materials and they are also the major source of soluble salts, sulfates and nitrates[13].

Other deteriorating agents like solar input, relative humidity and wind conditions also affect the dispersion and dilution of pollutants within a given area. The intensity and rate of weathering depends upon the stone, the surface area, and the levels of atmospheric pollutants, the orientation of the building, acid rain and rainfall[14].

The Agra Environment Management Plan[3] stated that actions taken for protection of Taj Trapezium Zone (TTZ) were targeted for protecting the structure of Taj Mahal and not Agra city or the TTZ. The actions taken for protection were mainly for repairing or maintaining the Taj structure and control of pollution through closing down of industries, it said. The report also emphasized that there was a need for a scientific study and innovative approach to achieve the desired results. Earlier the ICCROM-UNESCO Report of 199,7[10] had pointed on the conservation cum environmental concerns on the Taj Mahal monument. Thus there is a need to study, quantify and assess the actual environmental cum chemical species interacting in this complex scenario. This study has attempted to endeavor qualitatively the atmospheric and associated environmental inputs acting upon the area of the monument.

In line with this thought it was projected to analyze some significant environmental inputs from samples from the vicinity of the monument to visualize the possible chemical imprints acting upon the area.

1.1. Climate of Agra

Agra has a continental type of climate. It has three distinct seasons: summer, monsoon and winter. The monsoon season is from July to September, winter season from November to February and summer months are from April to June. The temperature ranges from 26^0C to 39^0 C during monsoon, the temperature ranges from 27^0 C to 47^0 C during summers, during winters the temperature ranges between 2^0 C to 15^0 C. The relative humidity ranges from 60 %to 90 %during winters, it ranges between 60% to 95 % during monsoon and it ranges between 30 %to 60 % during summers. The summers are characterized by high daytime temperatures ranging between 23^0 C to 44^0 C and low humidity 25-40%. The wind direction witnessed in the city is from North-West (prevailing wind) and South and Southeast (monsoon wind)[15]

1.2. Demographic and social profile

Agra has about 1400, 000 total populations and the population density is about 19.593 per sq. km[13].The population density is 897 persons per sq. km as compared to the national Indian average of 324.This data shows an immensely overcrowded city. The average literacy rate at Agra is 70%. The population has 55% males and 45% females, while the work population rate is 27%. The vulnerability assessment of the city conducted by various agencies like OXFAM, State Urban Development Authority, Agra Municipal Corporation have estimated that around 50% residents live in slums[16], while another study accounts the slums to be around 40%[3]. The urban area of Agra is divided into Nagar Mahapalika (local administrative civic body for city), Agra Cantonment Area, the Dayalbagh and Swamibagh Panchayats (Panchayats are local civic administrative bodies). The Municipal area has been divided into three main divisions, viz. the main city, Tajganj and the Trans Yamuna Area. The municipal area has 90 wards. The jurisdiction of the Agra urban area is under the Agra Development Authority (ADA).

1.3. Economic Base

The economy of Agra is based on industry, trade, commerce and tourism. Domestic, medium and small industries exist as a tradition. On a daily basis, the Taj Mahal is visited by 8-10 thousand tourists of whom 54% are foreign nationals. There are 12 major and medium scale industries and 7200 small scale units at Agra in various goods like pipes, cast iron fittings and allied fabrication goods, electrical items, leatherwear and shoes. The city has150 foundry units that produce cast iron pipe fittings, motor and tractor parts, weights and measures, diesel engines, pumping sets, generators, agricultural equipment's etc. The small scale industries comprise of textiles, cotton, wood paper products, leather goods, metal products, electroplating units, auto and engine parts etc. The handicraft industry is composed of zari, zardozi,(zari and zardozi are traditional medieval handicraft clothing in which some precious metal is embroidered on the clothes)marble and stone carving inlay works, carpet units. About 116 of these are exporting units. Agra is also famous for Petha (a type of local and traditional sweet) which is produced locally and consumes thermal energy.

1.4. Environmental issues

The solid waste management in the city is poor. Unmeasured solid waste is perhaps in the magnitude of 450 t/day. The total air pollution in the city from domestic, industrial, Petha units (sweets industry), vehicular source inputs, diesel generators (D.G. sets) is about 51 t/day[3,17]. Along with these Mathura refinery, Firozabad glass industries and brick kiln factories are also situated within 40km from Agra.[18]According to the report as stated in the following lines, at least 40% of the populace live in slums. People in slums use firewood, coal, cow-dung and its average consumption is 200-300kg/capita/year. Daily use of cow dung is around 4 hours/day. There has now been a new practice introduced by civic body to burn accumulated city garbage as the rapid measure to clear it contributing un-burn solid particulates in the local environment.

Agra has 292 notified industries, the majority of these are foundries in which the principal source of emission is cupola. The volume of the effluent gases discharged depends upon the cupola, melting temperature regimes, operation durations, nature of the charged material and finally the coke used. Gases are released during hot metal drawing and during casting. Agra is also famous for Petha. There are about 117 Petha units, which are small scale using wood and coal. The average wood consumption in these Petha units is around 5kg/day.

The fuels used in these industries are coal, coke, HSD, LPG and furnace oil. The most commonly used are hard coke, steam coal, wood and fuel oil.

Vehicles contribute a major source of air pollution. The total number of vehicles has grown at a tremendous rate of 57.7%during 1994 to 2000 and the numbers have increased. The vehicular pollution load in Agra city is around 15.6t/day.

Diesel Generator (DG) sets also contribute to the pollution input, as the diesel used for running the DG sets emit a considerable amount of airborne effluents. Much of these diesel powered engines are also used in lighting shops during power cut and for short transport in three wheelers use adulterated diesel with kerosene emitting voluminous un-burnt fuel as smoke.

Natural sources also contribute to the pollution scenario as the soil of Agra consists of loose alluvium, which thus becomes airborne easily. Considerable amount of windblown dust covers the city during summer months. Dust is the major contributor of particulates in the summers from April

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to June during which dust storms with high crustal loads and high wind speeds occur. Such dusty masses also remain suspended during summers in the atmosphere as hazes. The Suspended Particulate Matter (SPM) shows very high values and more so on days which witness dust storm episodes. Additional air pollution that has not been recognized till now is the contribution from the black particulate matters under nano dimension trapped in floating aerosol originated from the neighboring states through burning of the bio-waste from the crop fields and clearing garbage by burning at the city dump sites.

1.5. Air Pollution and monument conservation issues

Interest in the study of aerosol phenomena worldwide is justified by high particle emissions from natural and anthropogenic sources, high concentrations of gaseous precursors, relative humidity, weather conditions that favor stagnation of pollutants, low precipitation rates and water vapor in the atmosphere. Aerosols also have an impact on the weathering of historical buildings. The pollutants are transferred by two mechanisms-dry deposition and wet deposition. The external surfaces of a building with atmospheric effect of pollution evidences black brown or grey crusts and black scab like areas depending upon the deposition of the particles, rainfall, transformation within the crusts.

1.6. Sampling

The geographical area situated in a continental type of climate witnesses a temperature regime which radiates between 1^0 C in winters to around 47^0 C in intense summers within a year at Agra. Thus the monument falls in a temperature range in which a yearly thermal difference pattern influences geological processes conducive to surface weathering. Micro crust pieces' peel and fall off from places such as water spouts or areas of water passage naturally due to natural weathering phenomena. Dust is a natural phenomenon and is measured on a monthly basis as a 1- a standard measurement procedure called dust fall, 2- as a dust collected on a daily fixed cycled monitoring operation systems to measure Suspended Particulate Matter (SPM) from High Volume Samplers. The particle mode for dust characterization was on the coarse mode. The algal (cyano- bacterial) input into the dust fall, soluble inorganic and organic components of the aerosols have been determined. Marble crust samples, fresh marble used in conservation have been examined along with marble samples with algal growth. Dust has also been characterized based on seasonal conditions. The composite dust represents the airborne input on the annual dust profile.

