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A study on environmental corrosion of gilded heritage structures of Royal Palace Patan, Nepal

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This article presents the results of corrosion study carried out on 17th century gilded sample procured from the metallic golden window of Patan Royal Palace, Nepal. The characterization techniques employed in the study provide the detailed information about the environmental pollutants responsible for the corrosion and degradation of gilded window. The analytical results have revealed that the window has been made of pure copper sheet on which traditional mercury-amalgam gilding technique has been used. Particulate matters like elemental carbon, sulphur dioxide, chlorine and organic matter have been found to be the main factors responsible for the corrosion and degradation of gilded surface. The information obtained from the present study is expected to be the source of understanding and solution for the protection and conservation of the gilded heritage of Nepal.

Keywords: Mercury-amalgam gilding, Royal Palace Patan, Nepal, SEM-EDS, X-ray diffractrometry, FTIR

1 Introduction

Kathmandu valley has always been a melting pot for various cultures, religions, art and craft and an eclectic mix of the past and the present. Its exquisite monuments, sculptures and magnificent art make the valley hme to seven UNESCO Cultural World Heritage Sites. These monuments were defined by the outstanding cultural traditions of the Newars, manifested in their unique urban settlements, buildings and structures with intricate ornamentation displaying outstanding craftsmanship in brick, stone, timber and metal that are some of the most highly developed in the world.

The Kathmandu valley envelopes three glorious cities Kathmandu, Patan and Bhaktapur. Patan is the oldest of all the three cities of the valley and best known for its spectacular Patan Durbar Square. The former Royal Palace complex (Fig. 1(a)) is the center of attraction of Patan Durbar square and holds many masterpieces of artistic heritage. 17th century golden window, mounted to the exterior of Royal Palace building (Fig. 1(b)) is of high aesthetic values and stands as a symbol of the golden era of Nepal. The window obviously endured years of exposure to natural elements.

The surface layer presents various alterations, typically appearing as superficial formations and encrustations due to both products of metal corrosion and exogenous materials. Photos of before and after conservation of 17th century gilded window from Royal Palace Patan, Nepal is shown in Fig. 2. Today Nepal's mountainous and challenging topography and socio-economy make it a highly vulnerable country to climate change. Degradation to the environmental qualities in the valley is seriously hampering the national economy particularly the tourism sector and damaging these invaluable archeological and heritage site.

This is further to mention here that Nepal is suffering from air pollution which has emerged as the most visible components of environmental degradation in Kathmandu valley. The danger of heritage from air pollution comes from different gas sources that increase the corrosivity of the atmosphere. Most particles form in the atmosphere because of complex reactions of chemicals such as sulfur dioxide and nitrogen oxides, which are pollutants emitted from power plants, industries and automobiles. The main mechanism occurs when oxides of sulphur and nitrogen incorporated into rain, snow, fog or mist and form two strong acids: sulphuric and nitric acid also familiar as acid rains[1]. Acid rain primarily consists of HNO_3 (30%) and H_2SO_4 (70%). In dry atmosphere acid chemicals may become incorporated into dust or smoke which can deposit on buildings. In the presence

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of moisture these corrosive chemicals attack the surface materials and consequently damage metallic, wooden or building exteriors resulting to the loss of heritage. In Kathmandu valley, primary pollutant of H_2SO_4 is vehicular emission and industrial projects. The main reason for the elevated level of vehicular emission is the considerable number of poorly maintained heavy vehicles on congested streets, use of inferior quality and substandard fuels and lubricants, shortage of emission inspection facilities & maintenance system and a poorly managed transportation system[2].

