An Integrated Approach to Reducing Concentrations of Indoor-Generated Pollutants

by

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ABSTRACT

Air quality within museums and historical houses, at any one time, represents the sum total of all pollutants coming in from the outside environment plus all pollutants generated within, minus the sum of all processes which extract both. Therefore, indoor air quality is a dynamic process that varies not only by hourly, daily, weekly, and seasonal patterns but also as a function of facilities usage, exhibition schedules and maintenance. It is this ever changing character which makes estimation of air quality, particularly difficult to determine, and has coined the concept of the "building ecology" approach to indoor air quality.

For pollutants generated indoors, there are two broad classes of mitigation strategies - *chemical approaches* - which eliminate reactive species by adsorption, absorption, or chemical transformations, and *mechanical approaches* - which dilutes the concentrations of reactive gases or act as barriers that slow down their release rates. Since mechanical approaches are relatively simple to understand and easy to implement, they should be readily integrated into any abatement plan.

Introduction

In theory and practice, it is possible to built a display case or storage cabinet that is made of inert materials, is self-cleaning, buffers its internal relative humidity and provides some protection against photochemically-induced deterioration (Preusser, 1989). But in reality, there are probably thousands of microenvironments just in the United States alone that were built before these requirements were thought necessary or desirable. It was seldom imagined, for example, that some metals, shells, minerals and ceramics could be quickly corroded by organic acid vapors produced in these enclosures. As more attention is paid to this potential risk, more damage is inevitably found. In most instances, these cases or storage facilities cannot be feasibly replaced - what then to do? Is the situation hopeless?

Fortunately there exists a substantial body of knowledge on pollutant control which can be directed to retrofitting these types of microenvironments. Some of the "fixes" I'll suggest will be difficult to aesthetically implement and others might seem counterintuitive - like encouraging leakier display case rather than better sealed designs. Nevertheless, if a problem is know or suspected to exist, the basic approach described here is sound and will, in theory and in the laboratory, work well. The considerations I'll offer, will also relate work done by previous conservation researchers with the best of the recently developed mathematical models taken from the environmental engineering field.

Nazaroff and Cass (1986) developed models which predict pollutant concentrations indoors reasonably well. The elements of their treatment included flow rates between the museum building and outside and through the building's air conditioning plant; loss of pollutants to different types of walls and wall coverings; total surface area, volume; and the better known chemical reactions which take place in the gas phase, with and without additional photochemical inputs. Many of the observations recommended here stem from factors in this model which have not been specifically discussed in the conservation literature previously.

One of the realities of museum climatology is that gases move from areas of high concentration to those of low. This is true whether we are discussing water vapor, inert gases or air pollutants. This is usually overcome with respect to moisture by continuously supplying or subtracting water vapor. The active approach is by adding humidification or dehumidification in air conditioning plants or passively incorporating silica gel in display cases. In inert gas environments, a combination of impermeable materials and tight seals tend to be the time-tested solutions. But when it comes to controlling air pollution, the problem quickly becomes more complicated.

Figure 1 illustrates one solution whereby the principal line of defense is the museum shell backed up by filtration in the Heating, Ventilating, and Air Conditioning system (HVAC). Outdoor pollutants that still get into the building react with wall coverings resulting in virtually no outdoor pollutant gaining access to display cases. In this solution, the display case or storage rooms themselves are minor defense mechanisms and it is preferable to have them as leaky as possible, using the building to dilute and dispatch indoor pollutants that may be emanating from within.

Figure 2 is the other solution, one more easily applied in historical houses or buildings with no air filtration. Here the display case or storage vault is the principal defense. The museum shell is leaky because natural ventilation dominates, there is no loss of pollutants to a mechanical plant, and surface loss becomes the major protection mechanism outside storage and display. In this scenario, the physical barrier of the microenvironment is very important as is the ability of the microenvironment to control any pollutants that builds up within.

Cass et al.(1988) illustrates some of these points. Figure 3 shows what can be achieved by combining a chemical filter media while simultaneously reducing the rate at which outside air is taken into the building. Here, showing data for ozone in an air conditioned museum in Claremont, California, we see that lengthening the time for air to exchange by a factor of ten, results in a similar reduction in indoor concentrations. By slowing the rate highly polluted air is dragged into the building, other reactive surfaces, air chemistry and multiple passes through the HVAC system can deplete ozone concentrations in competition with air objects. Figure 4 shows that in an environment without chemical filtration and where natural ventilation dominates, the concentration inside a restricted air exchange microenvironment (here a display case with relatively wide gaps) can be quite low compared to its surrounding air.

In a different type of example, Passaglia (1987) discusses how document storage boxes can be either protective or non-protective to sulfur dioxide intrusion, depending upon whether or not SO_2 has an opportunity to react with the walls of the box, or simply enter through gaps in box construction.

A Closer Look At Microenvironmental "Fixes"

Relationship of Air Exchange to Concentrations

Mathematical models reduced to their most laconic form say that: indoor air pollution is the product of all processes which add pollutants and all those which subtract them. Each and every processes has a unique rate step, which may or may not be constant. Processes which add or subtract pollutants very slowly are less important than faster ones, and if any single fast additive process can be matched by a fast or faster subtractive one, pollutant concentrations will be displaced to lower levels. If we wish to match a release rate for formaldehyde with fast ventilation rates, it is easy to engineer very much faster subtractive processes (ventilation) that can dominate the slower additive ones (formaldehyde release). On the other hand, it's more commonly found that very slow, subtractive processes (diffusion) are completely dominated by faster pollutant release rates (Passaglia, 1987). The exact pollutant, its sources, sinks and the construction of the case or storage area, all work together to establish the actual concentration level.