2. Materials and methods:

To study the effect of weathering, chemical nature of the following- blue-green algae, airborne dust, soluble dust from dust fall, seasonal dust, water soluble portions of aerosols, samples were analyzed. There are zones near the water spouts, places protected from direct rainfall, niches, areas where water accumulation had taken place due to weak, weathered geological surfaces, from these zones crust pieces give away due to various geological and atmospheric impact factors.

Algal samples have taken from monthly dust fall, airborne dust from High Volume Samplers, natural peeled off pieces from the monument as crust pieces, water soluble fractions from dust fall, water soluble fractions of seasonal organic aerosols have been extracted from the glass fiber filter papers. Dust samples have been taken from High Volume Samplers representing major seasons as well as a composite dust profile has also been taken which contains the features of the annual dust load.

2.1. Sample preparation

A part of the black crust was washed with warm nitric acid, the residue was then leached with dilute sodium hydroxide and the filtrate was acidified with hydrochloric acid and vacuum evaporated to dryness. The black residue was washed with cold water thrice to remove any sodium chloride and subjected to TEM analysis.

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For mineralogical analysis the samples have been analyzed by a Seifert model Debye flex X-ray Diffractometer, with CrKα radiation and running conditions of 30mA, 40kV, scan speed 3.0°/min. Samples were analyzed within a range of 0-90^0.XRD plots were further refined by a Bruker AXS Software.IR analysis have been done by a FTIR Bruker Spectrophotometer (Vector 22 Model) working between 4000-400cm^{-1}. For elemental coupled with morphological and topographical analysis samples were subjected to a FEI Quanta 200 model computer controlled Scanning Electron Microscopy cum Energy Dispersive Spectroscopy (SEM-EDS) system. Transmission electron microscopy (TEM) images were taken using FEI TECHNAI-T-20 machine operated at the voltage of 200kV.

3. Results

X-ray data of summer, winter and composite mixture with PDF card no and mineral component is shown in a **Table 1**.

The XRD data revealed the soil oriented profile of the composite, summer and winter dusts. Composite dust represents the annual dust **(Figure 3)**. Quartz is the main mineral followed by illite, chlorite, montmorillonite, kaolinite, calcite, magnetite, hematite, mixed layer silicates.

Feldspars are represented by plagioclase, microcline and albite. The profiles of X-ray reflections are as per the standard Joint Committee on Powder Diffraction Standards (JCPDS)[19].

According to the JCPDS[19], XRD patterns one can observe the major and lesser reflections of the minerals. Among the major XRD reflections according to the JCPDS standard patterns, quartz gives reflections at 3.34, 4.23, 1.8, 1.54 and 2.45A^0. Subsequently mixed layer clay minerals give reflections at 12A^0illite gives reflections at 10, 4.48, 3.33, 2.61, 1.53A^0 kaolinite gives reflections at 7.17, 3.57, 1.62, 1.48 and 4.36A^0, chlorite gives reflections at 7.07, 14.1, 3.54, 4.72, 2.84A^0, orthoclase (alkali feldspar)gives reflections at3.31, 3.77, 4.22,3.24, 3.29A^0,albite (plagioclase feldspar) gives reflections at 3.19, 3.78, 6.39, 3.68 and 4.03A^0, calcite gives reflections at 3.03, 2.28, 2.09, 1.01 and 1.87A^0, hematite gives reflections at 2.69, 1.69, 2.51, 1.83 and 1.48A^0, magnetite gives reflections at 2.53 and 2.42A^0,montmorillonite gives reflections at 15, 4.0, 5.01, 3.02 and 1.5A^0.**(Figure 3).**The mineralogical results are based on major and lesser reflections.

3.1. Marble characterization: (Figure 4, Table 2)

3.1.1 Fresh marble: The fresh marble used in conservation showed all reflections of the calcite mineral. Calcite mineral showed a typical marble texture with distinct mineral patterns. The matrix showed an area with high crystalline features characteristic of perfect crystallographic lattices. The interfaces within the marble matrix were coherent.

3.1.2 Marble with black crust: The weathered marble with black crust showed weathering profiles and input of the soil oriented matter within its structure. The weathered mass depicted the impact of hydration combined with allied physical and chemical aspects. Hydration is a process resulting in the weathering of mineral matrices. Low crystalline zones were visible in the images. The zones gave impact of hydration along with presence of amorphous layers. Amorphous layers within the marble naturally have lower crystallinity. Loss of coherence between the interfaces could be assessed. The weathering products present in the black crust was soil inputs from dust like quartz, illite and magnetite. Marble weathering profiles were represented by calcium oxalate hydrate, ankerite, calcium carbonate hydrate.

3.1.3 FTIR of Marble Black Crust:(Figure 5,a) The IR spectra of marble black crust revealed carbonate bands at 2517cm^{-1}, 1799cm^{-1}, 1428cm^{-1}, 876cm^{-1} and 711cm^{-1}. The other mineral components are montmorillonite[35] at 606cm^{-1}, hematite[23] at 585cm^{-1} corresponding to the IR band range of 584-588cm^{-1}, quartz[37] at 457cm^{-1} corresponding to the IR band range of 455-450cm^{-1}, kaolinite[38] at 430$cm^{-1}$and organic carbons (as C-H vibration) at 2924cm^{-1} and 2873cm^{-1}.

3.1.4 FTIR of Organic content of the marble black crust (Figure 5,b): The organic content of the marble black crust showed CH_2 symmetric at 2924 cm^{-1} and CH_2 asymmetric at 2852 cm^{-1}, presence of esters at 1748 cm^{-1}, substituted aromatics at 1561 cm^{-1}, deformation of CH_3 and CH_2[24] at 1477 cm^{-1}

and 1377 cm^{-1}, asymmetric or symmetric stretching of esters and carbohydrates at 1146 cm^{-1}, aliphatic ethers[25] at 1085 cm^{-1} and aryl mono-substituted features at 739 cm^{-1} respectively.

3.2. Algal characterization (Figure 6)

The FTIR spectra of the blue green algae showed water absorption band at 3418 cm^{-1} conjugated with a protein structure, lipid bands[20] at 2923 $cm^{-1}$and 2852 cm^{-1}, protein amide [21] at 1637 cm^{-1}, C-H deformations of CH_2 or CH_3 groups in aliphatics[21] at 1463 cm^{-1} , carbohydrates[22] at 1026 cm^{-1},mixed Si-O deformations and octahedral sheet vibrations at 583 cm^{-1} and 518 cm^{-1} , while 467 cm^{-1} represents quartz[23] respectively .

3.3. FTIR of water soluble fractions of aerosols (Figure 7)

3.3.1 Summer season water soluble fraction of aerosols (Figure 7a): The summer season water soluble fractions of aerosols revealed asymmetric stretch[24] of CH_2, symmetric stretch[27] of C-H, stretch of CH_2[27], C=O of carboxylic , ketone or ester [28] at 1729 cm^{-1}corresponding to the IR band at 1725 cm^{-1},stretching of aromatic C=C [29] at 1600 cm^{-1} corresponding to the IR band range of 1595-1630 cm^{-1},C-H deformation of CH_2 and CH_3[28]groups at 1462 cm^{-1},O-H deformation of C-O stretching of phenolic O-H group or COO^- stretching and C-H deformation of CH_3 groups[30] at 1380cm^{-1}, C-O stretch and O-H deformation[27] of COOH and phenolics at 1274 cm^{-1} corresponding to the IR band range of 1260-1280 cm^{-1}, aryl sulfonic acid[31] at 1123 cm^{-1} corresponding to the IR band of 1121 cm^{-1}, C-O stretch and O-H deformation of COOH and phenolics[27] at 1072 cm^{-1}, aliphatic C-O-C or polysaccharides[27] at 1039 cm^{-1}, tri substituted aromatic rings[31] at 743 cm^{-1} corresponding to the IR band at 745 cm^{-1} respectively.