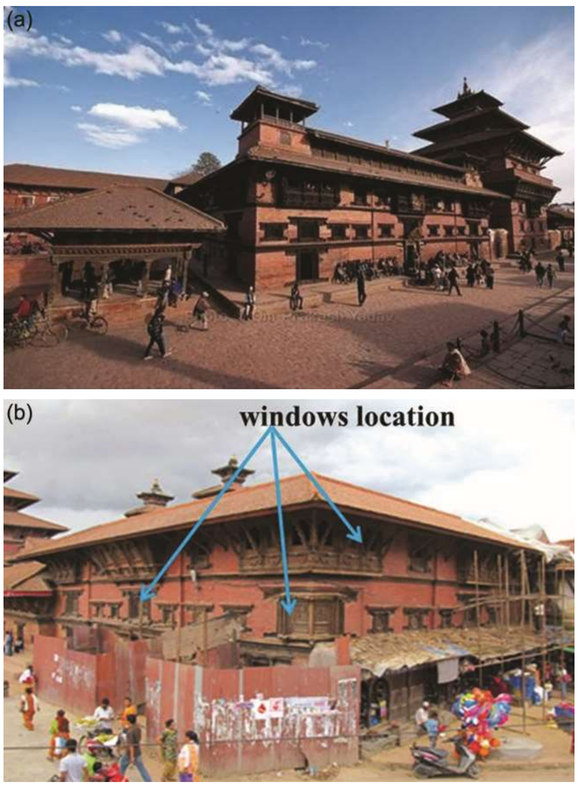

Fig. 1 — (a) Royal Palace Complex, Patan, Nepal and (b) Windows location-south-west wing.

Fig. 2 — Photos of 17th century gilded window from Royal Palace Patan, Nepal (a) before and (b) after conservation.

Level of pollution is further magnified by using leaded, substandard and adulterated fuel[3]. SO_2 has been found to go as high as 202 SO_2 $\mu g\ cm^{-3}$ and NO_2 to 126 $\mu g\ cm^{-3}$ particularly in winter months[4].

Furthermore, issues of power shortages have led to increased use of the power generators, as well as increased use of biomass burning and low- grade coal in over 110 traditional brick kilns in the Valley[5]. This has resulted in highly elevated particulate matter (PM) concentrations, which threatens the health of residents as well as damages heritage materials. Level of particulate matters in the atmosphere is so high that wearing a mask while going out of the house has become a daily ritual in Kathmandu valley.

Moreover, environmental condition has heavily deteriorated because of the bowl like topography of the valley (Fig. 3). The Kathmandu valley is oval shaped and surrounded by high hill range. The valley's unique bowl shape restricts wind movement and retains the pollutants in the atmosphere especially during period of thermal inversion over Kathmandu, where cold air flowing down from the mountains is trapped under a layer of warmer air which acts like a lid over a bowl thus preventing the escape of industrial and vehicle fumes and greatly enhances the likelihood of air pollution problems[6].

In the present study, the nature of pollutants present in atmosphere and their effect on the gilding windows surface during the years as contaminants from the environment have been studied in detail in order to know the cause of corrosion and degradation of heritage structures.

2 Experimental Details

A small sample of 17th century gold gilded window (7) was used in all scientific analysis. The scanning

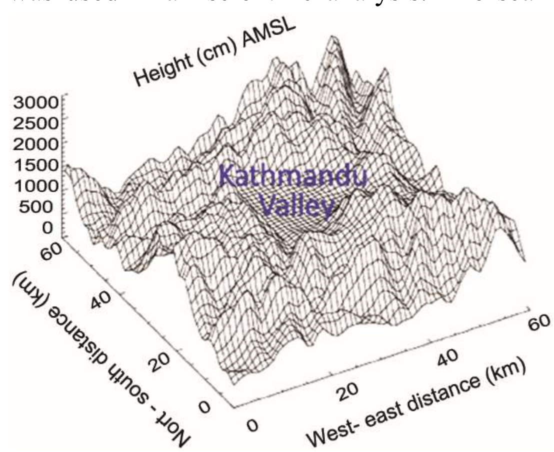

Fig. 3 — A topographic map of Kathmandu Valley and its surroundings (Courtesy: www.researchgate.net/figure/ 83578429).

electron microscope used for SEM analysis is a variable pressure SEM having tungsten filament, make Ziess, model -EVOMA10 operated at 20 kV with an attachment of EDX microanalysis system with a Si/Li, crystal detector, model INCA 250. EDX analysis and SEM images have been obtained simultaneously with an accelerating voltage of 20 keV and a beam current of 200 pA. Elemental compositional analysis of the gilding sample was carried out by using energy dispersive spectrometer (EDS) attached to the VPSEM. An FTIR spectrum was recorded in ATR mode in the wave number range of 400 - 4000 cm^{-1} using Agilent make FTIR spectrometer. X- ray diffraction technique was used to characterize the gilding sample for the identification of various elements and the different phases of the compounds present in the sample. X-ray diffractometer, make- Bruker Germany, model- D8 Advance having Cukα radiation of wavelength 1.548609 Å has been used in the present investigations.

