

Chemical agents of deterioration



09:00–10:45
21 September 2015



Chemical agents of deterioration

This session will cover what can be described, broadly, as pollutants, one of the ten agents of deterioration defined in an earlier session. For the purposes of the course, these will be divided into three categories.

Particulate pollutants

Outdoor chemical pollutants

Indoor chemical pollutants

Chemical agents of deterioration

- Particulate and gaseous pollutants comprise one of the ten agents of deterioration considered by conservators

Causes of loss or damage
<i>1. fire</i>
<i>2. water (e.g. ingress through roof, burst pipes)</i>
<i>3. criminal action (e.g. vandalism, stealing)</i>
<i>4. physical forces (e.g. vibration, dropping objects, building collapse)</i>
<i>5. pests</i>
<i>6. Light and ultraviolet radiation</i>
<i>7. contamination (e.g. dust, pollution)</i>
<i>8. incorrect temperature</i>
<i>9. incorrect relative humidity</i>
<i>10. dissociation (e.g. unregistered items, incorrect object location)</i>

Chemical agents of deterioration

Outdoor vs Indoor – why a distinction?

Little control of dust, particulates or gaseous pollutants generated in the broader environment. Depends on location, and on global, national and local practices and politics

Generally cannot stop outdoor pollutants at source, but rely on measures to exclude them

Greater control possible over the generation of particulate and gaseous pollutants within buildings through research, practice and policy

Particulate pollutants

Sources

Indoor and outdoor

Natural and human (anthropogenic)

Particulate pollutants

Outdoor sources

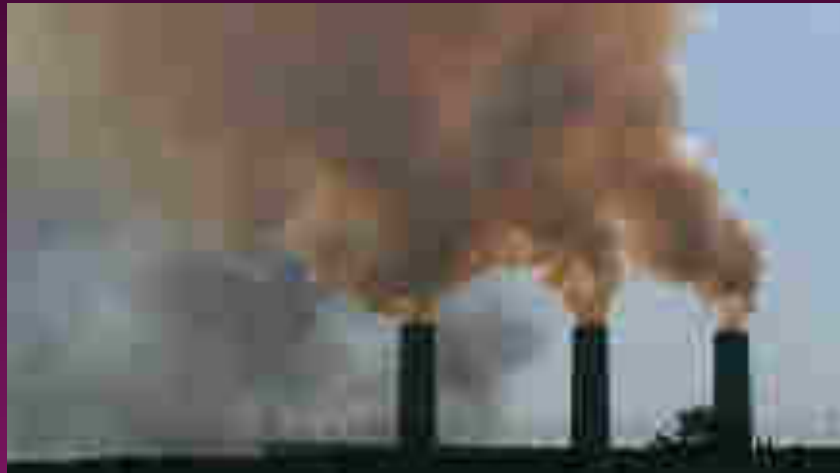
'General' dust from the breakdown of sand, soil, stone, concrete, brick, etc. or industrial activities. Common in urban environments but also in the rural settings from tilling of earth, pollen, pesticides, volcanic activity, etc.



Particulate pollutants

Outdoor sources

Particulates generated by burning fossil fuels and other materials – commonly called soot, but may not be entirely carbon due to incomplete combustion, which can make it 'sticky' and hence more soiling



Particulate pollutants

Outdoor sources

Suspended salt particulates can be generated in coastal setting from sea spray or in urban environments from efflorescence in buildings or the use of road salt in cold climates



Particulate pollutants

Indoor sources

Dust from the erosion of indoor plaster, brick or other finishes contributes to indoor pollution, particularly during building work

Suspended salt particulates can be generated from efflorescence in buildings



Particulate pollutants

Indoor sources

Human skin, hair and textile fibres shed by visitors are major components of indoor dust. These can aggregate into dust balls or 'bunnies'



Particulate pollutants

Indoor sources

Historically, indoor environments were affected by particulates generated by open fires and by cigarette smoking, both of which can produce 'tarry' or 'sticky' particles



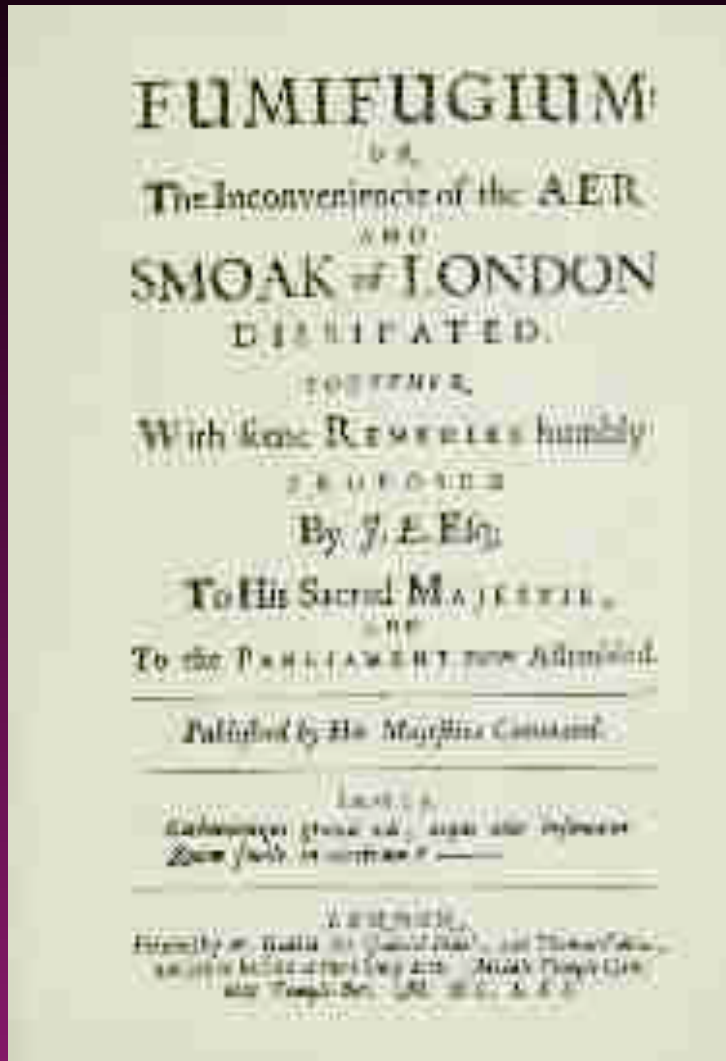
Particulate pollutants

Indoor sources

Outdoor dust brought inside with visitors



Patterns of particulate pollution



‘this horrid Smoake ... obscures our Churches ... fouls our Clothes, and ... spreads a Yellow upon our choycest Pictures and Hangings’: John Evelyn, 1661

Patterns of particulate pollution



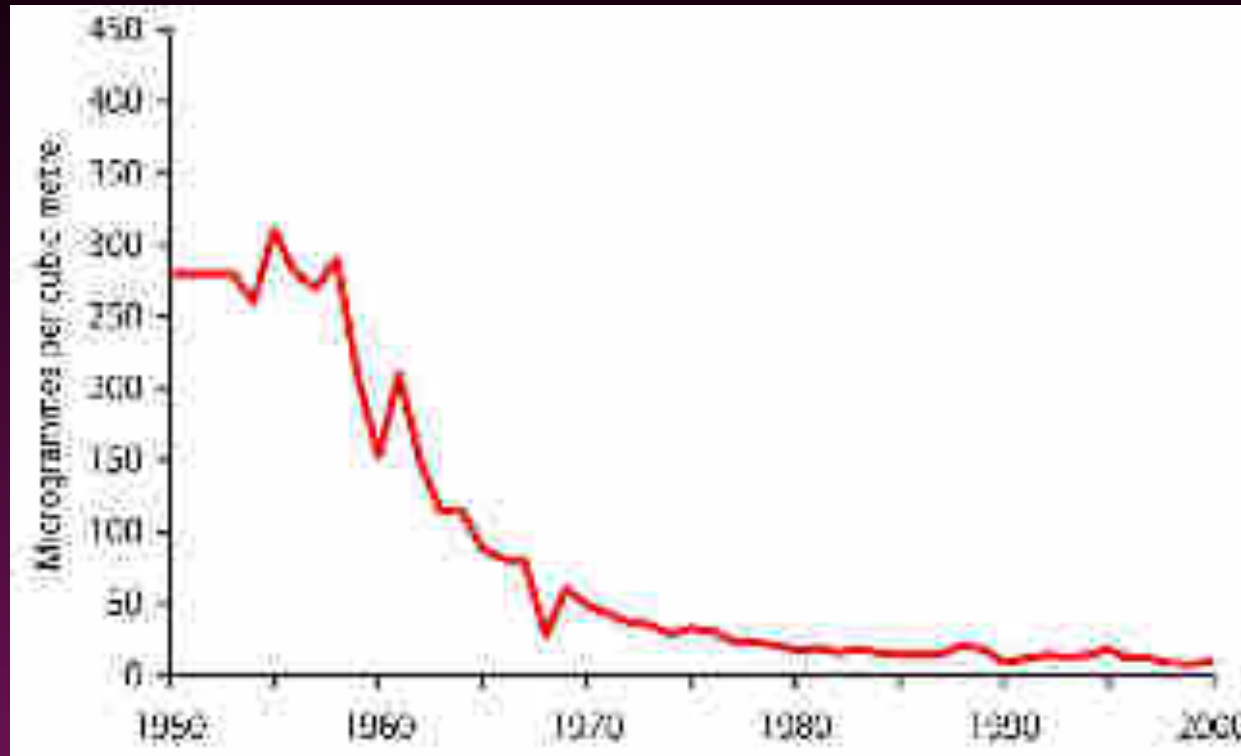
The smoke-blackened façade of the National Gallery,
London in c.1900

