Effects of Air Pollution on Cultural Properties:
The Measuring of Air Pollution and the Protection of Cultural Properties in the Historic City of Nara, Japan

<u>CONTENTS</u>:

The Effects of Air Pollution of Cultural Properties

1 Introduction

Cultural value created by our ancestors, and represent every sphere of their activities, including: political, economic, cultural, industrial activities as well as their daily life. Cultural properties are an indispensable part of our world; from them we obtain information about the history, culture, ideas and technologies that we use as a basis for considering our present and future, our society and culture.

Of the many types of cultural properties, the tangible cultural properties - buildings, handicrafts, paintings, statues, ancient documents, antiquities, materials of folk history and so on - are made of a variety of materials including metal, stone, wood, textiles, paper and leather, or a combination of these materials. With the passage of time and the effect of external factors such as the formation of mold, insect attack, changes in temperature and humidity, ultraviolet rays and so on, materials will deteriorate, gradually causing irreparable damages to the relic. This type of natural deterioration of cultural properties can be prevented using traditional repair techniques and through the application of chemical preservatives such as synthetic resins. Therefore, cultural properties can be restored and protected in most circumstances.

However, in recent years the deterioration of cultural properties caused by acid rain and other forms of atmospheric pollution has become a serious problem. Various atmospheric pollutants cause the corrosion, fading, discoloring or deterioration of the materials from which these cultural properties are made (Table 1). Atmospheric pollution penetrates into many places and has an adverse affect on many types of cultural properties. Now, more than ever, these cultural properties are in danger of destruction.

'Acid rain' refers to rain with a hydrogen ion concentration of 5.65 or below. Acid rain contains large quantities of atmospheric pollutants such as the negative ions SO_4^{2}-, NO^{3-} and Cl- and the positive ions Na^+, $NH4^+$, K^+, Ca^+ and Mg^+. Of these, the sulfur oxide (SO_x), nitrous oxides (NO_x), chloride ions (Cl^-) and other acidic substances are the primary cause of the deterioration of cultural properties.

Let us examine a few examples of the conspicuous damages caused by acid rain to cultural properties made of stone and bronze around the world.

2 Damages to Cultural Properties Made of Stone

Stone cultural properties in Europe, particularly buildings and statues made of marble, limestone, tuff and sandstone, are greatly affected by acid rain and atmospheric pollution. These substances dissolve the surface of the stone object, whereby decimating its value and in many causes can even cause the destruction of the object itself (Table 2).

(1) The Parthenon

The Acropolis sits on top of a hill visible from almost any point in the city of Athens, the capital of Greece. Since ancient times, this hill has been the center of political, cultural and artistic life in Athens. On top of this hill are temples that include the Parthenon of Athena Nike and the Erechtheion, while in the vicinity structures such as the theater, the Agora and the library have also been preserved. Together, these buildings are the symbol of ancient Greek civilization.

Built in the fifth century B.C., the Parthenon is a symbol of ancient Greek civilization while representing a worldwide battle to preserve cultural properties against atmospheric pollution. The Parthenon is constructed of excellent quality marble excavated from Mt. Pentelicon 10 kilometers to the east of the temple, while the statues were also created from excellent quality marble brought here from all over Greece.

Since the 1970's, the effects of acid rain and acidity in the atmosphere have been dissolving the pillars and statues of the Parthenon, resulting in a loss of their original details. Serious studies are underway to investigate the possibility of dismantling the entire structure and placing it on display in a museum for safekeeping. Athens is home to one-third of the entire population of Greece, and half of the country's cars and factories. As a result, there is a tremendous amount of atmospheric pollution caused by carbon dioxide, sulfur oxides, nitrous oxides, dust and so on. In 1988, the average yearly pH level of rainwater was about 5, but in 1992 levels of 9.0 $\mu g/day/m^3$ (12.0ppb) for SO_2, 120.0 $\mu g/day/m^3$ (30.7ppb) for NO_2 and 23.0 $\mu g/day/100cm^2$ Cl ions were recorded.

Acid rain, carbon dioxide, both sulfur and nitrous oxide compounds have brought about chemical changes on the surfaces of the buildings and marble statues on the Acropolis, transforming the beautiful semi-translucent marble into a white opaque plaster; there are even parts with ugly black splotches and are peeling in places. The chemical reactions are shown below:

The effect of air pollutant carbon dioxide on marble:
$CaCO_3 + CO_2 + aq \rightarrow Ca_2(HCO_3)_2^2$

The effect of air pollutant sulfur on marble:
$CaCO_3 + SO_2 + 0.5O_2 + aq \rightarrow Ca_2SO_4^2$ (ie. plaster) + CO_2

The effect of air pollutant nitrous oxide on marble:
$CaCO_3 + 2NO_2 + 0.5O_2 + aq \rightarrow Ca_2(NO_3)_2^2 + CO_2$

In the 1970's, air brushes were used to remove the dirty surface layer (the plaster layer) on the pillars of the Parthenon in order to restore the original colour of the marble. However, as this method actually removes the original surface, it is no longer used. At present, replicas of the beautiful sculptures on the friezes of the Parthenon and the pillars of goddesses at the Erechtheion have been installed on site, and the originals have been moved to a museum for safekeeping. Distilled water is currently being used to clean and remove the dirt from the surface of statues, and experiments are being performed and research is underway regarding the possibility of reversing the chemical reactions, whereby changing the plaster ($CaSO4 \cdot 2H_2O$) that has formed on the surface back into CaCO first, and then back into $CaCO_3$ (marble).

(2) Cologne Cathedral

The city of Cologne, located on the Rhine River in the central western part of Germany, has flourished ever since its establishment as a fortress in Roman times. Buried beneath the city are ruins covering an enormous area. Cologne Cathedral was originally established in the 4th century A.D. as a Christian church. It was subsequently expanded nine times. The present structure, built in the 14th century, is a massive Gothic cathedral with a 157-meter spire. Since that time, further additions have been built and repairs had been conducted by artisans affiliated with the cathedral. During its history, various stone have been used reflecting the period in which the work was done and the part of the structure that was being restored or expanded. In addition to sandstone, trachyte, tuff, basalt and other types of stone found in Germany, as well as at least eight varieties of French tuff have been used.