3 Results and Discussion

Scanning electron microscopy investigations can show the sample superficial texture at nanometric level, revealing shape and dimensions of particles that constitute the surface layer. Figure 4 represents the secondary electron (SE mode) SEM micrograph of the sample as procured from golden window of Patan Royal Palace, Nepal. The surface of the sample was not cleaned before putting into the scanning electron microscope (SEM) specimen chamber. SEM image revealed that the surface of the sample is composed of bright and some dark areas. The bright area in the micrograph represents the amount of dust particles containing carbonaceous compounds deposited as contaminants from the environment on the surface of the sample during the course of time. Large fraction of area of the sample consists of micro cracks throughout on the top surface of sample which may be developed due to the exposure to varied atmospheric conditions over the years. As per the gilding process used in the Nepal in the ancient years are concerned, very thin layer of gold (Au) used to be deposited on copper sheets by a long and cumbersome gilding process[7]. Thickness of the Au gilding depends on the amount of Au available[1]. This is further to mention here that the initiation of micro and nano cracks on the gilding surface may be created due to the variation in coefficient of thermal expansion of Cu (16.6×10^{-6} m/(mK), Au (14×10^{-6} m/(mK), and Hg (61×10^{-6} m/(mK). If the body is constrained so that it cannot expand, then internal stress will be caused or increased by an increase in temperature resulting in the localized stress and the strain at the gilding surface which are evident from the SEM image.

The same sample was also characterized for the identification of molecular structure of organic compounds which are expected to exist on the unclean top surface of the sample by using Fourier transform infrared spectroscopy (FTIR) technique. The typical FTIR spectra of the gilding sample are shown in Fig. 5.

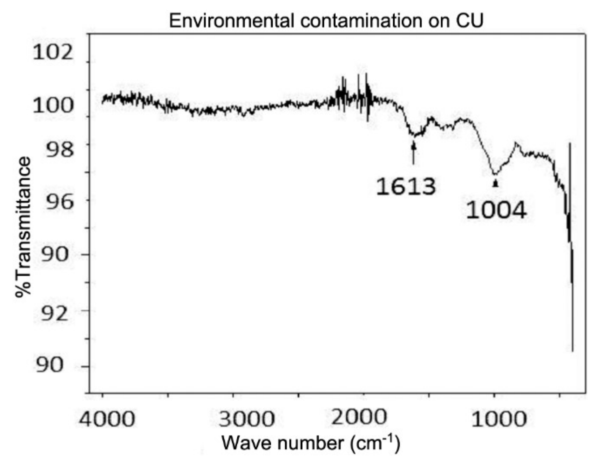

Fig. 5 — FTIR spectra of gilding sample showing C-C stretch and C-H bending.

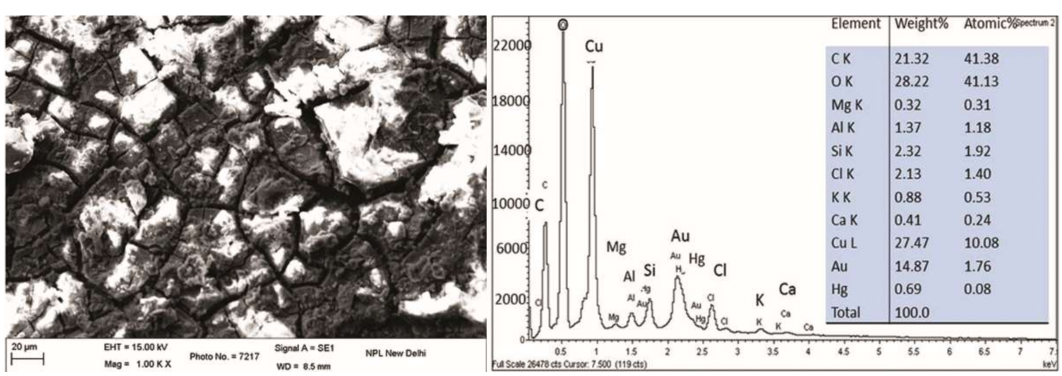

Fig. 4 — SEM micrograph of the gilding sample without cleaning its surface and EDS spectra.