3.3.2 Rainy season water soluble fraction of aerosols (Figure 7b): The rainy season water soluble fraction of aerosols showed symmetric stretch of C-H at 2924 cm^{-1}, stretch of CH_2 group at 2853 cm^{-1}, stretching of aromatic C=C[29] at 1597 cm^{-1} corresponding to the IR band range of 1595-1630 cm^{-1},C-H bending of CH_2 and CH_3 groups, COO antisymmetric stretching[30] at 1380 cm^{-1}, C-O stretching and secondary skeletal vibrations of aliphatic groups[32] at 1019 cm^{-1} corresponding to the IR band range of 1150-1000 cm^{-1} respectively.

3.3.3 Winter season water soluble fraction of aerosols (Figure 7c): The winter season water soluble fraction of aerosols showed symmetric stretch of C-H at 2924 cm^{-1} , stretch of CH_2 at 2854 cm^{-1} , ester aldehyde or ketone[31] at 1749 cm^{-1} corresponding to the IR band range of 1750-1700 cm^{-1} , CH_2, CH_3 asymmetric bending of aliphatics[21] at 1455 cm^{-1}, alkyl sulfonic acid[31] at 1376 cm^{-1} corresponding to the IR band at 1379 cm^{-1}, C-O stretch and O-H deformation COOH and phenolics[27] at 1268 cm^{-1} corresponding to the IR band range of 1260-1280 cm^{-1} , C-O stretching and secondary skeletal vibrations of aliphatic groups[32] at 1145cm^{-1} corresponding the IR band range of 1150-1000 cm^{-1}, stretching vibrations of S=O group in sulfoxides[31] at 1086 cm^{-1} corresponding to the IR band at 1087 cm^{-1},tri substituted aromatic rings[31] at 740 cm^{-1} corresponding to the IR band at 745cm^{-1},aryl monosubstituted[26] or C-H at 696cm^{-1} respectively.

3.4 SEM algal growth on marble (Figure 8a): To supplement the effect of the impact of algal attack on marble, weathered marble with algal inclusion was subjected to analysis under SEM. The algal growth and its impact on the weathered marble showed a structure similar to an organo-mineral complex[11]. The fibrillary nature of the cyanobacterial cell wall had penetrated into the marble matrix. The calcite grains showed invasion by small agglomerations of cyanobacterial cells closely attached to each other. Close associations of the algal cell formations showed that the weathered zones which had become more degraded had been inhabited by the blue green algae. Invasion by the cyanobacteria in the calcite mass was evidenced by cyanobacterial inclusions in the pores, pits and cleavages. The morphology indicated a major role of the algal invasion and subsequent colonization on the marble.

3.4.1 SEM EDS Analysis of algae (Figure 8b): The blue green algae were subjected to qualitative elemental and morphological analysis by a SEM EDS system which revealed the following:

3.4.2 Algal chemical analysis by SEM-EDS (Figure 8c): The blue green algae (cyanobacteria) which grow on the calcitic mass of the monument showed a chlorophyllous matrix cell structure

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based on natural organic polymers like proteins, sugars and phosphates. Some evidences of other microbialmass like fungal strains could also be ascertained.

Evidences of metal particulates embedded on the algal mass could be seen in the SEM images. The essentially plant based morphological structure also showed traces of metal particle inclusions on the chlorophyllous base. The elemental analysis by EDS gave imprints of phosphates, carbon and traces of Si, K, Fe adsorbed on the surface of the algae.

The SEM image of fresh marble shows **(Figure 9a)** marble specimen with a closed knit structure wherein the grains were close to each other; the grain boundaries were well defined. The structure was a compact one. The matrix showed perfect crystalline features, the interfaces in the structure were coherent. The calcium percentage in the EDS **(Figure 9b, c)** was around 97% with some silica around 3%.

The SEM image **(Figure 10a,b)** of a black crust sample showed a topography where the grain boundaries in the calcitic mass were loose and scattered, an amorphous like coating was visible, the weathering pattern was visible in the form of pits, pores, cracks and crevices. Amorphous layers indicated a lower crystalline nature of the specimen. The structure had imprints of weathered marble mass. Impact of hydration could be assessed which naturally indicated a lower crystalline structure. The EDS spectra **(Figure 10c, d)** gave the presence of Mn, Fe, Al, Si apart from the calcite. The presence of Si was from the calcite structure, whereas Al, Mn, Fe could be from the crustal input or from anthropogenic sources.

3.5. SEM-EDS spectra of airborne dust (Figure 11)

The EDS spectra of airborne dust represented an annual pattern of composite airborne dust. The elemental composition depicted a profile dominated by soil oriented elements (crustal elements) like Na, Mg, Al, Si, K and Ca. Some impressions of anthropogenic elements could be assessed by the presence of Ti, V, Mn, Fe and Ni. Fe could be from soil sources as well as from anthropogenic inputs.

The SEM images of the airborne dust in lesser magnifications showed a soil mineral matrix. The particles demonstrated a major aluminosilicate matrix with certain additions. The additions were presence of micro metal particles embedded within the dust. The soil mineral particles were characterized by irregular shaped, rectangular or rhomboidal particles. The aluminosilicate particles were associated with agglomerate formations in which the particles were closely attached to each other.

4. Discussion

The airborne dust profiles-composite, summer and winter showed the input of crustal minerals into the dust. The airborne dust incorporated coarse and fine aerosols. Composite dust or the annual profile of the dust showed a wide range of minerals. Under soil mineralogical considerations the dust represented the minerals of the local soil. The airborne dust gave a soil oriented profile which becomes airborne with the action of wind and meteorological phenomena. Among the minerals calcite, quartz and feldspars can be considered in the coarse particle mode[34].

Other minerals like kaolinite, montmorillonite and illite can be considered in the intermediate particle mode while magnetite and hematite can be considered in the fine particulate mode. The composite dust representing the annual dust gave a broad signature of the airborne minerals. The magnetic mineral Magnetite was present in the composite (annual) dust profile. Apart from these the other minerals were similar in the summer and winter seasons depicting that identical minerals were present within the area. Since the nature of the dust represents the parent material which is the soil, the dust showed that the dust was illitic as the soil material was illitic corresponding to an earlier study on the soils of the geographical region of Agra[35].

The elemental composition of the dust by EDS gave soil oriented elemental profile. Some elements like Na, Mg, Al, Si, K, Ca had crustal origin while Fe, Mn could be from soils or could be from anthropogenic source, while Ni, Cu, V and Ti indicated towards anthropogenic origin. In the overall elemental characterization, the base of the dust had crustal origin while inputs of industrial,signatures were visible. The airborne dust composition showed features of a typical

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crustal aerosol. The EDS spectrum showed that the ratio of Si/Al was 2.96 and ratio of Fe/Al was 0.95. These were in agreement with ratio of Si/Al of 2.7 and ratio of Fe/Al of 1-3 for crustal aerosols as reported by Rahn[36]. The elements represented showed a lithophillic nature of the dust. The elemental K/Fe ratio by EDS analysis was 0.47 which was in good agreement with a value of 0.4 for airborne coarse crustal material[37].

The wt % of Fe as analyzed by EDS in the airborne dust analyzed by EDS was 7.2% which was near the average weight % value of 6.7% of Asian dust. Thus the airborne dust represented a characteristic feature which resembled the nature of Asian dust[38].

The SEM images showed dust particles with irregular habits- octagonal and rhomboidal. Morphological nature showed that small particles were attached to large particles. The dust particles were attached in close proximity; this could be due to the strong cohesive forces within the particles. Presence of a dry environment like Agra which falls under a semi –arid zone of India could be a factor for such a particle habit. Some voids and minute gaps could be seen due to the presence of these odd shaped particles. Iron oxides in the dust get deposited on the monument surfaces by wind action. Iron aids in crust formation. Iron rich particle scan act as catalysts in various mechanisms leading to stone decay. Such a phenomena had been studied by Schiavon[39] et.al.

The microorganisms present in the weak zones of the monument can utilize the Iron oxides and related elements for their metabolic activity. SEM images of the dust particles gave a soil oriented profile and also indicated towards particles that could be from anthropogenic activity. The SEM images were dominated by irregular shaped particles which indicated crustal material but to some extent some metal input like Iron oxides, could also be assessed.