Present-day Cologne forms one corner of the Rhur industrial region. In the wintertime, the sky is typically overcast in northern Europe, causing the land to be blanketed in smoke and exhaust fumes from factories, household heaters, automobiles and so on. Pollutant gases containing a mixture of sulfur, chlorine and fluorine, together with acid rain and acid mist, produce adverse chemical reactions that attack the surface of the stones of Cologne Cathedral, forming crystals of calcite and dolomite which causes the peeling and chalking of the surface to a depth of about a centimeter. The result is a cauliflower-like deterioration while large holes measuring up to 15-20 centimeters in diameter have also been observed. At the Cologne Cathedral, Schlaitdorf sandstone components have sustained the most serious damage, as well as the higher parts of the structure that are exposed to the force of wind. In 1988, the average annual pH level of rainwater in Cologne was 4.6, while concentrations of 125.0 $mg/day/m^2$ of sulphur dioxide were measured in 1973.

Serious research into the preservation and restoration of Cologne Cathedral began in 1972. The black contamination on stone statues found on various parts of the structure was gradually dissolved with a natural chemical extracted from tree sap, and the statues were cleaned with distilled water. Two replicas were made of the statues that had suffered the worst damage. Of these, one was placed in the original position, while the other replica and the original statue were preserved as prototypes for future restoration. Statues that have sustained only minor damage and the walls of the structures that have deteriorated badly are being coated with acrylic resin in an effort to preserve them. Ultimately, the aim of the restoration effort is to clean the structure with chemicals made of natural materials and distilled water, and to restore it using traditional masonry techniques.

(3) Stone Cultural Properties in Japan and Other Parts of East Asia

The East Asian region also has many cultural properties made of many types of stone including marble, limestone, tuff, sandstone, andesite and granite. Stone objects include statues of persons and horses, obelisks, stone stupa and Buddhas, while stone statues and buildings of modern times also exist. The limestone stele with a thousand buddhas and dharani from the Liao Dynasty in China (11^{th} century), now part of the collection of the Kyoto National Museum, was brought to Japan in the early 1920's. For 45 years from 1927 to 1972, it was exposed to the elements, and gradually the surface was worn so smooth that the original inscriptions and designs can no longer be distinguished. Calcium sulfate has been detected on the piece, and the cause of the disintegration was determined to be acid rain containing sulfur oxides and atmospheric pollution.

At Meiji-mura in Inuyama, Aichi prefecture, Japan, the surface of the brick wall of St. John's Chapel is peeling away as a result of the formation of sodium sulfate and other crystals caused by acid rain. Similarly, the surfaces of the andesite and tuff tomb stones and Buddha statues in Oita prefecture are peeling away as a result of the formation of sodium sulfate, calcium sulfate and other crystals caused by acid rain.

Other damage has also been discovered, such as the discoloration of the marble at the Taj Mahal in India, and lead sulfate deposits on the stone Buddha at Le Shan city in China where rainfall is in the 4pH level range. Between 1985 and 1989, the pH level of rainwater measured at Seoul National University in Seoul, Korea was 4.2 -4.4, and the surfaces of the tomb stones and stone statues in the garden of the National Museum of Korea - national treasures that include works of granite, sandstone and tuff from the Three Kingdoms period, the Unified Shilla period and the Koryo period - were covered with dust and discolored to a gray hue. Corners of the limestone and tuff pagodas and statues in particular have been rounded off or have dissolved. This damage, too, was the result of acid rain and atmospheric pollution.

3 Damages to Cultural Properties Made of Metal

Metals featured in cultural properties include gold, silver, copper, bronze, iron and lead. Of these, bronze, an alloy made of copper and tin to which small quantities of lead, arsenic and other materials are added, is an excellent material in terms of its malleability, appearance and durability. When bronze is left outdoors for long periods of time, a fine dark layer of rust composed of basic copper carbonate gradually forms on the surface. As this rust progresses no further, it serves to protect the object from further corrosion or surface damage. Ancient peoples recognized this property of bronze and used it for a wide variety of applications that include buildings, commemorative statues and decorations.

However, even such otherwise durable bronze cultural properties that have been preserved for hundreds and even thousands of years have not escaped the effects of acid rain and atmospheric pollution. These chemical substances dissolve or break up the basic copper carbonate film on the surface, thus the bronze object becomes susceptible to corrosion by copper sulfate and basic copper chloride. As a result, the surface colour changes to a vivid yellow-green hue, and corrosion and deterioration are accelerated. (Table 3)

(1) The Bronze Garden Lantern of Todaiji Temple, Nara, Japan

The lanterns, which were made at the same time as the Great Buddha at the Todaiji temple, Nara Prefecture, in the middle of the 8th century A.D., were cast from an alloy of copper and tin (ie. bronze), and were originally covered in gold plating so that they would shine like pure gold. Although in the subsequent 1,250 years they have been exposed to the elements and the surface plating has been lost, the lanterns have retained their dark subdued appearance throughout the centuries. In the last 20 years, however, their colour has changed completely to a yellow-green hue, and concerns have been raised as to whether this is the result of atmospheric pollution.

Starting in 1987, researchers at Nara University measured atmospheric pollution in the northern part of the Nara basin that is home to the Todaiji temple and many other cultural properties. They also conducted studies and research into the effect of atmospheric pollution on cultural properties in the area. In these studies, the concentrations of sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and chloride ions (Cl^-) were measured at 19 locations around 9 cultural property sites. Test pieces, which included five types of metal panels, 11 colour panels, and cloth dyed with 5 colours, were exposed to the atmosphere. The changes in their appearance were monitored periodically and an analysis of the substances produced on their surfaces was performed in order to investigate the relationship between atmospheric pollution and metal corrosion and pigment/dye discoloration.

These studies found that the pH level of rainwater in the city of Nara was 4.7, while at Todaiji the measured concentration of various chemicals were 18.2 μg /day/100cm^2 (3.6ppb) for sulfur dioxide, 64.3 μg/day/100cm^2 (10.5ppb) for nitrogen dioxide, and 6.1 μg/day/100cm^2 for chlorine. Sulfur (S) and chlorine (Cl) were detected in the substances produced by metal corrosion; atmospheric pollution were found to have contributed to metal corrosion and the discoloration of pigments and dye to some extent. The effect of chlorine ions produced by the burning of rubbish was found to be particularly great.

Subsequently, an analysis of the rust on the octagonal gilt bronze lanterns conducted by the Tokyo National Research Institute of Cultural Properties detected the presence of sulfur (S) and chlorine (Cl) that resulted from pollution, while basic copper sulfate (brochantite $CuSO_4/3(OH)^2$ and antlerite $CuSO_4/2(OH)_2$) and basic copper chloride (atacamite $CuCl_2/3Cu(OH)_2$) were detected in the by-products of corrosion, thus verifying the results of the Nara University study.