Noise is observed in the data due to air gap. However, according to the standard IR frequency table, the peak at 1613 cm^{-1} corresponds to C-C stretch and peak at 1004 cm^{-1} corresponds to C-H bending on the surface of the sample. A little broadness can be seen in the higher side of wavenumber (i.e., 3500-3200 cm^{-1}) which can be attributed to presence of moisture. Presence of large amount of carbonaceous material revealed in the SEM image and EDS spectra are confirmed by the existence of C-C stretch as depicted in FTIR spectra.

Prior to SEM imaging the same sample was cleaned in the acetone followed by the ultra-sonication to remove the environmental contaminants on the sample's surface. Images A and B shown in Fig. 6, represent the SE mode SEM micrographs of the cleaned gilded sample. SEM image marked as A shows the chipped off areas at certain places in the sample which may be due to the exposure to different atmospheric conditions during time. SEM image marked as B revealed the presence of micro and nanocracks along with the evidence of pits at some places which are clearly indicated in the image. These pits may have been created due to the reaction of chloride or sulphate ions present in the environment as pollutant after forming the acids. The figure also shows the elemental compositional details of the corresponding areas of the sample.

Presence of various elements is depicted in the table shown as an inset of EDS pattern and also marked on the spectra peaks corresponding to different energies. Presence of elements like C, O, Si, Cl, Ca may be due to contaminants present in the atmosphere and the elements such as Mg, Al, K are expected due to the impurities in the copper sheet used for the gilding process. However, the presence of Au and trace amount of Hg proves that mercury-amalgam process was used in the making of golden window. This is further to be noticed here that the high amount of C in the EDS spectra still persists even after

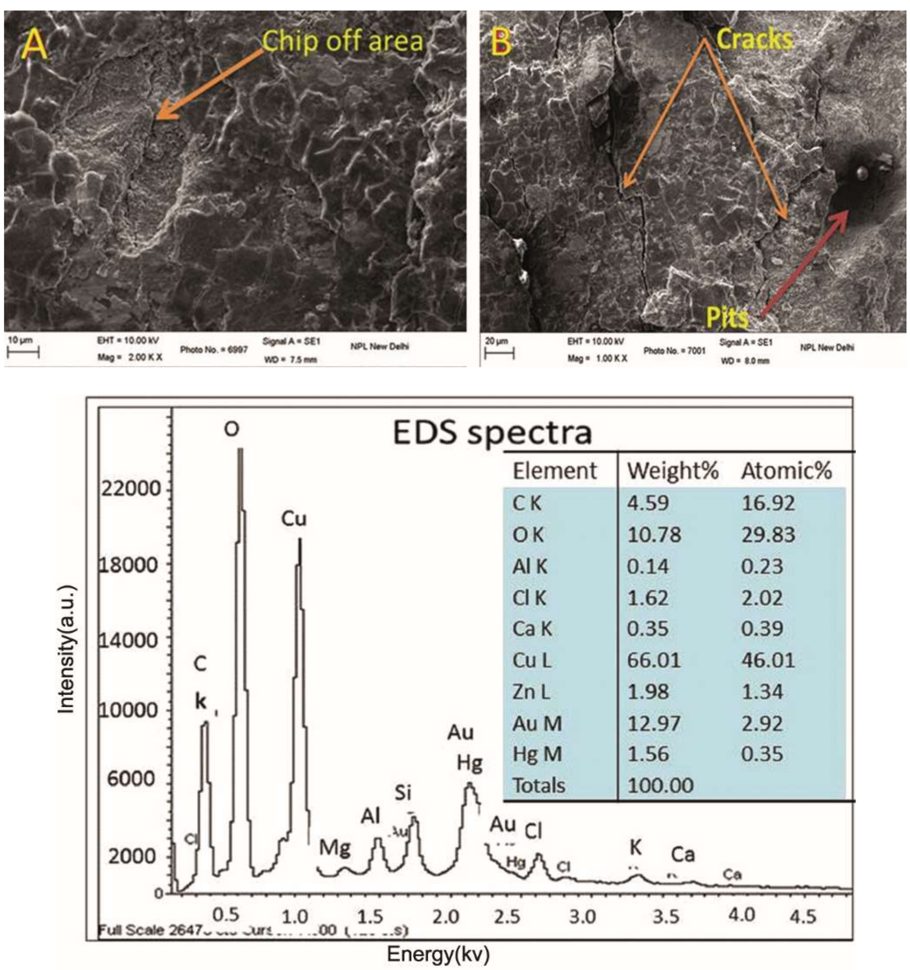

Fig. 6 — SEM images (A and B) of the chip off area and the EDS spectra of the corresponding area of the cleaned sample.

cleaning the sample with the acetone followed by the ultrasonication.