Patterns of particulate pollution



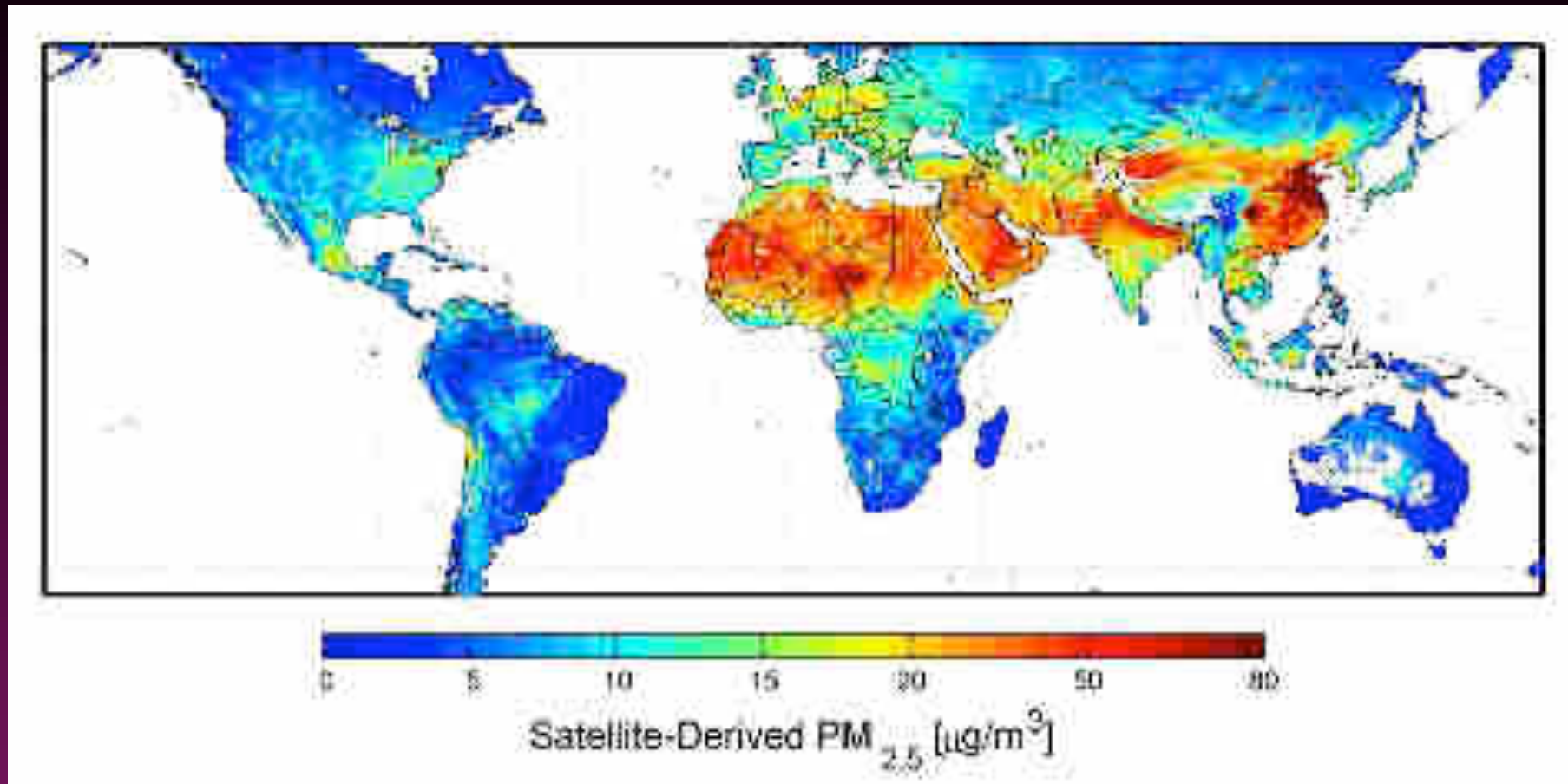
A particularly severe smog in London in 1952, which has been estimated to have caused 4000 additional deaths, was one of the factors leading to the passing of the 1956 Clean Air Act in the UK.

Patterns of particulate pollution



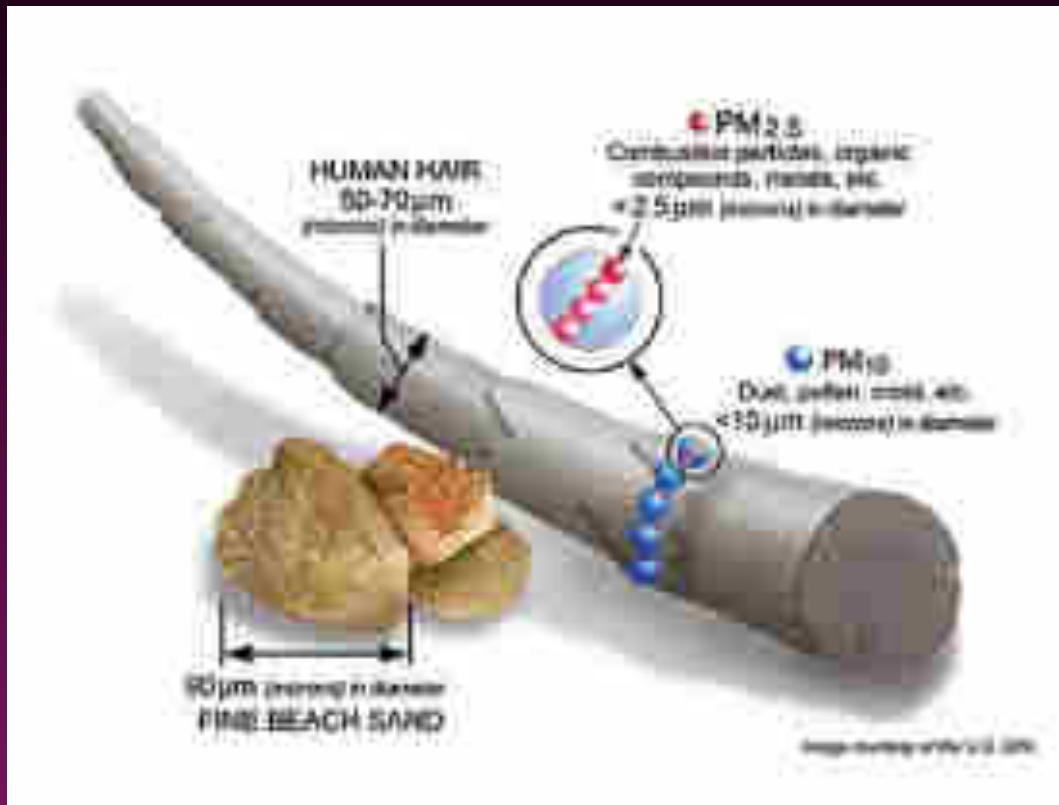
London smoke levels in the last half of the twentieth century

Patterns of particulate pollution



Levels of airborne small diameter particles derived from satellite data in 2001–2006

Patterns of particulate pollution



Definitions of PM₁₀ and PM_{2.5} derive largely from the health effect on the lungs of these particulates

Coarse dust particles (PM₁₀) are 2.5 to 10 micrometers in diameter. Sources include crushing or grinding operations and dust stirred up by vehicles on roads.

Fine particles (PM_{2.5}) are 2.5 micrometers in diameter or smaller, and can only be seen with an electron microscope. Fine particles are produced from all types of combustion, including motor vehicles, power plants, residential wood burning, forest fires, agricultural burning, and some industrial processes

Effects of particulate pollutants

Aesthetics

Dust can damage historic objects by altering their appearance, making them difficult to see and hiding historic information.