(2) Metal Cultural Properties Outside Japan

The Statues of Liberty which stands on Liberty Island at the tip of New York's Manhattan Island in the United States was given to the U.S. by France in the year 1886. In a 1980 survey, the copper plates set into the concrete were found to be severely corroded. As a larger quantity of corrosion products were found on the leeward side than on the northern side facing Manhattan, the corrosion was seen as the peculiar effect of atmospheric pollution. The pH level of rainwater in New York in 1985 was 4.3 and concentrations of 2.5 μg/ml of SO_4^{2-}, 1.5 - 2.0 μg/ml of NO^{3-} and 0.2 -0.3 μg/ml of NH_4^+ were measured.

The surface of the large bronze bell of Songdok-dea wang-sin Jong (Emile Jong) in the central garden of the Kyongju National Museum in Korea, also has yellow-green rust thought to be composed of basic copper sulfate and basic copper chloride. Acid rain with pH level in the low 5pH range falls in the city of Kyongju.

4 Conclusion

Any attempt to determine the effect of acid rain on cultural properties must take into account not only the pH level of rainwater but the substances contained in that rainwater. Furthermore, it is necessary not only to consider wet deposition such as acid rain but to also evaluate the total effect including dry deposition such as acid mist and gases.

The effects of atmospheric pollution build up year after year, and they cause damages to all cultural properties, whether they are in cities or in a rich natural environment, whether they are indoors or outdoors, and regardless of the materials from which they are made. Atmospheric pollution causes cultural properties to deteriorate at a rate up to several hundred times the speed of natural deterioration. In other words, cultural properties that have been carefully preserved for more than a thousand years can be destroyed in a few decades. As a result, we now face a major crisis.

Various methods of preservation can be considered for the protection of cultural properties from atmospheric pollution. However, together with the application of preservation methods, studies must be made about the environment surrounding cultural properties and environmental standards should be established urgently.

It is a truth common to all humanity that only by preserving the past - protecting our cultural properties and passing them on to the next generation - will we able to create the future.

Table 1: Atmospheric Pollution Affecting Cultural Properties

Type of Cultural Property	Pollutant	Effect
metal cultural properties	acid rain, acid mist, SOx, NOx, Cl^- etc.	corrosion, discoloration etc.
stone cultural properties	acid rain, acid mist SOx, NOx, Cl^- etc.	discoloration, deterioration etc.
wooden cultural properties	acid rain, acid mist SOx, NOx, Cl^- etc.	deterioration discoloration, etc.
wall paintings	acid rain, acid mist SOx, NOx, Cl^- etc.	peeling, discoloration etc.
oil paintings	ammonia	deterioration of oils, cloudiness of varnish
paper/leather	Sox, NOx, Cl^- etc.	discoloration, fading, deterioration
dyed and woven articles	acid rain, acid mist SOx, NOx, Cl^- etc.	discoloration, fading, deterioration
glass	acid rain, acid mist SOx, NOx, Cl^- etc.	cloudiness

Table 2: Damages to Stone Cultural Properties Caused by Acid Rain and Atmospheric Pollution

Name	Major By-products or Detected Substances Resulting From Atmospheric Pollution
(Athens, Greece) Parthenon/Erechtheion	calcium sulfate ($Ca_2SO_4^2$)
(Padova, Italy) Freccoes, Scroveni Chapel	calcium nitrate ($Ca_2(NO_3)_2^2$) calcium sulfate
(Venice, Italy) Marble statutes/walls, Church of San Marco	calcium sulfate
(Cologne, Germany) Stone statues/walls, Cologne Cathedral	calcium carbonate (calcite/$CaCo_3$) dolomite
(Le Shan city, China) Stone Buddha	iron sulfate
(Aichi prefecture, Japan) Brick wall, St. John's Chapel, Meiji-Mura	tenaraite(Na_2SO_4), aphthitalite($K_3Na(SO_4)_2$), trona ($Na_3H(CO_3)_2/2H_2O$), thermonatrite (Na_2CO_3/H_2O)
(Kyoto prefecture, Japan) Stone stela with thousand Buddhas and Dharani, limestone, Kyoto National Museum	calcium sulfate ($CaSO_4/2H_2O$)
(Oita prefecture, Japan) Andesite 5 ringed obelisk (Gorinto) etc.	NO_3, Ca etc.
(Oita prefecture, Japan) Beppu city Kunisaki tower / stone lantern (andesite)	SO_4^{2-}, Na etc.
(Oita prefecture, Japan) Acalanatha of rock-cliff sculptures, Fuko-ji Temple (tuff)	Ca, SO_4^{2-} etc.

Table 3: Damages to Metal Cultural Properties Caused by Acid Rain and Atmospheric Pollution

Name	Major Atmospheric Pollutants Detected
(Ibaraki prefecture, Japan) copper-plated roof of the inner shrine, Toshogu Otabisho Honden	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$)
(Tokyo prefecture, Japan) copper-plated roof of the Hyokeikan Tokyo National Museum	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$)
(Tokyo prefecture, Japan) copper-plated roof, Akasaka Rikyu	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$)
(Kanagawa prefecture, Japan) statue of Buddha, Kotoku-in temple	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$), lead sulfate
(Kyoto prefecture, Japan) copper bell/phenix images on roof, Amida-do, Byodo-in temple	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$)
(Kyoto prefecture, Japan) bronze decorations on 3-story pagoda, Joruri-ji temple	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$)
(Kyoto prefecture, Japan) “Kangaeru hito” (Thinking Person), Kyoto National Museum	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$)
(Nara prefecture, Japan) bronze garden lantern, Todaiji	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$) basic copper sulfate ($CuSO_4$ - $2Cu(OH)_2$) basic copper sulfate ($CuCl_2$ - $3Cu(OH)_2$)
(Okayama prefecture, Japan) 3-story pagoda, Hofuku-ji temple	basic copper sulfate ($CuSO_4$ - $3Cu(OH)_2$) basic copper sulfate ($CuCl_2$ - $3Cu(OH)_2$)
(Shimane prefecture, Japan) ornamental copper fixture, Hini-misaki Shrine	Cuprous chloride ($CuCl$)

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Measuring Air Pollution and the Protection of Cultural Properties in the Historic City of Nara, Japan

Summary

Nara is a famous historic city with many cultural heritage. The air pollutant levels in Nara are lower than in many other Japanese cities, but even this relatively low level of air pollutant affects many cultural properties. For example, in recent years the Todaiji temple's Hakkaku Toro (bronze lantern, 8th century) has corroded conspicuously and the Chogakuji temple's Sekito (tuff pagoda) has also been damaged.

Fig.1 the location of Nara City

For eight years, we have been measuring air pollutant at 12 locations outside and at 7 locations inside historic buildings or museums by the simple method of using a triethanolamin cylindrical filter (TEA-CF).