Airborne dusts tend to accumulate on the sensitive and weak weathered zones of the monument and can aid in crust formation. Such a study was given by Torok et.al which opined that dust and black crust samples from limestone buildings could be used as environmental indicators since both dust and crust accumulate air pollutants and act as memories of past pollution level[40].

The IR spectra of blue-green algae gave the presence of proteins, amide, lipids, aliphatic carbon, amides, carbohydrates and adsorption of clay minerals on the algal surface. The exterior surfaces have a composition of proteins and carbohydrates with which metallic species react. This view was given by Crist et.al[41].

Associated silicates were also visible which get attached to the algae by algal cell wall interactions with silicates within their proximity. According to Dodson et.al in the interaction of the metallic ions with the algae, crystalline Al_2O_3 and SiO_2 give their presence in the heterogeneous matrix of the algal cell wall[42].

The EDS spectra of the blue-green algae showed presence of Phosphates and Carbohydrates. Apart from these the spectra showed the presence of Fe, Si and K associated with the cell structure. Algae take these elements from the airborne dust and utilize them in their metabolic cycle. The presence of soil oriented elements like Fe, Si, Kin the EDS spectra of the algae address the same. The SEM images of the algae showed that the algal cell walls had a chlorophyllous structure testifying the organic nature. Within this structure presence of micro particles showed the possible adsorption of metal particles on the algal cell walls. According to Crist et.al in this scenario Si, Fe and Al elements concentrate at the cell wall surface by adsorbing onto the surface functional groups[41].

The SEM images of the algal growth on marble gave imprints of invasion by algal unicellular masses into the marble substrate showing colonization. An organo-mineral assemblage showed that the algal invasion was prominent within the system. The weathered marble mass was impregnated with cyanobacterial colonies scattered within the area. Such algal invasions could naturally result in the secretion of metabolic organic acids by which calcium oxalate hydrate salts were formed on the surface.

The XRD results of the marble black crust gave the effect of water percolation on the marble matrix, impact of cyanobacteria, as well as the impact of soil oriented minerals. With the joint action of water, cyanobacteria and soil minerals on the marble the weathering effects could be assessed. Calcium oxalate hydrate could be the action of oxalic acid secreted by the cyanobacteria. Ankerite formation may be due to action of iron oxides on the marble while calcium carbonate hydrate may

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have been formed by the action of water. The impact of airborne dust on the marble black crust could be seen by the presence of illite, kaolinite and hematite. Hematite may be from the soil or from anthropogenic sources. The IR spectra of marble black crust gave similar results. The spectral features showed presence of calcite, soil minerals on the marble viz. montmorillonite, kaolinite, hematite, quartz and organic carbon. The SEM images showed the weathering features of the marble, as compared with the fresh marble sample. Pits, pores, cracks were visible in the crust. Presence of an amorphous layer may have been formed by the action of water and further transformations in the physical and chemical profile. The fractures were uneven which showed the impact of water percolation. Since the amorphous layer of the crust had less crystallinity as compared to the fresh marble, the interfaces showed that the existing matrix had less coherence in the calcite grains and boundaries as compared with the fresh marble. The EDS spectra showed less weight % of Ca as compared with the fresh marble and also presence of Fe and Mn as transition metals on the crust.

The IR spectra of the water soluble fractions of the seasonal dust fall samples showed functional groups of a wide range of organic compounds. Within these carboxylic acids, ketones, esters, aromatics, phenolics, aryl sulfonic acids, polysaccharides, sulfoxides could be assessed. It was interesting to note that the water soluble portion of the rainy season profile gave few signatures of organic compounds due to obvious atmospheric scavenging of the aerosols during the rainy season. The summer season water soluble had the most organic compound signatures. Input of substituted benzene ring compounds could be assessed from the IR spectra of summer and winter season water soluble. The water soluble compounds in all the seasons were dominated by humic like substances (HULIS). HULIS have characteristics of natural organic matter. Natural organic matter is generally dominated by humic and fulvic substances. Some aspects of the IR spectra showed the presence of soot in the water soluble samples[43]. Bands at 1729, (summer and winter seasons) 1600 (summer and rainy season) and 1039 cm^{-1} (summer season) were in good agreement with bands of soot at 1720, 1620 and 1040cm^{-1} [43]. Presence of humic acids could also be assessed from a similar study[44]. The water soluble fraction of summer season aerosols showed signatures of C-H at 2958, 2928 and CH_2 at 2859 cm^{-1}. Humic like substances were represented at 1729, 1600, 1462, 1274 and 1039 cm^{-1}. Aryl sulfonic acids showed their presence by a band at 1123 cm^{-1}. Thus organo-sulfur particulate input was observed during summers. Phenolics and organic acids gave signature at 1072 cm^{-1}, carbohydrates/aliphatic could be assessed at 1039 cm^{-1} while band at 745 cm^{-1} could be assigned to aromatic structures. The water soluble winter season aerosols showed C-H asymmetric stretch at 2924 and stretch of CH_2 at 2854 cm^{-1}. Bands at 1749, 1455 and 1268 cm^{-1} could be attributed to humic like substances (HULIS). Sulfur compounds showed their presence with alkyl sulfonic acid at 1379 cm^{-1} and subsequently S=O group in sulfoxides was represented by band at 1086 cm^{-1} showing considerable amount of organo-sulfur compounds in the winter season. Presence of stretching and secondary vibrations of aliphatic groups could be assigned to a band at 1145 cm^{-1}. The winter season soluble aerosol also showed interesting features of aromatic structures –tri-substituted aromatic rings at 740 cm^{-1} and C-H deformation modes of Mono-substituted benzene ring at 696 cm^{-1}. The winter season in North India is characterized by unstable atmospheric conditions along with stagnation of aerosols. Thus the presence of aromatic structures in such an environment could be ascertained. The rainy season water soluble fraction showed asymmetric stretch of C-H at 2924 cm^{-1} and stretch of CH_2 at 2853 cm^{-1}. C-O stretching of aliphatic groups was represented at 1019 cm^{-1} while humic like substances gave their presence at 1463 and 1378 cm^{-1}. Study had shown humic acids were enriched in hydroxyl, carbonyl, carboxyl and aliphatic groups and relatively lacking in aromatic groups[44].

Calcium can be leached from limestone surfaces or chelated, once solubilized from the matrix, by hexauronic acids, carboxyl and hydroxyl groups[45]. Organic acids like oxalic, citric, gluconic, malic, succinic, amino acids, uronic acids may react with the stone via salt formation and complexation[46]. The impact of water soluble compounds present in the water soluble fractions remain to be assessed in the real sense. According to Saiz Jiminez and Hermosin, the black crust coatings on the structures of building materials located in urban environments have all kinds of organic compounds present in aerosols and particulate matter, which are transferred by dry or wet deposition. The composition of each crust is governed by the composition of the vehicular emissions, diesel engines have a strong

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influence[47]. However the direct impact of humic like matter on the marble substrate was difficult to assess. Finally, the careful examination of the black crust on marble by EMS imaging clearly showed the presence of airborne carbon particulate matters. Latest search on such particulates reveal that these in appreciable quantity contain carbon under nano domain as carbon nano tube, graphene oxide and nano carbon spheres. Such nano carbons are known to produce reactive oxygen species (ROS) under air and sunlight [48–51]. The readily available gaseous nitrogenous pollutant produced by auto exhaust and refineries on reaction with ROS readily produce reactive nitrogen species (RNS). These are capable to destroy marble surface inflicting permanent damage to such monument like Taj Mahal. The presence of nano carbons in the black crust can be clearly visualized in the TM images **(Figure 12).**