It can also give a place or object an appearance of being uncared for



Effects of particulate pollutants

Abrasion

Dust can interact with an object's surface, causing physical damage. Attempts to remove dust can cause damage by rubbing surfaces too hard, or cleaning away original materials



Effects of particulate pollutants

Ingraining

Where dust has been left in place a long time, it binds strongly to the surface of an object or infiltrates in to cracks and crevices, so that more complex and invasive cleaning techniques may be needed

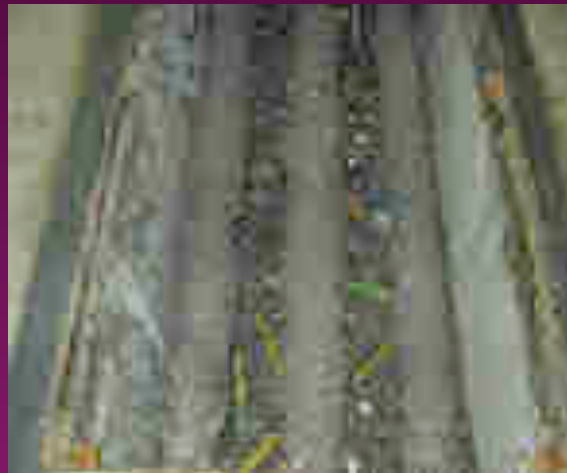
Effects of particulate pollutants



Attracting pests



As some components of dust are organic, they can act as a foodstuff for other organisms, potentially encouraging pests into the museum



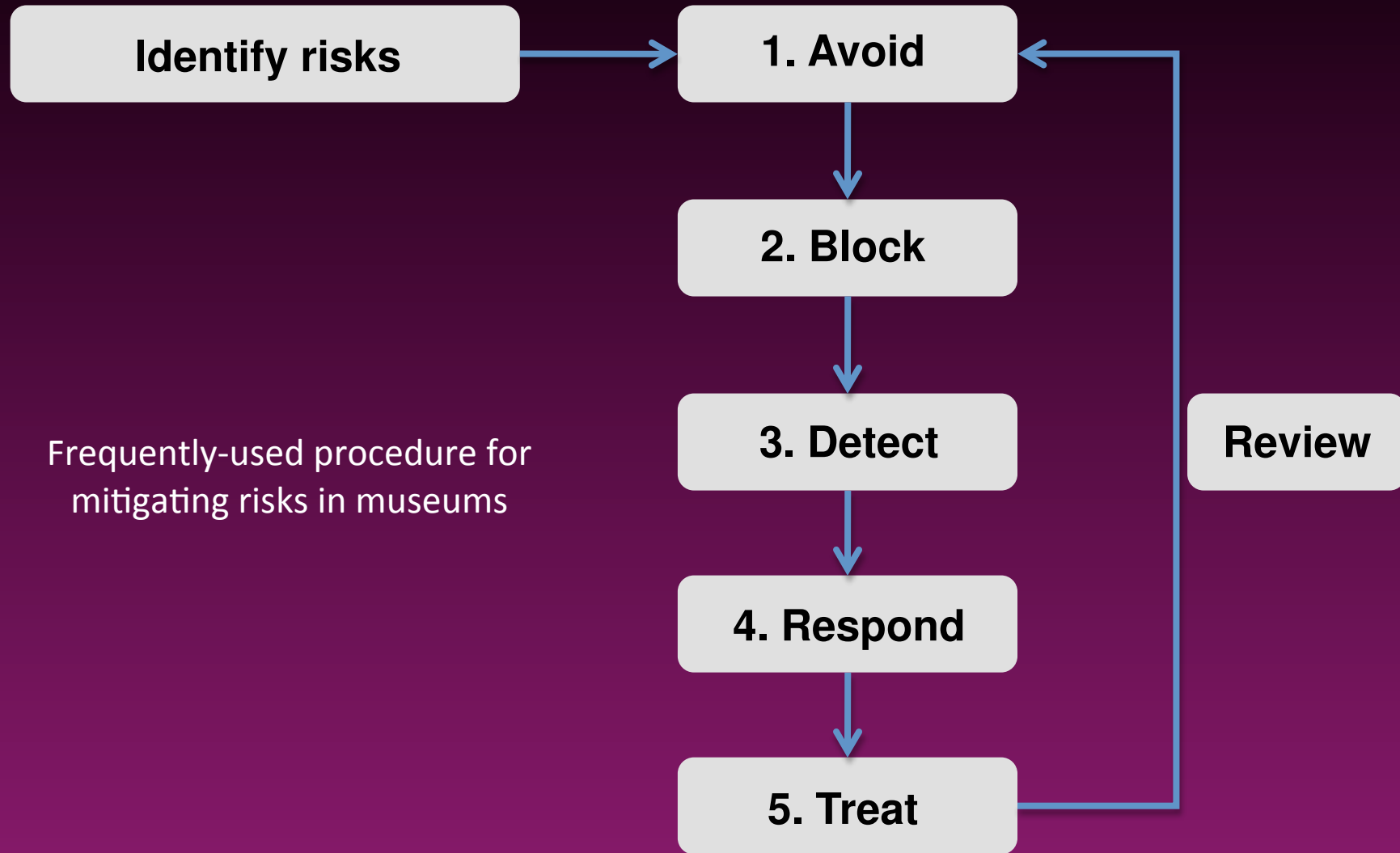
Effects of particulate pollutants

Chemical reactions

Particulates are not always chemically inert and may instigate reactions at surfaces on which they are deposited

Some particles contain metals, for example iron or lead, the latter primarily from lead additives to motor fuels, although its level has been much reduced by the introduction of unleaded petrol. Iron, however, is often present in particulate matter and has been implicated in the catalytic oxidation of sulphur dioxide (SO_2) to the potentially much more damaging sulphur trioxide (SO_3). When SO_2 or SO_3 dissolve in moisture in the air or water on the surface of the object they produce sulphurous or sulphuric acid respectively, which can be extremely deleterious.

Mitigating particulate pollutants



Frequently-used procedure for mitigating risks in museums

Mitigating particulate pollutants

Avoid

Move the museum to a less polluted area!

Fit and close doors and windows: use double doors or revolving doors with positive air pressure at entrances

Use dust mats (and sticky dust mats near building work)



Mitigating particulate pollutants

Avoid

Fit filters to air circulation equipment or within the air conditioning plant if used

Some control of larger particulates is possible by fitting screens to windows

But remember that these will all need to commitment to maintain and replace



Mitigating particulate pollutants

Block

As appropriate place objects in display cases and glaze two-dimensional works of art

Use well sealed drawers, boxes, crates or dust covers for objects in store or during closed periods in historic houses

But there are potential drawbacks to sealed boxes and cases – as will be seen later



Mitigating particulate pollutants

Block

Design routes to keep a distance between visitors and sensitive objects on open display – also avoids greasy hands on objects

Use droggets on floors to protect historic surfaces and trap dust



David Saunders



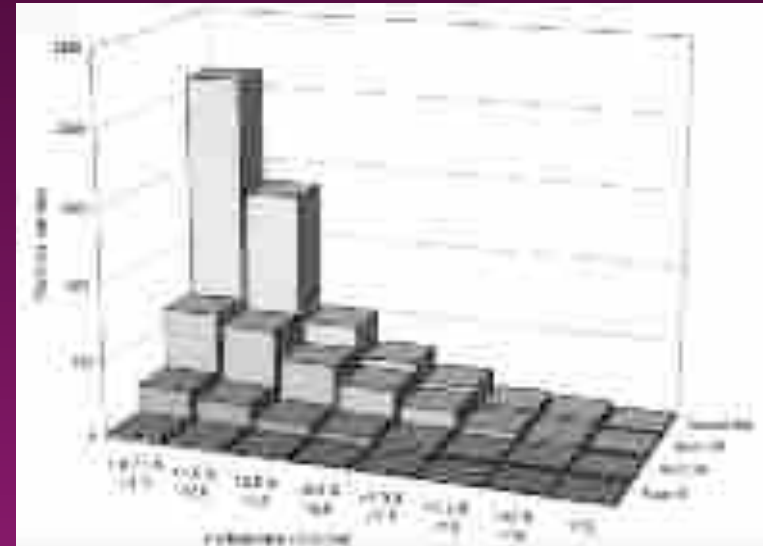
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Mitigating particulate pollutants

Detect

Entrained dust measurement – using meters mostly designed for occupational health. Indicates the distribution of particles sizes and the dust can be retrieved from the filter for analysis

Drawbacks are that these meters are expensive and indicate the level of dust in the air not that on objects



Mitigating particulate pollutants

Detect

Deposited dust assessment using 'sticky' slides and looking at loss of gloss – can also be used to place dust under a microscope to assess its content

Comparatively low cost and low technology



Group exercise

The now-derelict house and a collection of objects associated with an important historical local figure has been given to the museum by her family. The collection comprises limestone busts, furniture, books, letters, clothing and jewellery

Thinking only for the moment about particulate pollutants, what measures will you need to take to convert the room below into a suitable display space for this mixed collection?

Briefly, can you imagine how decisions you make to mitigate pollutants might affect the risks from other agents of deterioration



Outdoor chemical pollutants

Main gaseous pollutants

Reduced sulphur gases

Oxides of sulphur

Oxides of nitrogen

Ozone

Outdoor chemical pollutants

Reduced sulphur gases

Mainly hydrogen sulphide (H_2S) or carbonyl sulphide (COS)

Hydrogen sulphide was the principal contaminant in *miasmata* or organic emanations from people or animals, including those associated with poor public hygiene

Field's experiments during the first quarter of the nineteenth century involved exposing samples to 'foul air by suspending it beneath the seat of a privy'. He found that lead-containing pigments were blackened by this 'foul air'



Outdoor chemical pollutants

Reduced sulphur gases

The main current anthropogenic sources of hydrogen sulphide are the paper and petroleum industries. In the rural environment, hydrogen sulphide is emitted by oceans, volcanic and geothermal activities, marshes and vegetation



Effects of outdoor pollutants

Reduced sulphur gases

Some metals (notably silver), metal compounds and metal-containing pigments react with reduced sulphur gases to create black or dark-coloured sulphides. Lead-containing pigments are darkened by the formation of black lead sulphide.