Typical results collected are as follows: at outside test locations, the nitrogen dioxide (NO_2) level is 56.1 -132.4 $\mu g/100cm^2$/day (9.6 -16.6 ppb/day), the sulfur dioxide (SO_2) level is 13.1 - 52.6 $\mu g/100cm^2$/day (3.4 - 5.1 ppb/day) and the chloride (Cl^-) level is 4.2 - 13.9 $\mu g/100cm^2$/day. At the inside locations, the NO_2 level is 7.5 - 32.9 $\mu g/100cm^2$/day (4.1 - 7.2 ppb/day), the SO_2 level is 0.3 - 3.6 $\mu g/100cm^2$/day (under 2.8 - 3.0 ppb/day) and the Cl^- level is 1.1 - 5.0 $\mu g/100cm^2$/day. Experiments on exposing test pieces of materials to the atmosphere revealed that metal and colored cultural properties are susceptible to damage by even a low level of air pollutant.

At Nara Park, NO_2 levels were 28% lower in wooded areas than near principal roads, and 52% lower in virgin forest areas. The percentage difference between NO_2 levels measured on the principal roads and in the virgin forest areas is about the same as that between the outside and the inside of the Todaiji temple's Kyoko (wooden storehouse).

In order to protect cultural properties, we must reduce the level of air pollutant, apply treatments to cultural properties, and establish wooded green belts as a protective buffer zone around them.

1. Observation of Air Pollution in Nara City

In 1989 we started a study in the Northern Nara Basin, where a number of cultural properties including national treasures and important cultural assets exist at close proximity. The purpose of the study was to grasp the effect of air pollution on cultural properties, and to eventually find effective measures to protect cultural properties from being damaged by air pollution.

Many cultural properties in Nara have recently been inscribed on the UNESCO World Heritage List .

(1) Observation Sites

Monthly as well as semiannual observations of the effect on the properties were conducted at 19 locations of 9 sites, including: the Nara University, Heijo-kyuseki Site (the ruins of Heijo Palace), Yakushiji temple, Hannyaji temple, Shosoin Store, Todaiji temple, Kofukuji temple, Kasugataisha shrine and Jurinin temple. Daily observations were also conducted at 81 locations in Nara Park.

(2) Measuring Procedures and Results

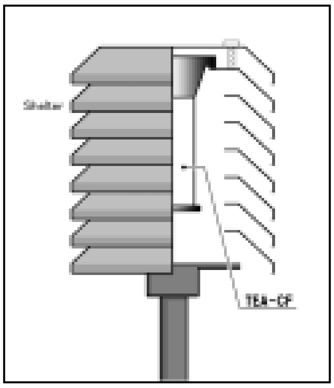

Fig.2 TEA-CF filter

Sulfur dioxide (SO_2), Nitrogen dioxide (NO_2) and chlorine ion (Cl^-) were measured using a method of absorbing the pollutants known as TEA-CF; a cylinder made of cellulose filter paper with a surface area of 100cm_2(Fig.2) was dipped into a 29.6% solution of tri-ethanol amine (2,2',2"-nitro-tri-ethanol, $N(CH_2CH_2OH)_3$=149.49). The treated TEA-CF was then set in a sheltered location at 1.8m above the ground level. The shelter was calibrated to allow 20% aeration. The filter was then aerated for one month before being collected for elution. The pollutants in the sample were then identified and analyzed using ion-chromatography.

In Nara Park, one-day-exposure NO_2 trapping capsules (AP capsule) were also placed at 81 locations within an area of 1.6km^2. The capsules were collected and pollutant concentrations were calculated by using a colorimeter with a saltzman reagent. The data of SO_2 distribution, NO_2 and Cl^- concentration at one month exposure that were recorded during the period between January and December 2000 are shown in Table 1 and Fig.3 (converted and expressed in “per day values”).

The SO_2 concentration observed were 3.6, 3.9, 3.4, 4.3, 3.9 and 4.0 ppb/day at Todaiji temple, Kofukuji temple, Kasugataisha shrine, Jurinin temple, Yakushiji temple and the Heijokyuseki site respectively. Locations with a concentration over 7.0 ppb/day turned out to have been in an industrial area at the south of the intersection of the National Road No.24 and No.369, suggesting that emissions from factories and traffic were the source.

The NO_2 concentration observed was 10.6, 14.5, 9.7, 14.7, 14.4 and 15.0 ppb/day at Todaiji temple, Kofukuji temple, Kasugataisha shrine, Jurinin temple, Yakushji temple and Heijokyushi site, respectively. Locations where high concentrations of over 30ppb/day were observed were located near the intersection of the National Roads No.24 and No.369, suggesting that exhaust from traffic was the main source. The distribution of SO_2 and NO_2, was highest in the central region of the Northern Nara Basin, and there was a gradual decrease in concentrations at sites located further away in all directions.

The level of Cl^- observed was 4.4, 4.3, 2.6, 9.8, 8.7, 11.0 and 15.7 μg /100cm^2/day at Todaiji temple, Kofukuji temple, Kasugataisha shrine, Jurinin temple, Yakushiji temple, Heijokyuseki site and Nara University, respectively. High concentrations of over 18.8 μg/100cm^2/day were observed at locations in the vicinity of Narayama Hills. The conspicuous differences in the concentration distribution patterns of SO_2 and NO_2 were attributable to the exhaust from the nearby incineration facility.

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Table 1: SO_2 distribution, NO_2 and Cl^- concentration

Measuring Site		SO_2 (μg)	SO_2 (ppb)	NO_2 (μg)	NO_2 (ppb)	Cl (μg)
Nara University (Library)	outside	21.1	3.7	56.8	11.5	8.5
	inside	0.5	<2.8	12.0	4.7	0.6
	within glass case	0.5	<2.8	1.5	3.5	0.6
Heijokyuseki site	outside	16.5	3.5	60.7	11.6	6.7
Yakushiji temple	outside	12.9	3.4	56.0	10.9	5.5
Hannyaji temple	outside	12.4	3.3	41.3	10.0	4.3
Shosoin store	outside	12.1	3.3	39.7	8.8	3.5
Tsusakamon Gate	outside	7.2	3.1	37.5	8.3	2.4
Todaiji temple (Store house)	outside	10.0	3.2	38.6	8.6	3.5
	inside	0.9	<2.8	19.6	5.9	0.8
	within wooden box	0.1	<2.8	0.2	<3.3	0.4
Kofukuji temple (Museum)	outside	9.1	3.2	56.1	10.9	2.5
	inside	0.9	<2.8	25.3	6.7	0.9
	parking lot	12.9	3.4	64.7	12.0	3.2
Kasugataisha shrine	outside (virgin forest.)	7.4	3.1	31.3	8.0	1.9
	inside (museum)	0.8	<2.8	14.8	5.2	0.9
	parking lot	10.6	3.2	40.5	9.0	3.7
Jurinin temple (Main hall)	outside	19.2	3.7	57.4	11.1	6.0
	inside	1.2	2.9	33.6	8.3	0.8