5. Conclusion

The characterization of the airborne species and the substrates upon which these atmospheric species interact have been studied for the Taj Mahal monument at Agra, India. The atmospheric aerosol inputs, their impact, transformation and results are not simple and straightforward but are an amalgamation of different processes. Atmospheric inputs get added to a process of complex biochemical involving free radical weathering mechanisms. In this process inorganic crustal minerals like airborne dust, air borne carbon dust with nano carbons, organic aerosols, natural organic matter like Hulis, cyanobacterial cellular mechanisms and allied metabolic processes act upon the stone matrix and make the weathering phenomenon a complex one. A recent report of erosion of Aravalli mountain range extending the Thar desert may enhance dust storm drifted by the wind current toward the site of the discussion.[52]

We could not quantify on the specific data of aerosols, their residence time, deposition mechanisms and further transformations which act upon the effective impact area. A clear strategy of such a type would be helpful for a long term study on the monument vis- a- vis its environment. However, it is true that we have to keep globally clean environment. It will not help much to clean only the nearby zone as drifting of aerosol particles is global that is not confined to the place of its origin but drifted all over to the globe.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 24 June 2019 doi:10.20944/preprints201906.0239.v1

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Figure 1. The Taj Mahal

Figure 2. Areas near water spouts having black crust zones

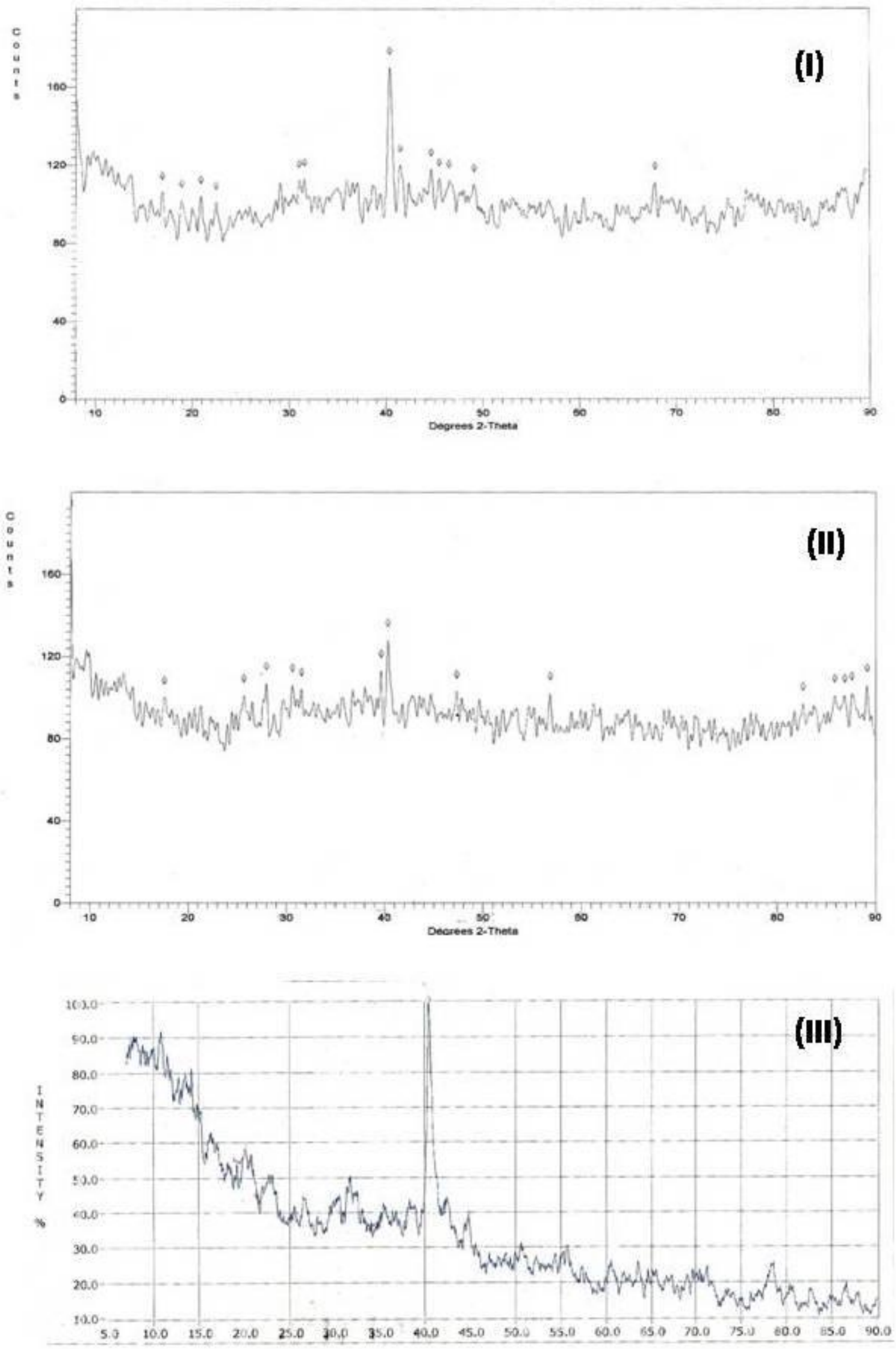

Figure 3. Dust characterization: summer (I), winter (II) and composite (III) dust profiles

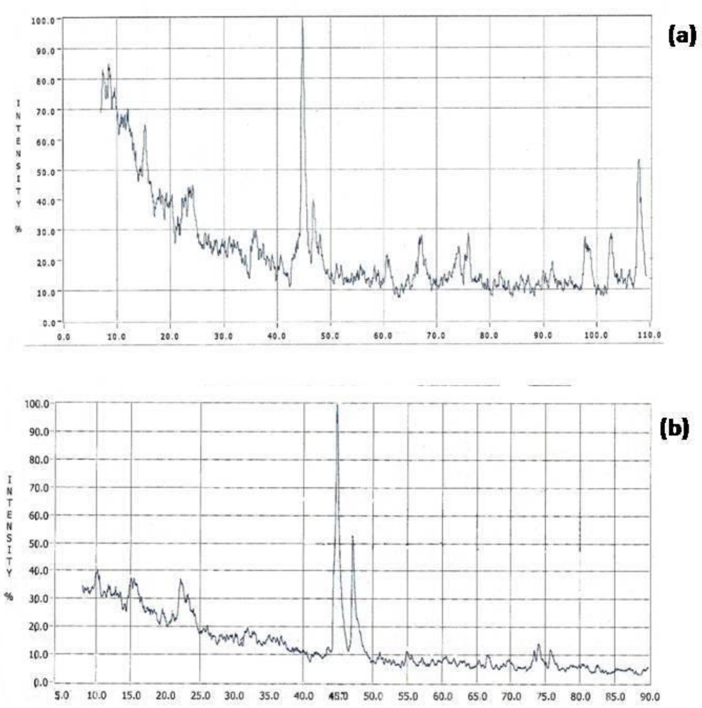

Figure 4. XRD spectra of Fresh Marble (a) used in Conservation and Marble with black crust (b)

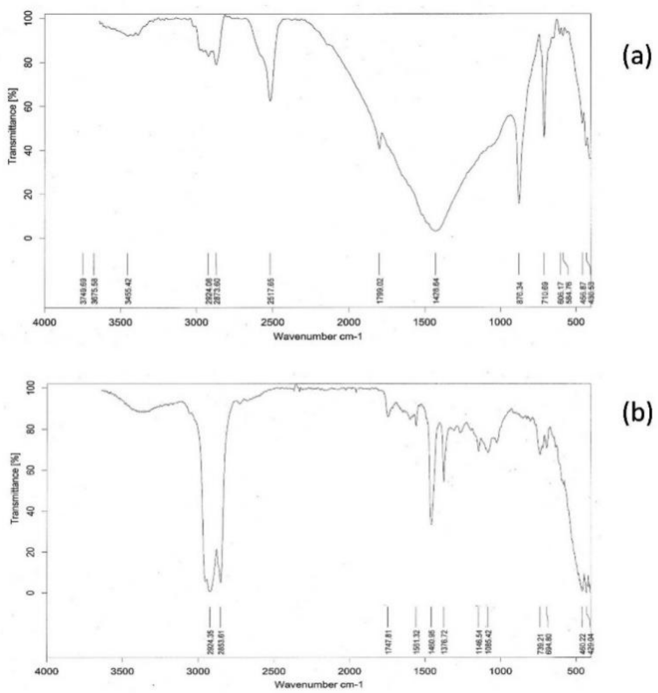

Figure 5. FTIR Spectra of Marble with black crust (a), organic content of the marble black crust (b)