(more on this in the section on indoor pollutants)



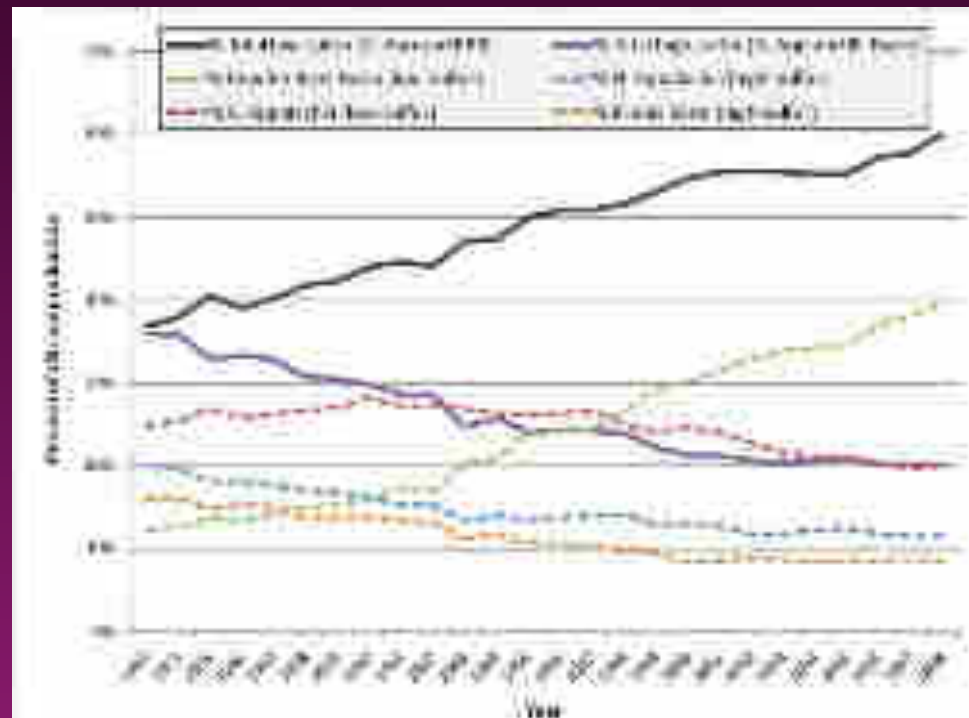
Veduta dell'interno del tempio d'Iside in Pompei...
George Hackert c. 1780–1800



Outdoor chemical pollutants

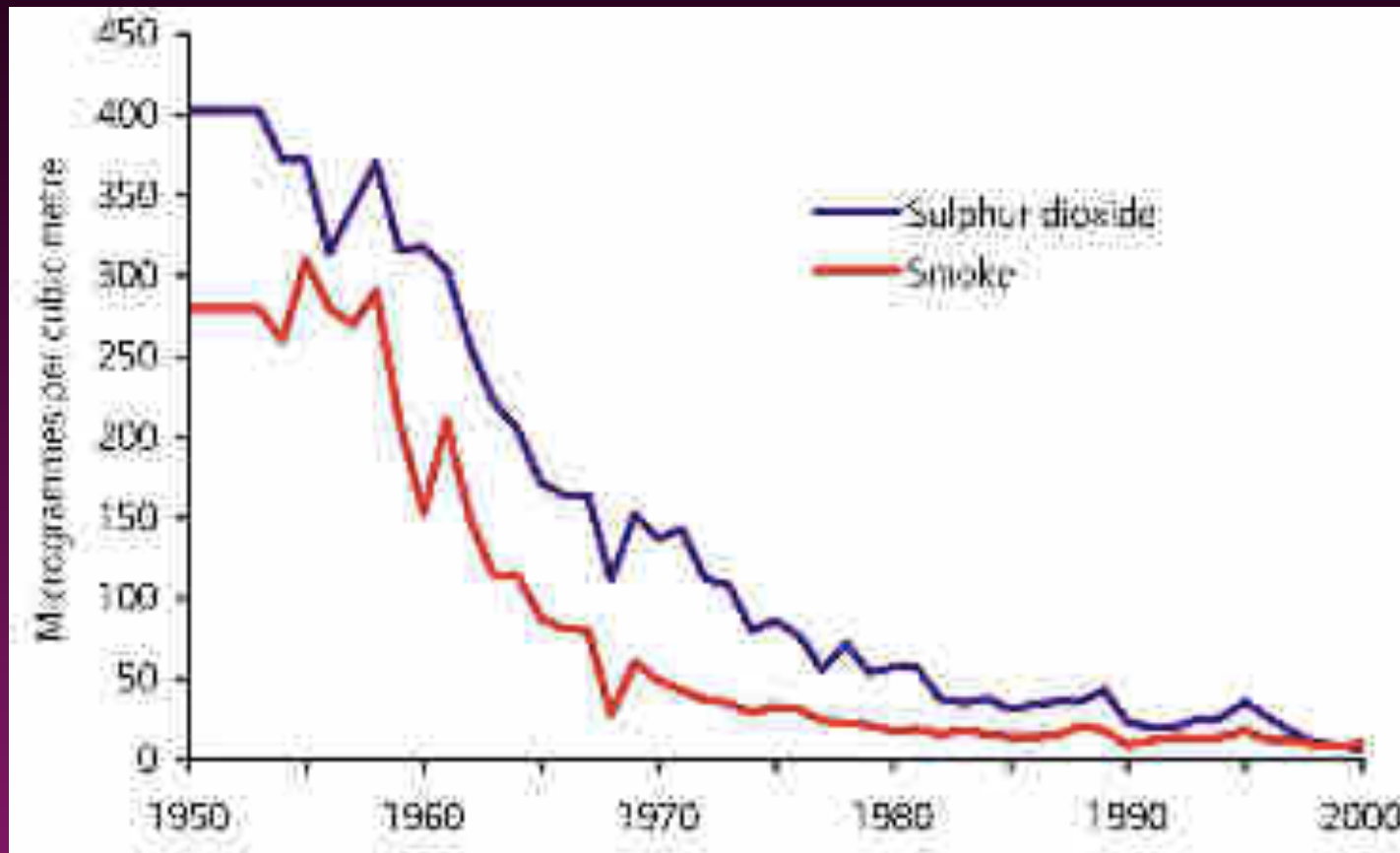
Oxides of sulphur

Principally sulphur dioxide (SO_2), the current and historic main source of which is the burning of sulphur-containing fossil fuels. Historically, the sulphur content of these fuels was much higher



Patterns of chemical pollutants

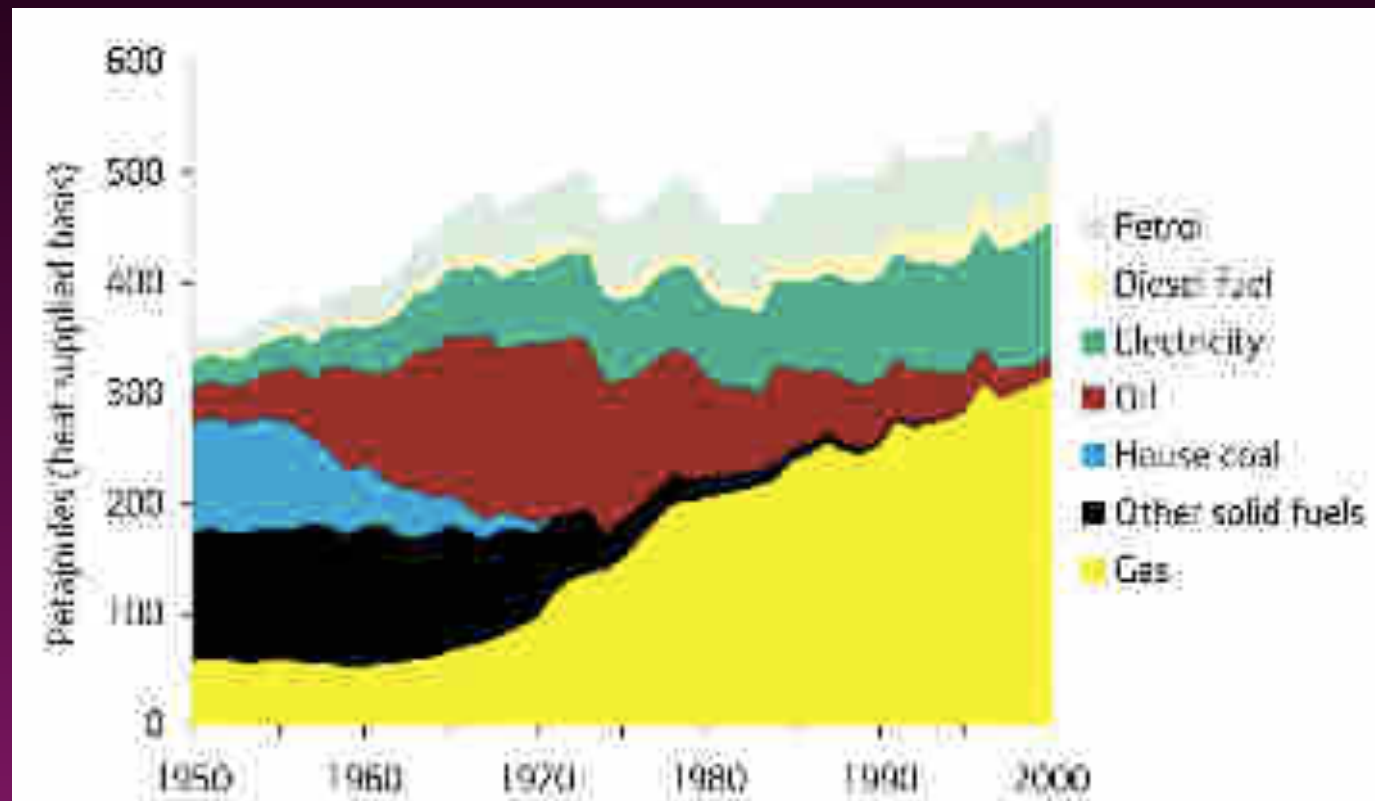
Oxides of sulphur



London smoke and sulphur dioxide levels in the last half of the twentieth century