μg= μg/100cm²/day
ppb=ppb/day(by empirical formula:SO^2 (ppb)=0.043 × μg SO^2/100cm /day+2.8,
NO^3 (ppb)=0.043 × μg NO^3/100cm /day+3.3)

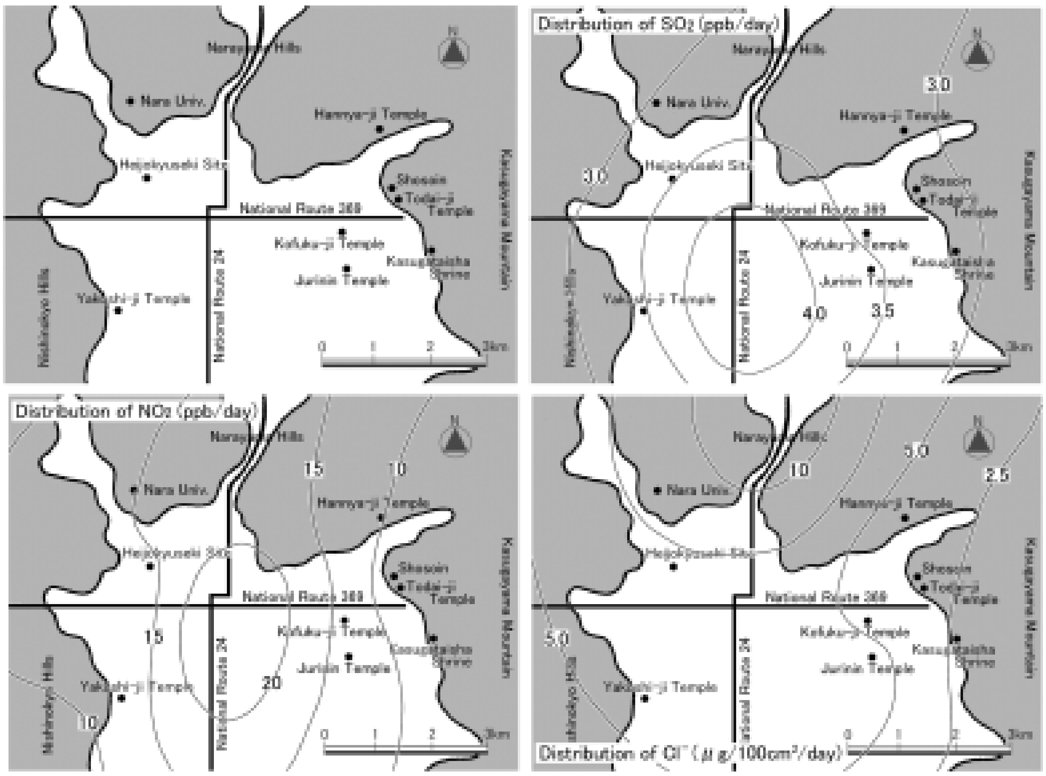
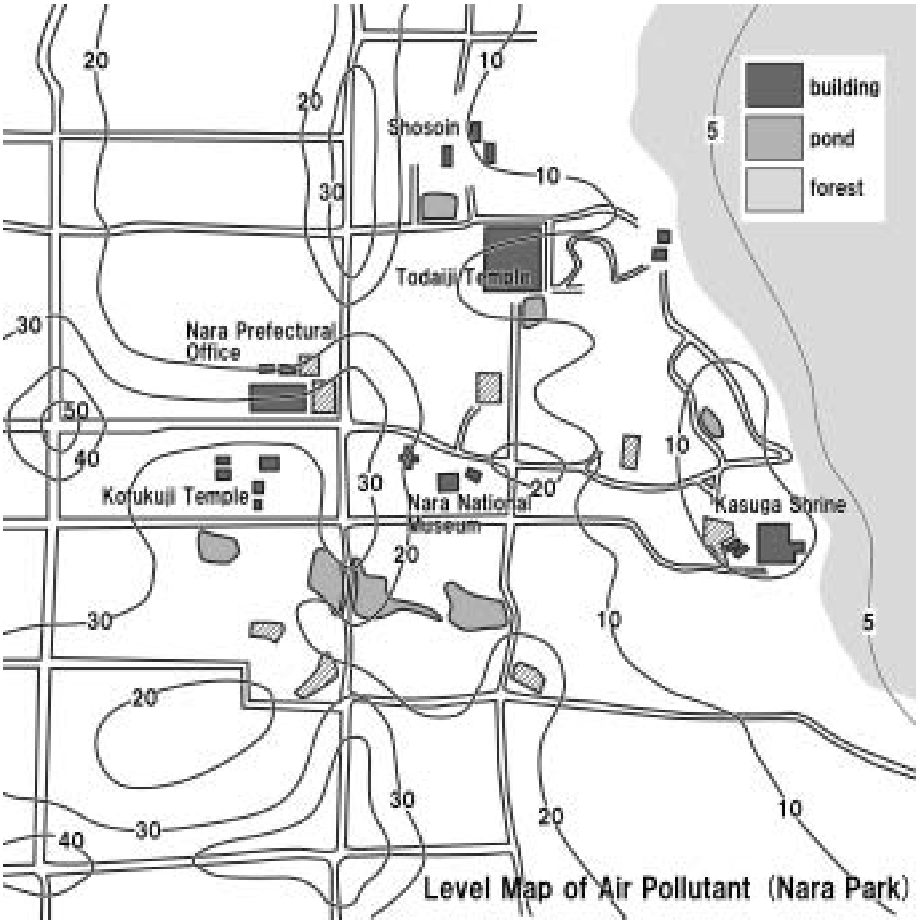


Fig.3 Observation sites and level maps of air pollutant Northern Nara Basin



The distribution of NO_2 concentration, which was measured by the use of one-day-exposure AP capsules in Nara Park, is shown in Fig.4. NO_2 concentration reached as high as 20 to 30 ppb/day along the busy National Road No.369 and the Nara-Tenri-Sakurai Road. It was also higher in and around the parking lots, indicating that exhaust from cars is the source.

In contrast, NO_2 concentration was low in the Kasuga virgin forest, Nagi (Podocarpus Nagi) virgin forest to the south west of the Kasugataisha shrine and forests in the southeast of Todai-ji Daibutsuden (Hall of the great Buddha). This indicates that forests prevented NO_2 from penetrating (and diffusing) and that they also filtered NO_2.