Variation in the quantity (weight%) of Au and Hg as obtained in the EDS spectra as depicted in Figs 4 and 6 may be due to the non- uniformity of the gilding layer on the copper processed in those days. Presence on Zn in very low wt% was also seen in the EDS spectra which may be in the form of impurity in the copper.

An effort has been made to identify the thickness and the uniformity of thin layer of Au coating during the gilding process (Fig. 7). Cross sectional SE mode SEM image as depicted in Fig. 8 clearly revealed that the gilding layer is not uniform. Thickness of the gilding layer is found to vary between 12 to 20 micrometers. Presence of Hg is not revealed in the EDS spectra (Fig. 7) as expected as per the traditional gilding technique in the Nepal is concerned, since the Hg was supposed to be sublimed during the repeated heat treatment.

X-ray mapping of gilded sample is presented in Fig. 9. Distribution of various elements like oxygen, sulphur, chlorine, copper and gold has been revealed in the mapping originated from different energy levels of the element present in the sample. It is evident from the X-ray mapping images that a sufficient amount of sulphur and chlorine is present on the top surface which is responsible for the initiation of corrosion and degradation (chipped off) of the gilded surface during the course of time.

X-ray diffraction technique was used to further characterize the gilded sample for the identification of various elements and the different phases of the compounds present in the sample. A typical diffraction pattern of the gilded sample has been shown in Fig. 10. From the XRD data it is observed that the sample mainly composed of copper and gold present due to gilding process used in ancient times in Nepal. Diffraction peaks oriented along (111), (200), (220) direction found to be of copper matching with the

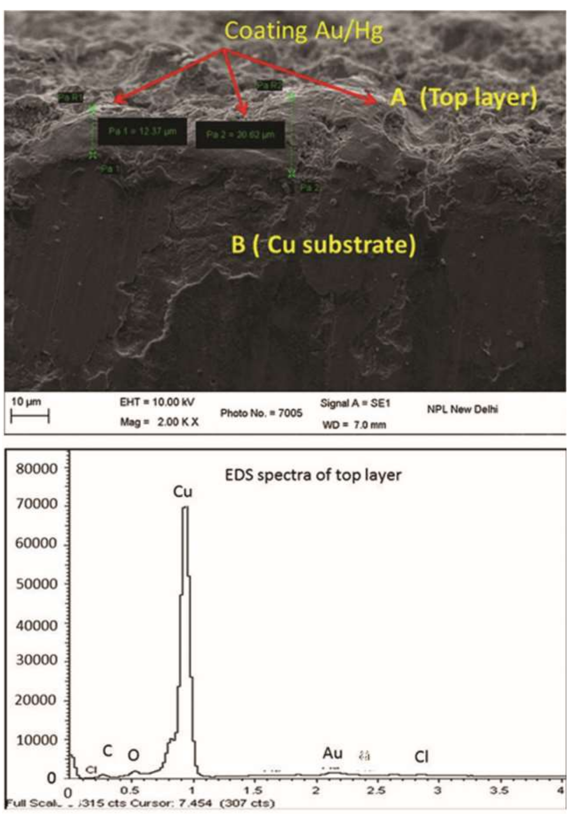

Fig. 7 — SEM image of cross sectional view and the EDS spectra of same area.

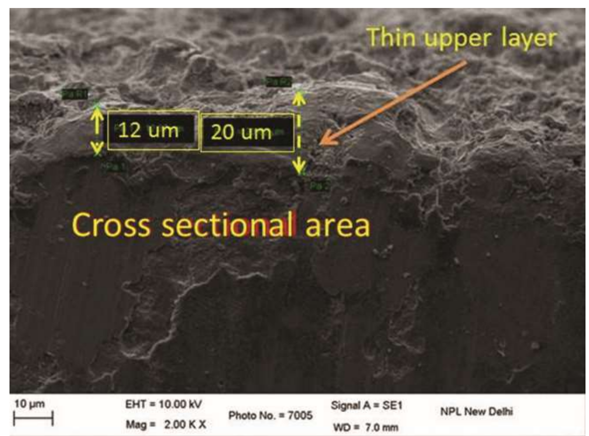

Fig. 8 — SEM image of cross sectional view of the sample indicating the variation in thickness.