Patterns of chemical pollutants

Oxides of sulphur



Changing patterns of fuel use in London in the last half of the twentieth century

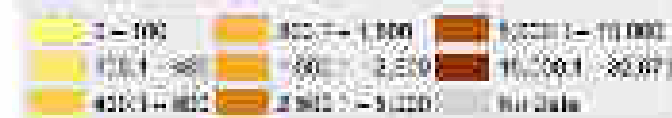
Total SO₂ Emissions, 1970: National and Regional Data Set by Source Category, Version 2.86

Historical Anthropogenic Sulfur Dioxide Emissions



The data shown in this total SO₂ emissions map are derived from the 1970
 National Inventory of Air Quality (NIAQ) for the United States, the National
 Inventory of Air Quality (NIAQ) for the United Kingdom, the National Inventory
 of Air Quality (NIAQ) for the Netherlands, and the National Inventory of Air
 Quality (NIAQ) for the Federal Republic of Germany.

Total SO₂ Emissions (Kilograms)



Global Emissions of Air
 Quality Information Network
 (GEAIN)



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Total SO₂ Emissions, 2005: National and Regional Data Set by Source Category, Version 2.86

Historical Anthropogenic Sulfur Dioxide Emissions



This map shows the total SO₂ emissions by country for 2005. The data is based on the Global Anthropogenic Sulfur Dioxide Emissions Database (GASD) for the year 2005. The map is based on the data from the Global Anthropogenic Sulfur Dioxide Emissions Database (GASD) for the year 2005.

Total SO₂ Emissions (kilotonnes)



Global Anthropogenic Sulfur Dioxide Emissions Database (GASD) for the year 2005. The map is based on the data from the Global Anthropogenic Sulfur Dioxide Emissions Database (GASD) for the year 2005.



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Effects of outdoor pollutants

Oxides of sulphur



In the 1850s, Michael Faraday described the effect sulphurous acid (produced by combination of the sulphur dioxide and water generated during the combustion of coal) had on a 'copper apparatus' at the Athenaeum club-house, producing a 'large body of sulphate of copper'.

He also called attention to the deterioration of leather armchairs caused by acid gases

Effects of outdoor pollutants

Oxides of sulphur



The damage from sulphur dioxide or sulphur trioxide is most severe if moisture is present to dissolve these gases to form sulphurous or sulphuric acids

Calcium carbonate is converted to calcium sulphate by prolonged exposure to acidic conditions, affecting limestone sculptures and wall paintings in fresco

Conversion of the chalk (calcium carbonate) to calcium sulphate causes a change in volume, which can cause surface disruptions ranging from the appearance of small 'pustules' on the surface to severe delamination

The crust of calcium sulphate formed on damaged limestone buildings is often black, as its formation can be accompanied by smoke deposition

Effects of outdoor pollutants

Oxides of sulphur

In addition to leather, observed by Faraday, other organic materials such as wood, cotton, wool and silk are attacked by the acids formed from SO_2

Acid-catalysed hydrolysis of cellulose- or protein-based textiles is responsible for weakening fabrics, which yellow and embrittle

A few acid-sensitive pigments, e.g. ultramarine, are affected by dissolved SO_2



Outdoor chemical pollutants

Oxides of nitrogen

Although oxides of nitrogen are present in the air from natural sources, levels have increased in urban areas during the twentieth century, due to high-temperature combustion processes that oxidize atmospheric nitrogen to nitric oxide (NO) or nitrogen dioxide (NO₂)

Of the oxides of nitrogen, nitrogen dioxide is of most concern to the conservator; it can dissolve in water to form nitrous acid, which, on aerial oxidation, yields nitric acid, a strong acid and oxidant

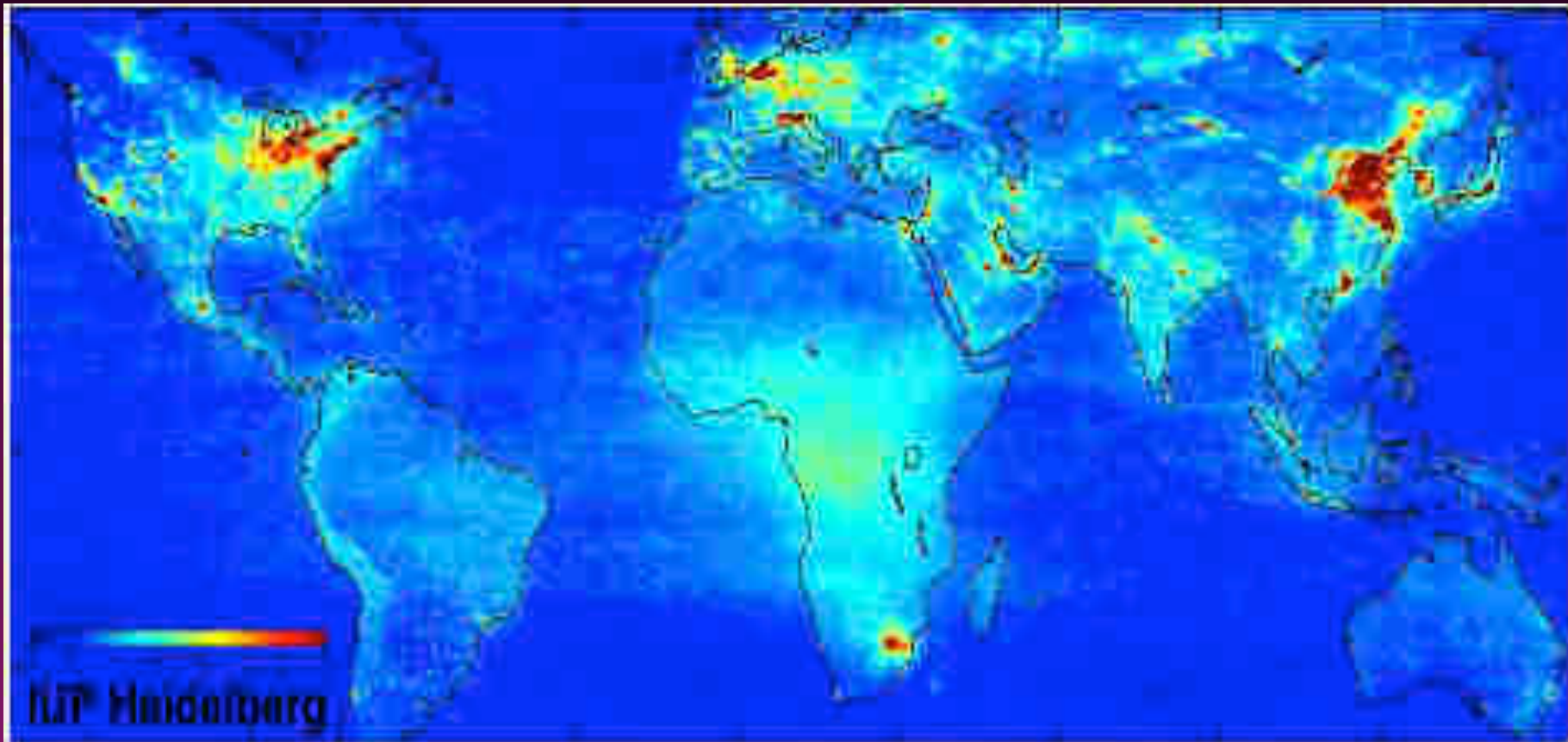
The behaviour of nitrogen oxides demonstrates the two main dangers from pollutant gases