2 The Effect of Air Pollution on Test-Pieces (Metal Plates, Pigments)

(1) Measuring of the Results

The effect of air pollution on cultural properties was evaluated by making use of test-pieces. Five kinds of metal samples (silver, copper, iron, lead and tin) were used to represent the materials making up parts of cultural properties. The metal samples that were used measured 50mm×30mm×1mm (length, width, thickness), however, the thickness of the tin sample was increased to 2mm.

Fig.5 Metal and pigment test pieces in screen

Measuring Site		Sulfur(mg/100cm^2)				Chlorine(mg/100cm^2)			
	Metal Plate	Silver	Copper	Lead	Tin	Silver	Copper	Lead	Tin
Nara Univ.		2.3	7.0	11.1	0.4	10.4	3.7	3.9	0.9
Heijokyuseki Site		1.7	3.3	6.6	0.3	8.1	3.6	3.4	1.0
Yakushi-ji Temple		2.1	3.6	8.6	0.3	7.1	2.6	2.7	0.9
Todai-ji Temple		2.0	5.4	7.7	0.1	7.9	2.9	3.3	0.7
Kofuku-ji Temple		1.3	3.0	7.3	0.1	5.1	1.7	1.6	0.6
Kasugataisha Shrine		1.6	3.3	7.3	0.1	4.1	0.9	1.1	0.4

Table 2 Sulfur and Chlorine level in the substance formed of the metal plates (after six months exposure to the external environment)

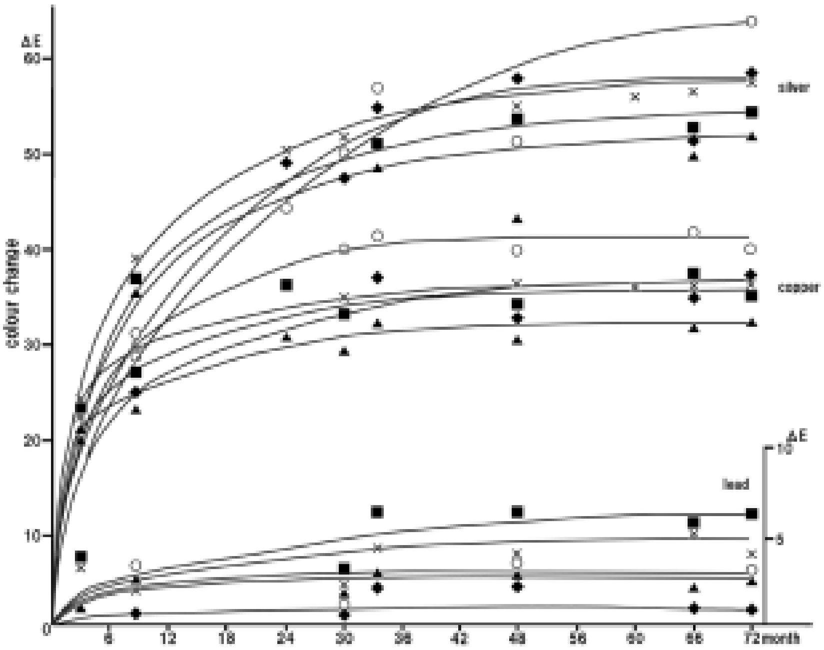
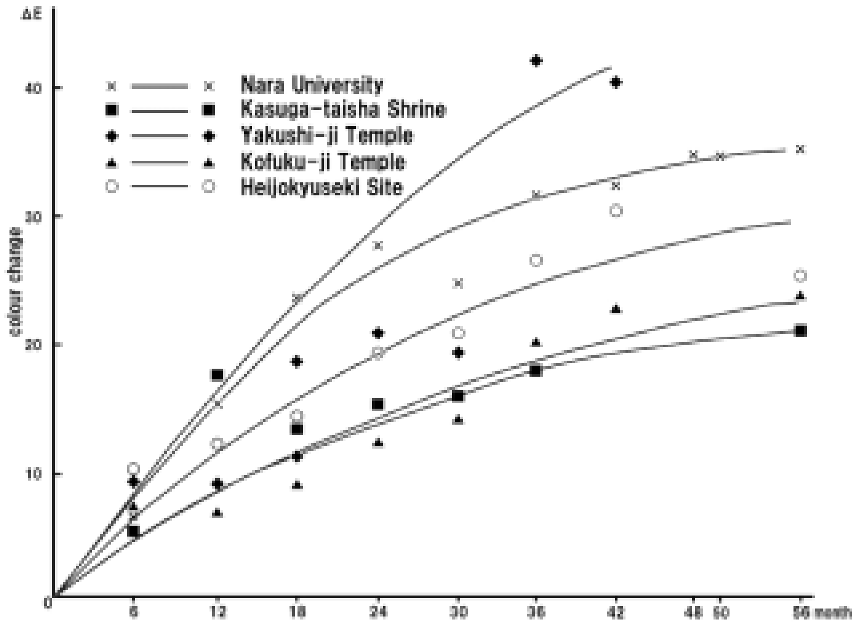
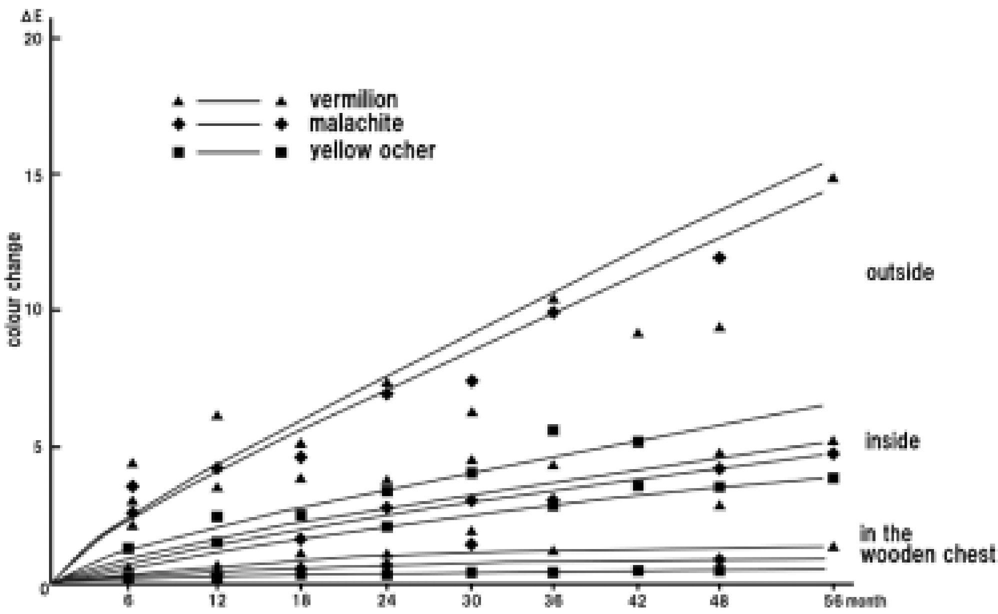


Fig. 6. Metal Colour Change





These metal pieces were exposed to the external environment for a continuous period of six months, twelve months and twenty-four months. Changes in their colour and weight were measured, and the rust that developed was also analyzed.