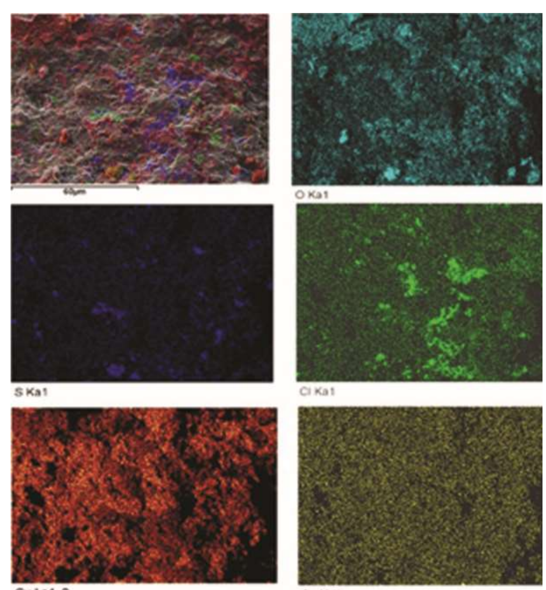

Fig. 9 — X-ray mapping of gilding sample showing maps of different elements.

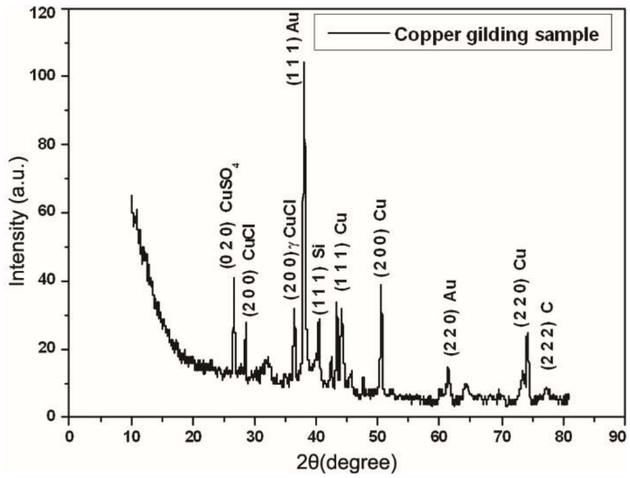

Fig. 10 — XRD pattern of the gilding sample showing various elements on the surface.

standard data JCPDF file No. 892838. However, the peaks of Au oriented along the (111) and (220) direction are found to be in good agreement with standard data of JCPDF file No. 893697. Presence of carbon and silicon reflection peaks in the diffraction pattern may be in the form of contaminants from the environment. Detailed analysis of the diffraction data also revealed the existence of $CuSO_4$ (JCPDF file No. 721248) along (020) plane, γ CuCl (JPDF file No.811841) along (200) plane and CuCl (JCPDF file No. 822117). Presence of $CuSO_4$ and CuCl phases in the diffraction pattern may be due to the presence of sulphate and chloride ions as contaminants from the environment and responsible for the corrosion or degradation in the form of pits on the surface of the gilding sample.

4 Conclusions

Detailed analysis of the gilded sample procured from 17th century golden window of Patan Royal Palace, Kathmandu valley, Nepal revealed that pollutants from the atmosphere such as sulphur and chlorine and carbon are deposited on the gilded windows surface as contaminants from the environment and is found to be responsible for the initiation of corrosion of the heritage structures. Presence of $CuSO_4$ and CuCl phases as depicted in XRD results are found to be the main factors responsible for the degradation of the surface of the gilded window.

It is evident from the pollution level in Nepal that tons of dust particles, SO_2, NO_2, hydrocarbon, are emitted in the atmosphere which is found to be causing damage to many historical buildings and artifacts that represents the cultural heritage of the valley. The bowl like topography hinders wind movement and retains the pollutants in the atmosphere especially during period of thermal inversion over Kathmandu, where cold air flowing down from the mountains is trapped under a layer of warmer air, which acts like a lid over a bowl. Topography and climate-induced disasters together have accelerated vulnerabilities and risks to heritage in Kathmandu valley, Nepal. These are contentious concerns where Nepal needs to factor in national needs. There should be strategic approach towards promoting progressive and affordable standards for fuel quality, and regulating vehicle emissions to ensure compliance with air quality.

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