Acidic degradation

Oxidative degradation

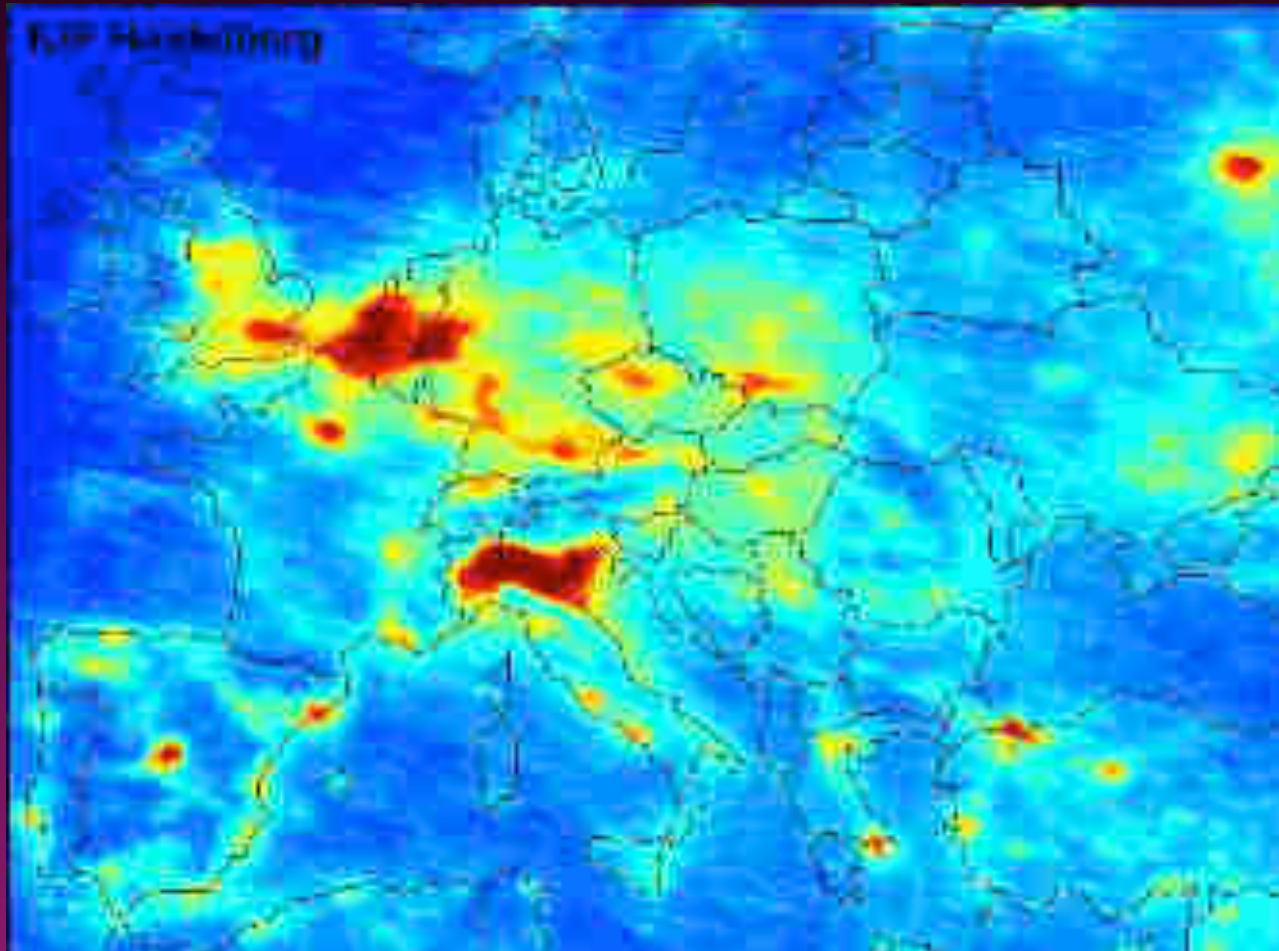
Patterns of chemical pollutants

Oxides of nitrogen



Patterns of chemical pollutants

Oxides of nitrogen



Outdoor chemical pollutants



Smog over Mexico City

Effects of outdoor pollutants

Oxides of nitrogen

As nitric acid is of a comparable strength to sulphuric acid, it might be expected to corrode metals, attack calcareous stone and damage textiles in the same manner, were it not for its volatility, which reduces its effect

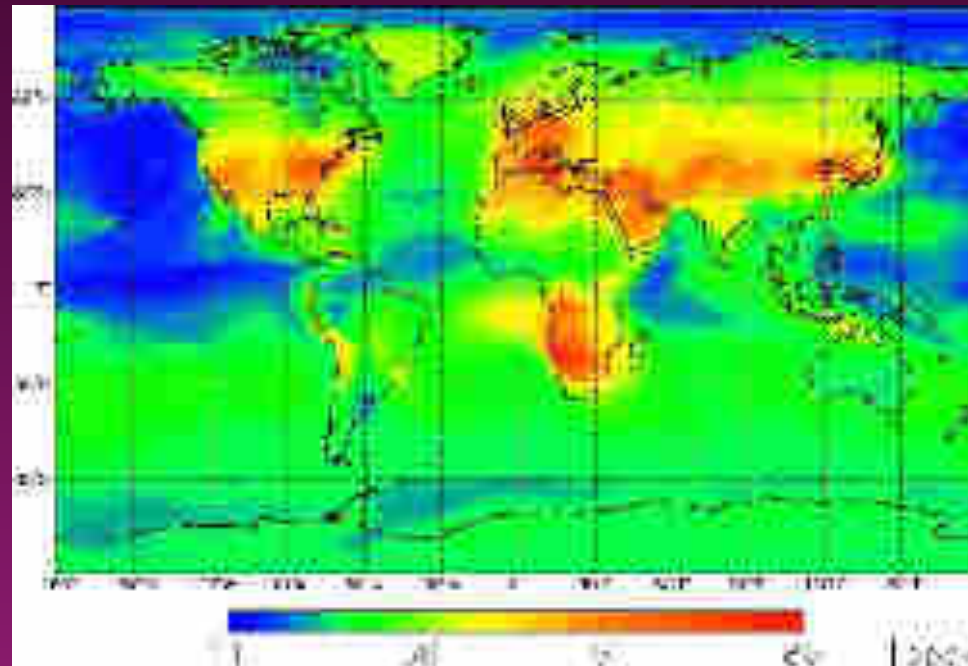
There is little specific evidence to relate the presence of NO_2 to damage, as it is usually present alongside other potentially damaging gaseous pollutants, such as SO_2

Nitrogen dioxide has, however, been shown to affect iron gall inks, some synthetic dyestuffs, the arsenic sulphide pigments orpiment and realgar, and a few traditional organic colorants, both on silk and paper

Patterns of chemical pollutants

Ozone

Ozone is a strong oxidant formed naturally in the atmosphere and by anthropogenic activity. It is highly reactive and often reacts or is adsorbed before reaching objects



Effects of chemical pollutants

Ozone

Oxidants have been implicated in the embrittlement and cracking of textiles, rubber and plastics, the fading of pigments and dyestuffs and the oxidation of some fossil and mineral specimens

As ozone is so reactive that it is often adsorbed by the surfaces within buildings so that generally very low levels have been recorded (although this may unfortunately mean that it has already reacted with objects)

Effects of outdoor pollutants

Pollutant-object interactions on open display or storage			
Object	Pollutant	Damage	References
Paper and papyrus (cellulose)	sulphur dioxide, nitrogen dioxide, ozone	increased brittleness, yellowing, friability due to weakened structure	Baer 1985, Johansson 2000, Menart 2011
Textiles	nitrous oxides	reduced tensile strength	Baer 1985
Textile dyes	ozone, nitrogen dioxide	Fading of dyes and pigments	Thompson 1986, Grosjean 1988
Rubber	ozone	reduced flexibility and cracking	Grosjean 1988
Colour photographs, natural organic colourants on paper	ozone, nitrogen dioxide	fading	Bard 1980, Fenech 2010, Whitmore 1987, 1988, 1989, Grosjean 1993, Salmon 1993
Pigments	ozone	fading	Cass 1991
Stone	sulphur dioxide	mechanical damage due hydrated sulphonated salts	Braun and Wilson (1970). Hoke (1978), Wiczorek-Ciurowa (1988)
Leather	sulphur dioxide	crumbling	Spedding 1971, Tétreault 2003

After PAS 198:2012

Mitigating outdoor pollutants

While the levels of gases present in the atmosphere outside a building are generally out of the control of heritage professionals, pollution control for health reasons has driven down levels in many urban centres

For example, since 1993 all new cars sold within the European Union have been fitted with catalytic converters that ensure efficient (up to 90%) conversion of carbon monoxide and hydrocarbons to carbon dioxide and water and the reduction nitrogen oxides to nitrogen.

Mitigating outdoor pollutants

The general levels within museums can only be limited if air ingress is very tightly controlled

Sealing a building is difficult, expensive and may have other unforeseen consequences – e.g. on the moisture levels in the fabric and interior

The pollutants mentioned here can be reduced by fitting chemical – e.g. activated carbon – filters to the air circulating or air conditioning systems, but these require costly monitoring and upkeep



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Mitigating outdoor pollutants

Local control of levels of gases can be achieved by using display cases that have filtered air supplies and a positive air pressure

Scavenger materials can be used locally to react with acidic gases

Again, sealing objects in enclosures – in this instance they need to be very well sealed if they are to keep out gases – can have other effects

(These issues are dealt with more fully in the context of indoor pollutants)

In the nineteenth century, walls were painted with distemper containing lead white and paintings were backed with lead white primed canvases to absorb SO₂

Mitigating outdoor pollutants

Detect

Meters are available to measure the levels of most common pollutants, but these can be expensive – particularly if not used regularly

Sampler and diffusion tubes are available to monitor common outdoor and indoor pollutants – some are self indicating but others need to be sent away for analysis

Need to check the level of sensitivity is appropriate



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Indoor chemical pollutants

Main gaseous pollutants

Reduced sulphur gases

Oxides of sulphur

Oxides of nitrogen

Ozone

Acetic acid

Formic acid

Formaldehyde

Acetaldehyde

Ammonia and amines

Other volatile organics

Indoor chemical pollutants

Indoor sources: wood

Each sugar unit in the hemicellulose component of wood contains mildly basic hydroxyl groups, a number of which are acetylated in the form of ester groupings that can easily be hydrolyzed to produce **acetic acid**

Hardwoods contain 4–6 % of hemicellulose by weight of wood
Softwoods contain 1–2 % of hemicellulose by weight of wood



Formic acid is also released by wood, although to a lesser extent

Indoor chemical pollutants

Indoor sources: wood

Wood	Type	Acetic acid / mg m ⁻³	Formic acid / mg m ⁻³
Afromosia	Hardwood	2480 ± 175	162 ± 16
Oak	Hardwood	1740 ± 15	60 ± 10
Obechie	Hardwood	1570 ± 58	168 ± 23
Beech	Hardwood	1500 ± 27	133 ± 17
Mahogany	Hardwood	1250 ± 102	171 ± 19
Cherry	Hardwood	952 ± 48	46 ± 28
Ash	Hardwood	883 ± 37	161 ± 49
Teak	Hardwood	509 ± 58	89 ± 17
Birch	Hardwood/Softwood	698 ± 38	116 ± 3
Larch	Softwood	1890 ± 297	101 ± 18
Red Pine	Softwood	1460 ± 26	18 ± 6
Oregon Pine	Softwood	495 ± 32	153 ± 65
White Pine	Softwood	447 ± 90	68 ± 12
Yew	Softwood	132 ± 139	187 ± 66

Gibson and Watt, *Corrosion Science* (2010).