Plates of cryptomeria (Japanese cedar) measuring 150mm×120mm×10mm (length, width, thickness) were used as substrates for testing pigments that represent the colouring materials used in cultural properties. The whitewashed cedar plates were painted with five coatings of pigment over an area of $120mm^2$. Several coatings were applied to achieve a uniform colour. The colours used in the test were indigo blue, ultramarine blue, azurite, malachite, cochineal, vermillion, red oxide of ion, burnet sienna, yellow mauve, yellow ocher and white, while glue (non pigment) was also tested. The test pieces were exposed to air and the changes were measured every six months (Fig. 5).

(2) Metal Plates Analysis and Colour Change Observations

After the six months exposure, four out of five kinds of metals were subjected to quantitative analysis using a fluorescene analysis technique to determine the sulfur (S) and chlorine (Cl) content of the rust formed on the surface of the plates. The results are shown in Table 2. The quantity of detected S and Cl in the rust turned out to be, in general, proportionate to the respective concentration of SO_2 and Cl in the environment. This indicates a positive correlation between air pollution and the content of pollutants in the rust formed on the metal plates. The colour on the metal surfaces (prior to and after the 72 months exposure) were monitored. The change in colour is shown in terms of ΔE (Fig. 6).

(3) Colour Change of Pigments

The change of colours of eleven different pigments is shown in terms of ΔE in Fig. 7 and 8. These pigments contain metallic elements. Considering the fact that humidity contributes to the changes in colour, it is obvious that there is a correlation between air pollution and the changes in colour that were observed.

3. The Effect of Air Pollution on Cultural Properties

(1) Sources of Air Pollutants and their Concentration Distribution

Areas with higher nitrogen dioxide (NO_2) concentration are located in the vicinity of the intersection of National Road Route No.24 running through the Nara basin from south to north and National Road No.369 which crosses the basin from east to west. This suggests that exhaust from cars is the source of nitrogen dioxide.

Areas with higher sulfur dioxide (SO_2) concentration are located in the vicinity of the industrial area south of the intersection of National Road No.24 and No.369. This shows that factory emissions are the main source of sulfur dioxide.

The area with higher chlorine (Cl^-) concentration is located at Narayama Hills, which suggests that the exhaust from the nearby incineration facility is the main source of chlorine.

(2) Diffusion of Air Pollutants

The greater the distance from the source, the more the polluted air diffuses itself and its concentration decreases. Concentrations are lower indoors than outdoors, lower within casings (such as wooden chests) than within a building, and lower in a ferroconcrete building (which is more airtight) than in a wooden building.

(3) The Azekura Style Building and the Use of Trees against Air Pollution

The Azekura style storehouse is an indigenous Japanese building, and features an elevated floor with a log house style of construction (Fig. 10). This type of storehouse together with the use of wooden chests provides a storage condition that is comparable to that of the controlled environment inside a museum. It protects the cultural properties, to a similar extent as the latter, not only from the varying temperature and high humidity of the Japanese climate, but also from the effects caused by air pollution. The Azekura-style building and ferroconcrete buildings, both of which allow the admission of open air, have about the same degree of filtering and purifying effect as that of a dense forest buffer.

(4) The Effects of Air Pollution on Metal Based Cultural Properties

The content of sulfur and chlorine (rust) that developed on the surface of metal test-pieces were proportionate to the concentration of sulfur dioxide (SO_2) and chlorine (Cl^-) in the air to which the pieces were exposed. Based upon such test results, it may well be inferred that similar chemical changes and their consequential effects such as discoloration / deterioration are applicable to metal cultural properties, such as hanging lanterns, garden lanterns, temple bells and Buddhist images.

(5) The Effect of Air Pollution on Coloured Cultural Properties

When it comes to pigments, changes in colour involve very complicated phases of chemical reaction. However the concentration of pollutants in atmospheric air and the degree of discolouration of pigments were observed to have been proportional to each other and were positively correlated. It may well be inferred that the colours on buildings, sculptures, paintings, dyed textiles are undergoing similar chemical changes.

4. Conclusion

When cultural properties are exposed to polluted air, they undergo a continuous process of deterioration / discolouration. The accumulation of even an extremely small change daily may lead to the relic to wear out eventually. This is illustrated in the case where a 0.5mm thick copper plate which is expected to last 40 to 50 years under ordinary conditions corroded and developed a hole within a decade. The speed of deterioration is much faster than estimated; in other words, we are facing a grave situation where priceless cultural properties which have been well preserved for more than a millennium could extinct within a mere few decades.

In order to protect cultural properties from air pollution, several methods, including the reduction of the source of pollutant, are feasible. For example, the following measures can be applied to outdoor objects:

- moving them farther away from the source of pollution;
- building shelters to keep them safe from the effects of rain and wind;
- planting trees as buffers against polluted air (Table 3);
- and possibly applying treatments to cultural assets for preservation.

For transportable items, possibilities include storing them indoors, encasing them or applying preservation treatment to the object.

Table 3. Air pollutants level and mitigation percentage between measuring

Measuring Site		NO_2 μg (ppb)	NO_2 mitigation percentage	SO_2 μg (ppb)	SO_2 mitigation percentage	Cl^- μg	Cl^- mitigation percentage	remarks
Todai-ji Temple (Store House)	outside	61.7 (10.6)	100.0%	18.0 (3.6)	100.0%	4.4	100.0%	8th century wooden building
	inside	29.4 (6.6)	47.6	1.4 (<2.8)	7.7	0.8	18.2	
	in the wooden chest	1.2 (<3.3)	1.9	0.8 (<2.8)	4.4	0.4	9.1	
Jurinin Temple (Main Hall)	outside	96.4 (14.7)	100.0	34.1 (4.3)	100.0	9.8	100.0	12th century wooden building
	inside	51.9 (9.2)	53.8	2.2 (2.9)	6.5	0.7	7.1	
Kasugataisha Shrine	parking	70.4 (11.6)	100.0	18.4 (3.6)	100.0	4.4	100.0	
	in the Virgin Forest	55.9 (9.7)	79.4	13.0 (3.4)	70.7	2.6	59.1	
	in the museum	12.1 (4.7)	17.2	0.6 (<2.8)	3.3	1.0	22.7	reinforced concrete
Kofuku-ji Temple (Museum)	outside	94.6 (14.5)	100.0	20.3 (3.9)	100.0	4.3	100.0	reinforced concrete
	inside	39.6 (8.0)	41.9	1.5 (2.8)	7.4	0.8	18.6	
Nara Park	on T-K Line Road	(12.0)	100.0	-	-	-	-	
	grassy area	(9.9)	82.5	-	-	-	-	
	Man-made forest	(8.6)	71.7	-	-	-	-	
	virgin forest	(5.7)	47.5	-	-	-	-	