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Peer-reviewed version available at Heritage 2019, 2, 129; doi:10.3390/heritage2030129

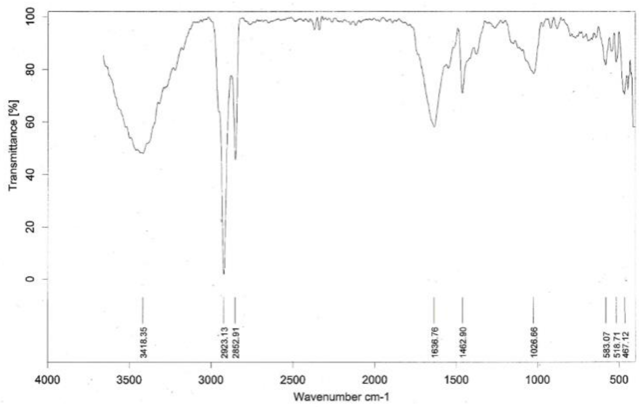

Figure 6. FTIR Spectra of Blue Green Algae

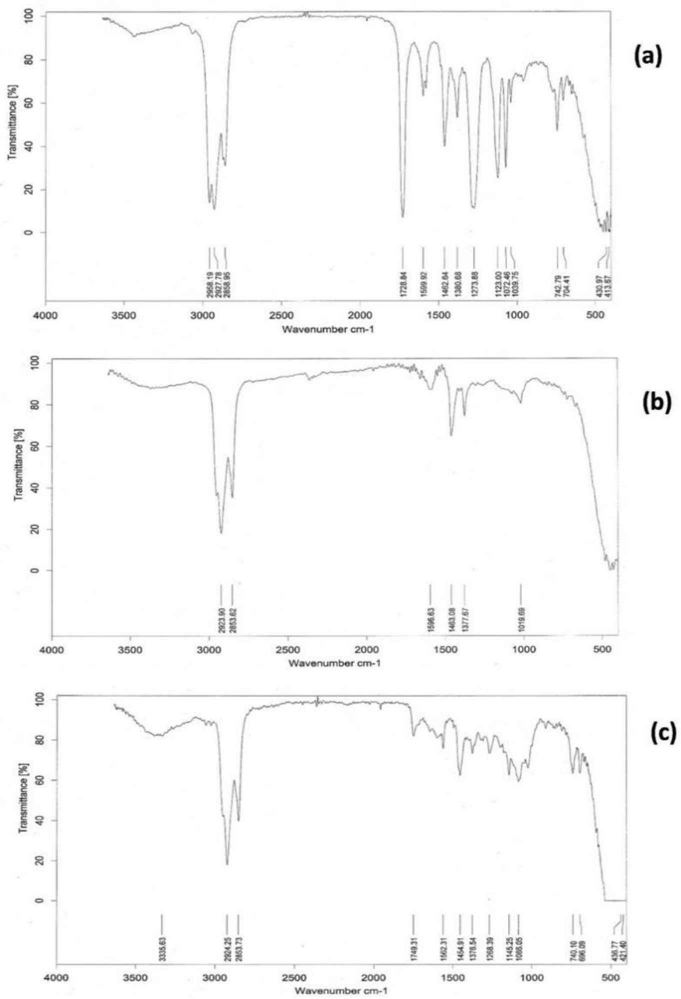

Figure 7. FTIR Spectra of a) Summer, b) Rainy season, c) Winter season water soluble fraction of aerosols

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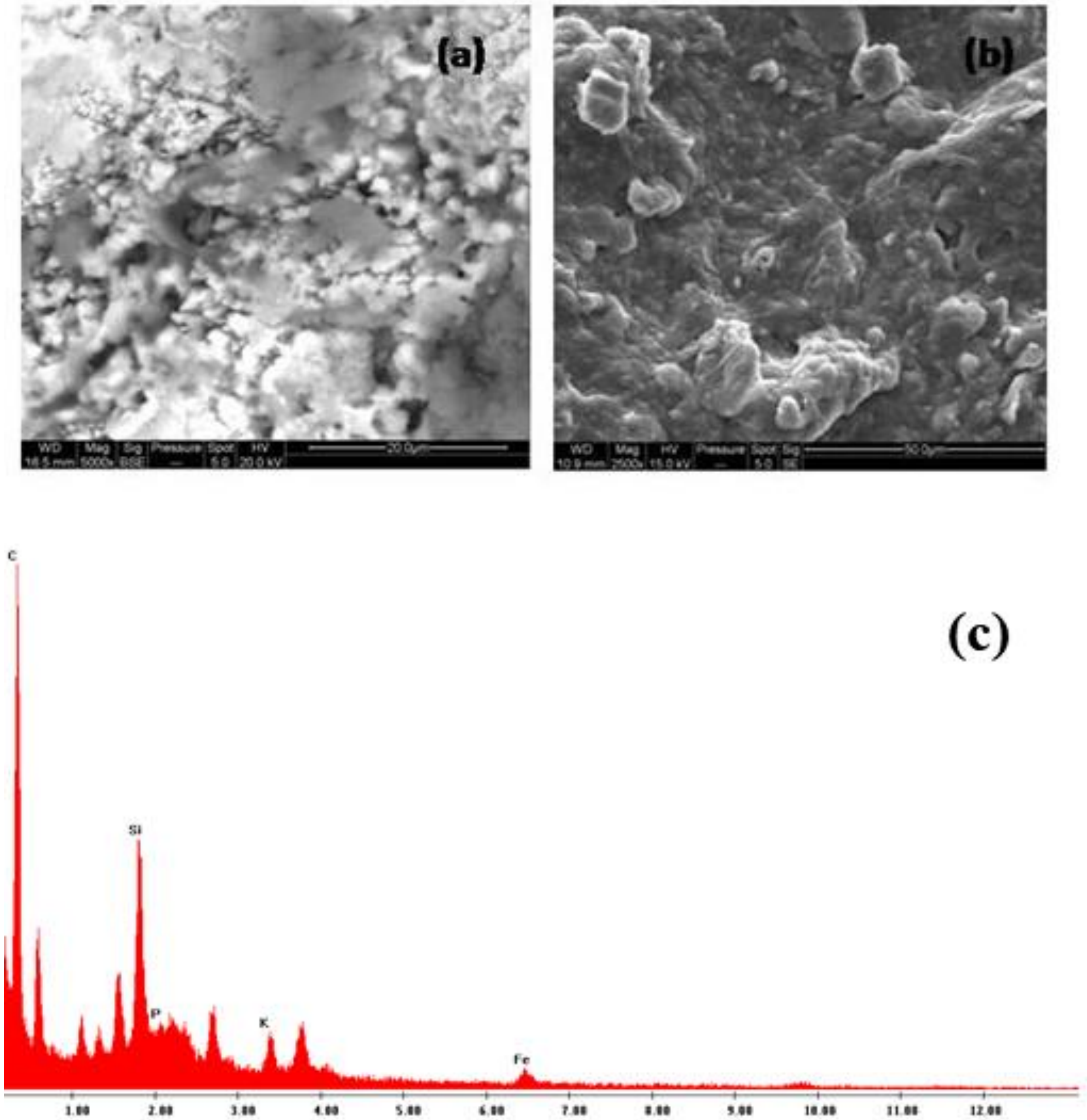
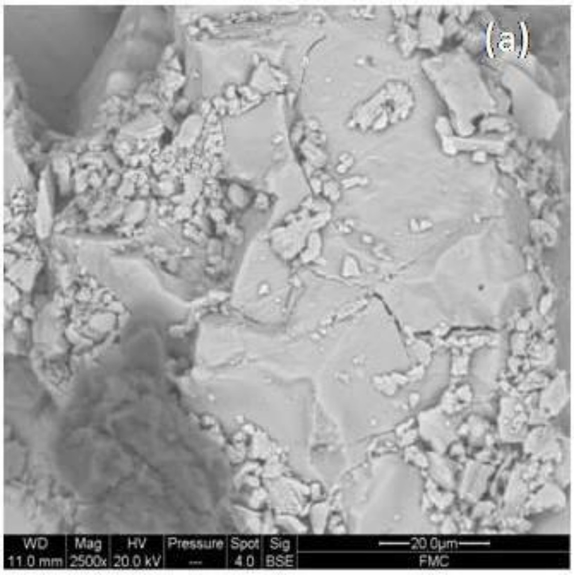
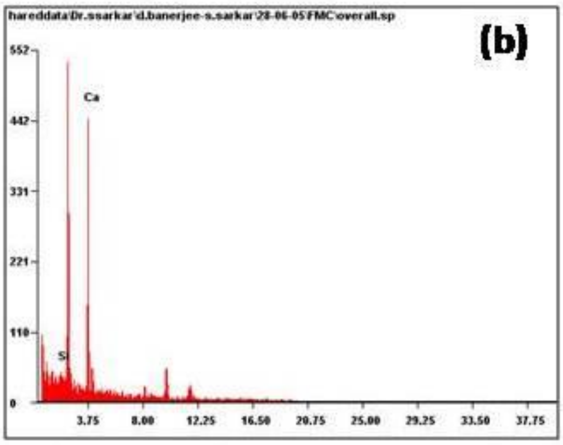