Indoor chemical pollutants

Indoor sources: wood substitutes

(Plywood, particle board and fibreboard: MDF)

Synthetic boards contain urea–formaldehyde resin binders, with up to 0.04 % free formaldehyde in the wood which can be released rapidly

Bound formaldehyde is also present, which can be released in the long term through the hydrolysis of various bonds within the components

Reducing the free formaldehyde content will decrease the immediate release but not the long term effect, as the resin binders contain methylol groups (up to 17–20%) which are a source formaldehyde



Indoor chemical pollutants

Indoor sources: paint

A principal source of formic acid due to the oils/additives added to the pigments (e.g. turpentine)

Immediately after application a complex mixture of organic acids and aldehydes is released from paints with drying oils. After a few days the main emissive vapour is formic acid, which can continue to be released for up to 15 months

Paints formed by oxidative polymerization (oil-based, alkyd and oil-modified urethanes) release formaldehyde and peroxides during curing



Solvents from acrylic and nitrocellulose based paints also emit corrosive vapours

Indoor chemical pollutants

Indoor sources: resins

Polyvinyl acetate (PVA: wood glue) emits acetic acid and is more corrosive than acrylic adhesives. The volatiles produced include acetaldehyde in addition to acetic acid

A high concentration of pollutants is produced immediately after application, as these are emitted during the curing process



Indoor chemical pollutants

Indoor sources: proteinaceous material

Proteinaceous materials containing the amino acid cysteine, notably including wool and silk, emit reduced sulphide gases due to the hydrolysis of the cysteine, particularly when damp or wet

Visitors are another potential source, with some research indicating that a person may release approximately 100 mg per hour



Most research focuses on hydrogen sulphide, but some researchers believe the most damaging form is dimethyl- or carbonyl sulphide – hence the use of the general term ‘reduced sulphur gases’

Indoor chemical pollutants

Indoor sources: objects (Cellulose acetate)

Cellulose acetate objects can suffer from a phenomenon commonly referred to as 'vinegar syndrome', which is the release of acetic acid vapour from the polymer by acid hydrolysis of side-chain acetyl groups. The acetyl groups then react with water to form acetic acid



The smell of vinegar (acetic acid) often alerts conservators to the onset of decay as most human noses have a very high sensitivity to acetic acid

Indoor chemical pollutants

Indoor sources: objects (Cellulose nitrate)

Cellulose nitrates were among the first plastics invented. However they easily degrade, producing large quantities of nitrous oxide vapours, which in turn can hydrolyse to produce nitric acid



The type of collections most at risk are probably archival film materials

Indoor chemical pollutants

Sources of internally generated pollutants

Source	Pollutant	References
Acrylic and nitrocellulose paints	acetic acid (ethanoic acid), solvents	<i>Donovan and Moynehan (1965), Tétreault (1992)</i>
Cellulose acetate items, cellulose triacetate film	acetic acid (ethanoic acid)	<i>Allen et al. (1987), Allen et al. (1990), Aubier (1996), Edge (1992), Edwards, H.G. et al. (1993), Quye (1998), Ram (1994)</i>
Cellulose nitrate items and photographs	camphor, formaldehyde (methanal), nitrous oxides	<i>Edge (1990), Jutier et al. (1987), Miles (1955), Phillips et al. (1955), Wolfrom et al. (1955), Yarsley et al. (1964)</i>
Plastics, rubber	acid vapours	<i>Knotková-Čermáková and Vlčková (1971)</i>
Polyisoprene rubber (carpet backing), vulcanised rubber, wool and certain sulfide minerals	reduced sulphur gases	<i>Brimblecombe et al (1992), Donovan and Stringer (1971), Sease et al. (1997), Waller (1999b)</i>

Indoor chemical pollutants

Sources of internally generated pollutants (continued)

Source	Pollutant	References
Poly(vinyl chloride)	hydrochloric acid	<i>Kelen (1983)</i>
Resins / coatings	acetic acid (ethanoic acid), formic acid (methanoic acid), solvents	<i>Tétreault (1992), Tétreault and Stamatopoulou (1997)</i>
Wood	acetic acid (ethanoic acid), formic acid (methanoic acid)	<i>Arni et al. (1965), Budd (1965), Clarke and Longhurst (1961), Donovan and Moynehan (1965), Donovan and Stringer (1971), Farmer (1967), Gibson and Watt (2010), Grzywacz and Stulik (1993), Knotková-Čermáková and Vičková (1971)</i>
Wood-based panels (sealed with urea-formaldehyde or phenol-formaldehyde resins)	formaldehyde (methanal)	<i>Andersen (1975), Grzeskowiak et al. (1988), Lehmann (1987), Matthews et al. (1986), Meyer et al. (1985), Myers (1984), Myers and Nagaoka (1981)</i>

Effects of indoor pollutants

Acetic acid

The Dutch process for making lead white pigment – which effectively encourages the corrosion of lead by acetic acid – has been known since antiquity

In 1787 the corrosion of lead close to oak beams in church roofs was noted and a report of 1874 documented the corrosion of lead and zinc by vapours from oil of turpentine

In 1928 lead-covered telephone cables next to yellow pine were found to corrode, indicating that woods other than oak could cause damage



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Effects of indoor pollutants

Acetic acid

Lead objects are among the most sensitive to the presence of acetic acid vapour

Under certain conditions corrosion will be observed in just a few days and the lead is irreversibly converted from the metal to basic lead carbonate and/or lead formate



Effects of indoor pollutants

Acetic acid

In 1899 George St Loftus Byne attributed the salt formation on shell specimens to a reaction of the surface with an organic acid (although he thought the acid derived from the dead mollusc)

A Babylonian baked clay tablet at the Semetic Museum at Harvard University that had previously been in good condition exhibited a white efflorescent salt in 1913 after it was placed in a cherrywood case



Byne, *Conchology* (1899)

Effects of indoor pollutants

Acetic acid

Modern instrumentation allowed the crystals responsible for so-called Byne's disease to be identified as a combination of calcium acetates and calcium acetate formate, produced by the action of acetic and formic acids on the calcium carbonate of the shell



Tennent and Baird, *Studies in Conservation* (1985)

Effects of indoor pollutants

Acetic acid

In objects that contain chlorine – particularly archeological objects that have been buried in saline or marine environments – calclacite (calcium acetate chloride pentahydrate) crystals form on the surface on exposure to acetic acid



van Tassel, *Acta Crystallographia* (1958)

Effects of indoor pollutants

Acetic acid

An example of an even more complex process is so-called efflorescence X

It was found on different objects including ceramics in 1971 and was reported to contain calcium, acetate and chloride – in other words to be similar to calclacite

(it was at first thought to be calclacite, which is very widespread)



FitzHugh and Gettens, in *Science and Archaeology* (1971)

Effects of indoor pollutants

Acetic acid

Efflorescence X was shown to be a more complex salt, to containing calcium, acetate, chloride and nitrate: $\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl}(\text{NO}_3) \cdot 6\text{H}_2\text{O}$. The salt was christened thecotrichite and has subsequently been found as a common efflorescence on objects that also contain nitrates (presumed to derive from the burial environment or from conservation treatments)



The different acetate and formate salts produced by the action of acetic and formic acids on objects are often difficult to distinguish, even using modern instrumentation

Gibson, *et.al.*, *Analytica Chimica Acta* (1997)

Effects of indoor pollutants

Objects: cellulose acetate

Cellulose acetate hydrolyzes over time to releases acetic acid. This acetic acid induces further acid hydrolysis of the polymer chain (chain scission) reducing the chain length (depolymerisation) in a catalytic destructive cycle

Eventually, this cycle leads to structural collapse



Spiral Theme Naum Gabo, Tate

	Acetic acid mg m ⁻³	Formic acid mg m ⁻³
Sculpture in case	7583	n/a
Sculpture in cupboard	148	230
Sculpture in charcoal-lined container	193	12

Gibson (2015).