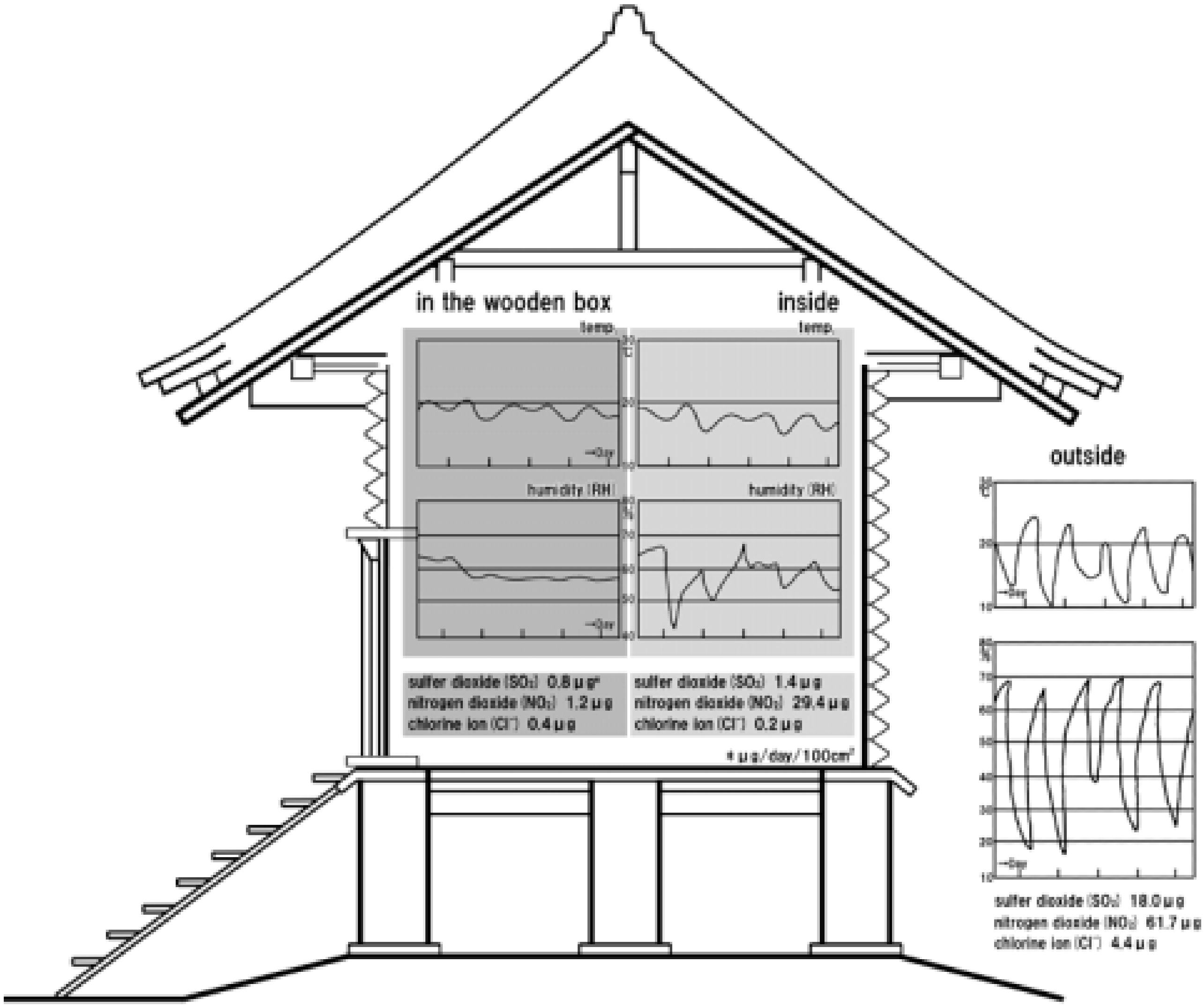


Fig. 10. The level chart of air pollutant at Todai-ji

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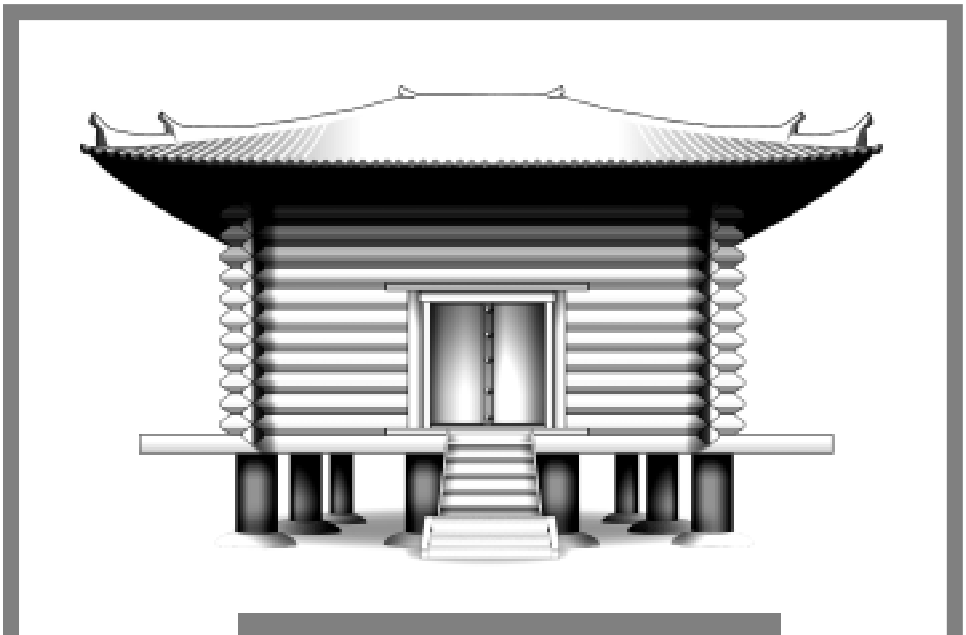

Azekura Style

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