Figure 8. SEM image of a) algal growth on marble, b) algae and c) EDS spectrum of algae

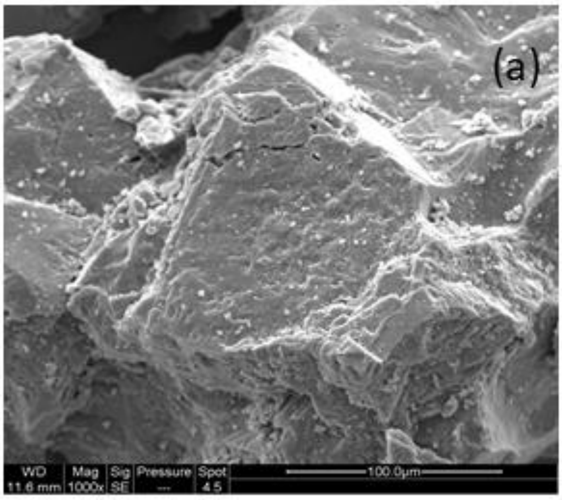


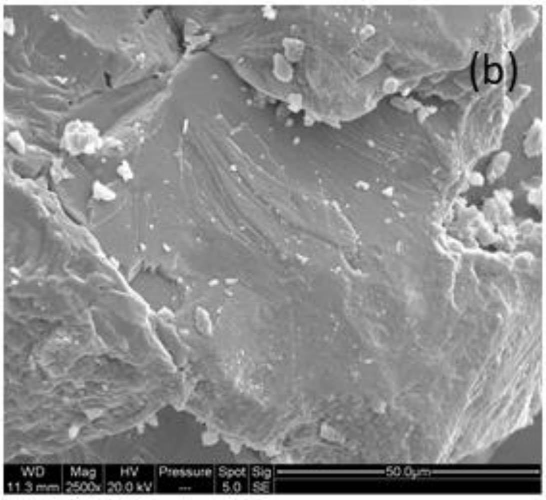


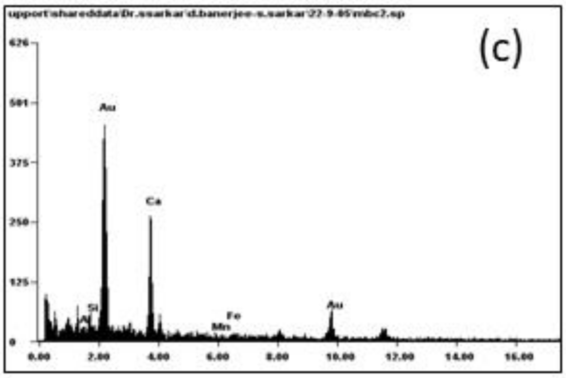
(c)

Element	Wt%	At%
SiK	02.95	04.16
CaK	97.05	95.84

Figure 9. EDS spectra of fresh marble (marble used in conservation)



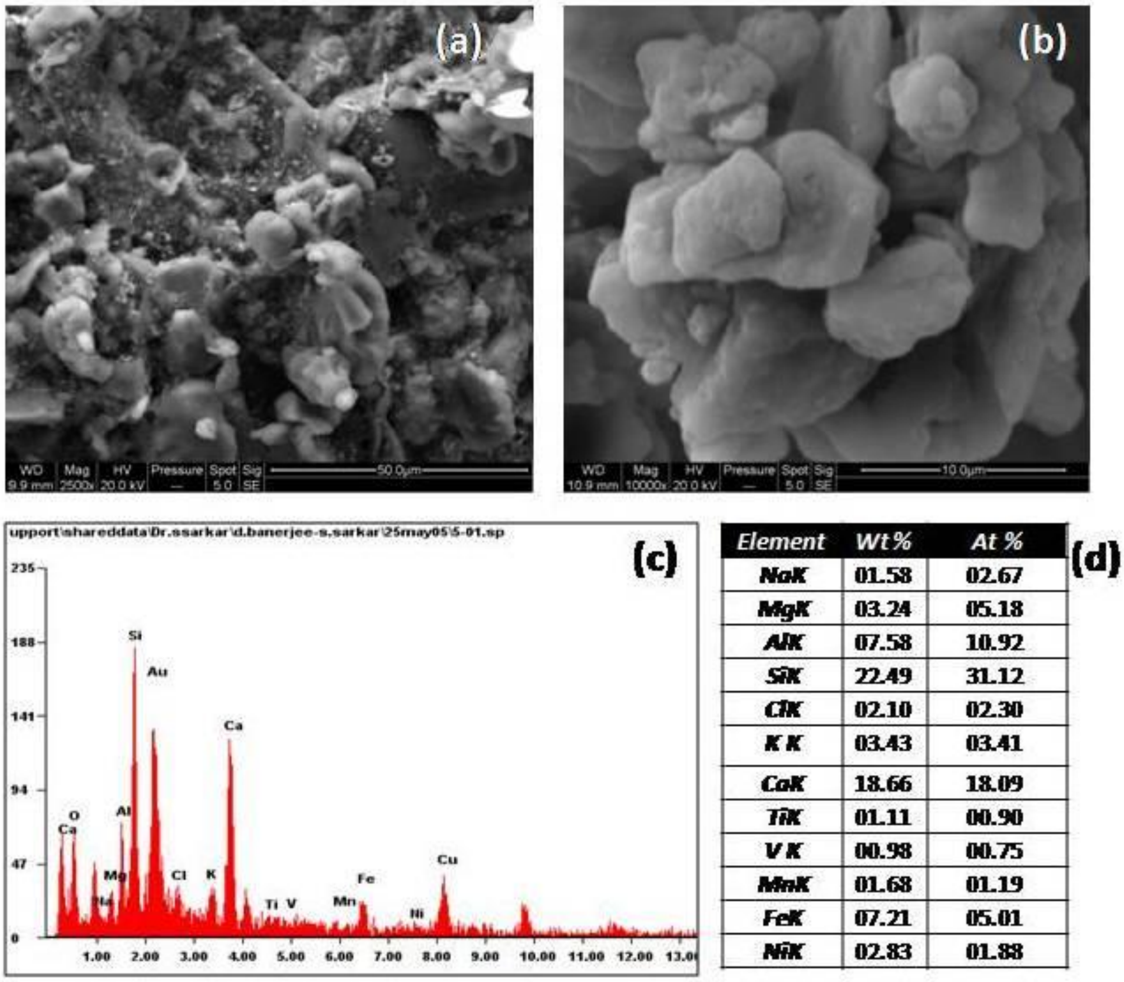




(d)