Effects of indoor pollutants

Objects: cellulose nitrate



Acidic-autocatalytic depolymerisation of cellulose nitrate leads to loss of structural integrity and complete collapse of objects

The tissue paper around the puppet shown here had discoloured and become fragile, alerting conservators to a potential problem. On examination the legs of the puppet had completely – and irreparably – fragmented

The degradation of cellulose nitrate film has led to explosions in film archives, which is why many are now housed in bunkers and stores outside towns and cities

Effects of indoor pollutants

Objects: paper

Paper decays over time where the principle degradation process occurring is the decomposition of cellulose, in particular, reactions occurring at the hydroxyl groups and the glycosidic links.

This degradation takes place via two mechanisms, oxidation and acid hydrolysis.



Effects of indoor pollutants

Objects: composite objects

Offgassing from one component – in this case the cellulose nitrate beads – can damage other materials, tarnishing the silver alloy components in this necklace



Effects of indoor pollutants

Synergic effects: moisture and heat

Thecotrichite (and other associated salts) will not precipitate when the relative humidity (RH) is low (< 20–30 %) regardless of the acid concentration in the environment

Metal corrosion rates are also retarded at < 20 % RH

Most deterioration processes will be reduced by lowering the RH and/or temperature, but these measures may induce internal stresses in objects

For a mixed collection containing objects that are moisture sensitive it may not be feasible to apply such low RH and temperatures and there are practical difficulties in maintaining these conditions

Effects of indoor pollutants

Pollutant-object interactions in enclosures			
Object	Pollutant	Damage	References
Historic soda silicate glass	formic acid (methanoic acid) / formaldehyde (methanal)	white salt formation formed on surface weakens structure of glass	Knockart 1978, Robinet 2004, Robinet 2007
Limestone, ceramics, fossils, pottery	acetic acid (ethanoic acid)	salts form on the surface of item leading to severe pitting and disruption of glazes	Van Tassel 1958, Fitzhugh 1971, Wheeler 1993, Gibson 1997, Gibson 2005, Linnow 2007
Shells, Eggs	acetic acid (ethanoic acid), formic acid (methanoic acid)	white salts form on the surface of item leading to pitting	Byne 1899, Nicholls 1934, Agnew 1981, Tennent 1985
Copper	acetic acid (ethanoic acid)	transformation of copper metal to green copper-based salts	Lopez-Delgado 1998 Thickett 2000

Effects of indoor pollutants

Pollutant-object interactions in enclosures (continued)

Object	Pollutant	Damage	References
Lead	acetic acid (ethanoic acid), formic acid (methanoic acid), formaldehyde (methanal)	transformation of lead metal to white salts. Severe pitting and/or complete destruction of small items such as coins/tokens	Coles 1957, Fitzhugh 1971, Hatchfield 1986, Tennent 1993, Edwards 1997, Tétreault 1998, Allan 2000, Raychaudhuri 2000, Clarke 1961, Donovan 1965, Donovan 1971, Knotkova-Cermakova 1971, Streigel 2000, Thickett 1997
Silver	reduced sulphide gases	transformation of silver metal to silver sulphide causing pitting, tarnishing and blackening of metal surface	Oddy 1973, Daniels 1979, Franey 1985, Brimblecombe 1992, Sease 1997, Pope 1968

Effects of indoor pollutants

Pollutant-object interactions in enclosures (continued)

Object	Pollutant	Damage	References
Zinc	hydrogen sulphide and nitrogen dioxide	Transformation of zinc to salts causing pitting	Svensson 1996, Clarke 1961, Donovan 1965, Donovan 1971
Lead based pigments	hydrogen sulphide	formation of black spots	Wohlers 1966
Paper (cellulose)	acetic acid (ethanoic acid), volatile organic compounds (VOCs)	increased brittleness, friability due to weakened structure	Strlic 2011

Mitigating indoor pollutants

Avoid

Consider whether an enclosed environment for storage or display is the best solution for objects or groups of objects and what the threshold values for pollutants should be

Identify those materials in the collection that are liable to be sensitive to deterioration by particular pollutants and group according to these criteria (this may not be possible as a priority may be to group in response to another – greater – risk)

Consider ventilating enclosures periodically to release a build up of gases (assuming that this does not adversely affect the objects in other ways such as letting in dust and changing the humidity level)

Mitigating indoor pollutants

Summary of published monitoring

Pollutant	Location	Concentration / mg m^{-3}
Acetic acid	Outdoor concentrations	0.3–30
	Rooms	40–100
	Wooden storage or display cabinets	80–3200
	Degrading cellulose acetate collections	900–100000
Formic acid	Outdoor concentrations	0.1–20
	Rooms	0.1–30
	Wooden storage or display cabinets	2–2000

Gibson (2015).

“The materials used to construct the enclosures, as well as the items themselves, shall be evaluated to ensure they do not emit gaseous pollutants to an extent that would be expected to cause unacceptable and irreversible change in the contents” PAS 198-2012

Mitigating indoor pollutants

Avoid

Most common route for museums is to establish a database of 'safe' materials that can be used in enclosed storage or display environments using a material testing method such as the so-called Oddy test

Certain materials should be avoided – for example those containing sulphur – and all other woods, wood products, paints, adhesives, silicones, rubber and dyed fabrics should be tested

Even after testing it is good practice to allow three to four weeks between applying paints, adhesives, etc. and placing objects inside airtight enclosures to allow them to cure and offgas (clearly schedules do not always contain this period)



Mitigating indoor pollutants

Material testing

An internationally used method is the so-called Oddy test

It assesses the affect of materials on three metal coupons (lead, silver and copper) during an accelerated ageing test in moist conditions at 60°C for one month

Visual assessment and comparison with other test results are used to classify materials into one of three categories

Unsuitable

Suitable for temporary (short term) use

Suitable for permanent (long term) use



Mitigating indoor pollutants

Oddy testing: method



Mitigating indoor pollutants

Oddy testing: method



Mitigating indoor pollutants

Oddy testing: issues

Test set-up



Mitigating indoor pollutants

Oddy testing: issues

Assessing deterioration



Mitigating indoor pollutants

Oddy testing: issues

Lack of parallel between the test situation and installation in the enclosure – e.g. different paint application methods and curing times or different batches of fabric

Materials that do not react with the metal coupons but which might cause damage – e.g. certain paint solvents

Mitigating indoor pollutants

Block: wrappings and coatings

If materials that produce indoor pollutants must be used they can sometimes be rendered less damaging by sealing them

Barrier foils (e.g. Moistop) can be applied over wood or wood-based materials to prevent their vapours reaching the objects. Alternatively liquid coatings can be applied, although care needs to be taken that these coatings do not themselves constitute a source of damage

Coatings have also been applied to objects to protect them, e.g. the practice of lacquering metals, but care is needed to ensure the coating is not damaging and that it can be removed later without adverse effect

Mitigating indoor pollutants

Block: sorbents

A wide range of solid sorbents have been used in display environments; their performance depends on the type of pollutant to be reduced

The sorbents either adsorb the gaseous molecules by physical adsorption – the gas molecules become trapped in the pores of the sorbent – or they react with pollutant to form benign or non-volatile material; the latter are sometimes called scavengers or sacrificial materials

In either case the pollutant is removed from the air



Most sorbents can become saturated over time and need to be monitored and replaced. If neglected, the absorbed gases can sometimes be released by a change in temperature creating a very hazardous atmosphere for objects

Mitigating indoor pollutants

Block: sorbents

In storage, materials can be introduced into a sealed or semi-sealed environments that preferentially absorb or react with pollutants

Particularly in storage, sorbent boxes or papers (e.g. Solander boxes and acid free or Microchamber paper) can be used to surround objects

Other alternatives include films or bags that selectively react with certain pollutants – e.g. the Intercept bags designed to reduce silver and other tarnish



David Saunders



IIC- ITCC September 2015

Mitigating indoor pollutants

Block: sorbents

In some cases the sorbent can be used as part of an air recirculating system – e.g. silver pumps used in showcases at British Museum



Materials testing

Block: sorbents

Sorbent type	Acetic acid	Reduced sulphur gases	Formaldehyde
Activated carbon (KCO ₃ or (KOH)	good	good	poor
Activated charcoal cloth	good	poor	medium
Activated alumina	good	very good	medium
Molecular sieves	medium	medium	poor
Zinc oxide catalyst		very good	

Mitigating indoor pollutants

Detect

As with outdoor pollutants, meters, air samplers and passive diffusion tubes are available – with same advantages and drawbacks but the addition challenge of use in a sealed environment

Coupons – which might be sacrificial materials themselves – are sometimes used to give a visual indication of the atmosphere in an enclosure



Coupons of lead, copper and silver are commonly used to screen for organic acids and aldehydes, chloride vapours and reduced sulfide gases, respectively

Group exercise

Your museum is lending a collection of coins – struck from various metals – and ceramic vessels used in the meting of these metals during coin making. All were recovered from an archaeological context

You have been asked to write a brief specification of the show case in which these will be displayed while at the borrowing museum

What will be your concerns in terms of gaseous pollutants and what will you therefore include in the specification?

During the loan it is decided that the collection will be shown at a second museum in the same country three months later. The objects will be packed and stored locally before being transported to the second city.

How will this affect the scope of your specification?

Acknowledgements

Dr Lorraine Gibson
Department of Pure and Applied Chemistry
University of Strathclyde

Colleagues at the British Museum and National Gallery, London
Particularly

Dr Capucine Korenberg
Julie Phippard