Element	Wt%	At%
AlK	01.30	01.99
SiK	00.00	00.00
CaK	84.77	87.59
MnK	06.74	05.08
FeK	07.20	05.34

Figure 10. SEM images of Taj Mahal marble black crust



Element	Wt %	At %
NaK	01.58	02.67
MgK	03.24	05.18
AlK	07.58	10.92
SiK	22.49	31.12
ClK	02.10	02.30
K K	03.43	03.41
CaK	18.66	18.09
TiK	01.11	00.90
V K	00.98	00.75
MnK	01.68	01.19
FeK	07.21	05.01
NiK	02.83	01.88

Figure 11. SEM and EDS spectra of composite airborne dust

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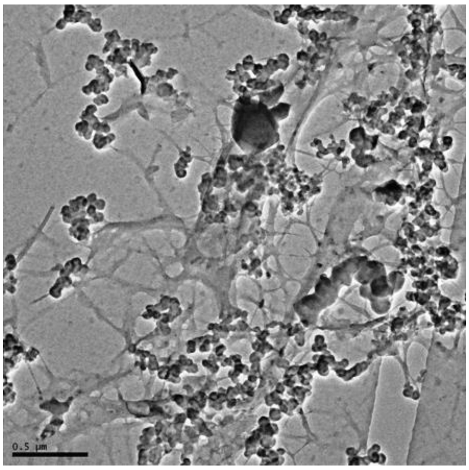
Peer-reviewed version available at Heritage 2019, 2, 129; doi:10.3390/heritage2030129



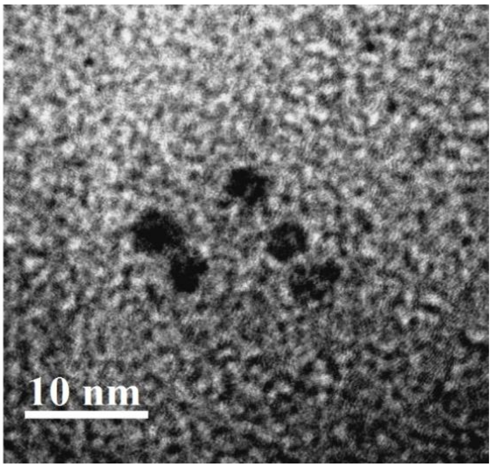


Figure 12. TEM images: Left side: low resolution showing the presence of assorted nano carbon particles of different shapes and sizes. Right side: a focused zoomed resolution image showing the nano carbon particles in less than 5 nm size.

Table 1. Dust characterization: summer (I), winter (II) and composite (III) dust profiles

1 **d A⁰ Exp**	**2** **d A⁰ Exp**	**3** **d A⁰ Exp**	**d A⁰** **Std**	**PDF** **Card no**	**Mineral Component**
		12.23	12.0		Mixed layer silicates
		10.4	10	31-968	Illite $KAl_2(Si_3Al_{10})(OH)_2$
7.79	7.5	7.23	7.12	78-2110	Kaolinite$Al_4(OH)_8Si_4O_{10}$
6.97			7.07	13-3	Chlorite$Mg_2Al_3(Si_3Al)O_{10}(O_8)$
		6.8	6.5	003-0016	Montmorillonite $(NaCa)O.3(AlMg)_2SiO_{10}(OH)_2nH_2O$
6.31			6.39	9-458, 003-016	Plagioclase Feldspar,$NaAlSi_3O_8$-$CaAl_2Si_2O_8$ Montmorillonite(6.5)$(NaCa)O,3(AlMg)_2Si_4O_{10}(OH)_2nH_2O$
		5.17	5.0	31-968, 003-0016	Illite $KAl_2(SiAlO_{10})(OH)_2$, Montmorillonite $(AlMg)_2(Si_4O_{10})(OH)_2nH_2O$

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	5.16		5.16	003-0016	Montmorillonite$(NaCa)O,3(AlMg)_2Si_4O_{10}(OH)_2nH_2O$
	4.75		4.72	13-3	Chlorite$Mg_2Al_3(Si_3Al)O_{10}(O_8)$
		4.7	4.7	13-3	Chlorite$Mg_2Al_3(SIAl)O_{10}(O_8)$
	4.34		4.48	31-968	Illite$KAl_2(Si_3AlO_{10})(OH)_2$
4.28			4.26	19-926	Microcline$KAlSi_3O_8$ (Potassium Aluminium Silicate)
	4.22	4.20	4.22	19-926	Microcline$KAlSi_3O_8$(Potassium Aluminium Silicate)
		4.36	4.2	19-926/46-1045	Microcline $KAlSi_3O_8$/Quartz SiO_2(4.42)
		3.66	3.66	20-554	Albite $NaAlSi_3O_8$
3.32	3.32	3.31	3.34	46-1045	QuartzSiO_2
3.23			3.24	19-931	Orthoclase Feldspar$KAlSi_3O_8$ Montmorillonite (3.25) $(NaCa)O,3(AlMg)_2Si_4O_{10}(OH)_2nH_2O$
3.01	3.32	3.00	3.03	05-0586	Calcite $CaCO_3$
		2.95	2.95	19-926	Microcline $KAlSi_3O_8$
2.75	2.85	2.68	2.7	33-0664	HematiteFe_2O_3
	2.4	2.53	2.53	76-1849	Magnetite Fe_3O_4
		2.50	2.51	33-0664	Hematite Fe_2O_3
		2.47	2.49	05-0586	Calcite $CaCO_3$
		2.29	2.28	05-0586	Calcite $CaCO_3$
	1.66		1.69	33-0664	HematiteFe_2O_3

Table 2: XRD of fresh marble and marble with black crust

Sample	**d A^0 Std**	**d A^0 Exp**	**PDF Card no**	**Mineral Component**
fresh marble	2.45	2.49	05-0586	$CaCO_3$
	2.27	2.28	05-0586	
	2.10	2.09	05-0586	
	1.90	1.91	05-0586	
	1.87	1.87	05-0586	
Marble with black crust	12.0	11.79		Mixed layer clays
	10.02	10.32	31-968	Illite $KAl_2(Si_3AlO_{10})(OH)_2$

	5.93	5.93	75-1313	Calcium oxalate hydrate (Whewellite)$CaC_2O_4H_2O$
	5.02	5.08	31-968	Illite $KAl_2(Si_3AlO_{10})(OH)_2$
	4.91	4.98	31-968	Illite $KAl_2(Si_3AlO_{10})(OH)_2$
	4.33	4.33	15-20	Calcium carbonate hydrate $CaCO_3H_2O$
	3.57	3.58	78-2110	Kaolinite $Al_4(OH)_8Si_4O_{10}$
	3.03	3.01	05-0586	Calcite $CaCO_3$
	2.9	2.86	33-282	Ankerite $Ca(FeMg)(CO_3)$
	2.63	2.66	15-20	Calcium carbonate hydrate $CaCO_3H_2O$
	2.53	2.56	19-629	Magnetite Fe_3O_4
	2.45	2.45	46-1045	Quartz SiO_2
	2.08	2.08	05-0586	Calcite $CaCO_3$
	1.91	1.91	05-0586	Calcite $CaCO_3$
	1.87	1.86	05-0586,33-0664	Calcite $CaCO_3$,Fe_2O_3,(1.83)

Author Contributions: DB has collected samples through field work from the building site and other sources and the raw images and the relevant data were extracted from the samples in the laboratory and analyzed under the supervision of SS. The first draft manuscript has been written by DB and then both the authors worked on this draft which was finally checked by SS. Both the authors have given approval to the final version of the manuscript.

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Abbreviations

Reactive Oxygen Species (ROS), Taj Trapezium Zone (TTZ), Particulate Matter (PM), Agra Development Authority (ADA), Diesel Generator (DG), Suspended Particulate Matter(SPM), Scanning Electron Microscopy cum Energy Dispersive Spectroscopy (SEM-EDS), Transmission Electron Microscopy (TEM), humic like substances (HULIS), reactive nitrogen species (RNS).

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