Virtually all examples of phenomenon like "matburn" and other forms of acid migration or lignin decomposition products transfering to higher grade papers in sealed frames, probably would not occur in frames where a laminar air flows parallel to bevelled mat cuts, whisked these products out the back of the frame. While such micro-, dare I say, nanoscaled HVAC systems for picture frames seems ludicrous, it's a similar instinct that drives the idea and practice by paper conservators of leaving open the corners of Mylar encapsulation.

Although it would not be feasible to use high ventilation rates to protect objects in sealed frames, there are numerous situations like cabinetry where high ventilation rates are probably responsible for a lack of visible deterioration, provided however, that the next larger contiguous air volume is not more polluted than the smaller or adjacent one. The difficulty in proving that high ventilation rates are working alone, is that it's not as easy to say why something is not deteriorating as it is to say why it is.

Cecily Druzik (1991a) found in her extensive museum sampling study, that generally, the concentration of formaldehyde predictably followed the rates of air exchanges within galleries, storage rooms and display cases (Figure 5). As the air exchange rate increased, the formaldehyde concentration decreased: galleries had the lowest concentrations, display cases, the highest, and storage vaults were intermediate. While aldehydes and organic acids are normal components of urban air pollution, their outdoor concentrations are usually not as high as those often found to cause damage indoors and much lower still in non-urban areas.

Effects of Sacrificial Surfaces

Since we know much more about the behavior of outdoor-generated pollutants than indoor-generated ones at this point, I'll illustrate the importance of pollutant loss to walls using ozone, sulfur dioxide, nitric acid vapor, and nitrogen dioxide, then proceed to show how it works with indoor-generated pollutants.

High losses of sulfur dioxide have been observed in museums (Hackney, 1984) and in laboratory tests (Parmar, 1991a,b). Hackney found concentrations levels only 25% the outdoor levels. Parmar's loss rates for SO_2 on Plexiglas alone, a material considered to have relatively low reactivity, were the highest of any pollutant he examined. Finally, many have observed the very high rates of SO_2 sorption shown by paper and other cellulosics (Williams II, 1990; Edwards, 1968). Nitric acid is equal to, if not greater, than sulfur dioxide in its loss to walls. So great is this loss on nylon for example, it can be quantitatively removed this way. J. Druzik et al. (1990) presented data in which ozone concentrations ranged from high, medium or low in rough correlation to the air exchange rates of the building. Houses had low levels, air conditioned building **without** chemical filtration were intermediate, and highly ventilated structures were the highest. Nitrogen dioxide, on the other hand, has lower reactivity than the other pollutants just mentioned and accordingly, it's typically found in higher concentrations indoors (Hughes, 1983; Hisham, 1989). In all these instances, loss of pollutant to surfaces was the dominant reason for lower indoor/outdoor concentration ratios.

Turning to indoor-generated pollutants, Figure 6 illustrates what happens when other materials are present in competition with cultural artifacts for pollutant scavenging. Line 1 is of a silver object in a Plexiglas case where the half-loss time for hydrogen sulfide is 6.8 hours. By adding another 700 square centimeters of silver surface, the half-loss time is reduced to 1.82. By comparison, line 3 is for 20 grams of activated carbon in an empty case and shows a half-loss time of 0.88 hours. For either instance, 2 or 3, most of the hydrogen sulfide would have ended up harmlessly on surfaces other than the silver object you wanted to protect. Silver protection with colloidal silver dispersed in paper or cloth work this way.

Padfield's suspicion that buffered lining papers or boards would be generally helpful in drawers and cabinets follow from this phenomenon (Padfield, 1982)..

Effects of the Surface/Volume Ratio

Figure 7 demonstrates a very subtle aspect of enclosures - how just the surface-to-volume ratio alone can effect the rate at which a pollutant is lost to walls. Here line 1 represents the concentration decay of ozone in an empty display case. By placing a smaller box within the larger case, we increased the surface area relative to the free volume. This resulted in a decay rate almost twice as fast than that of the more voluminous case. One of the reasons, ozone concentrations decrease so quickly in the Fenyes Mansion (J. Druzik, 1990) is that, like private homes, it has a remarkably high surface area; the rooms are small, hallways long and narrow, convoluted Victorian wood molding everywhere, and plenty of books, tapestry and cloth upholstered furniture. Here we have a combination of high surface area and many types of reactivities.

Coatings and Barriers on Emitting Surfaces

Figure 8, taken from work carried out by Hatchfield and Carpenter (1987) at the Harvard University Art Museums, plots the efficiency of five coating systems applied to birch-veneered particleboard as barriers to formaldehyde emission. A reduction in emission in the range of 60-90% seems quite reasonable for paints and varnishes. Still better yet might be a polymer/foil laminate or a combination of strategies. John Burke (1991) has researched the area of solid film barriers extensively, as have others, and has identified a few that would work if all else fails.

Chemical Sorbents

Of course the most effective means of "passive" control is carried out with chemical sorbents, and Figure 9 radically displays it. In this study from Parmar and Grosjean

(1991a), equivalent weights of potassium permanganate on an alumina substrate and crushed activated carbon are compared in terms of their sulfur dioxide removal rates. If this experiment were duplicated with a "active" system (say a small cartridge of sorbent on a fan hidden below the decking of a display case or a free-standing unit in storage) the effects would be much more dramatic.

Remove the Offending Materials

Frequently it is possible to remove an offending material and replace it with a more stable one. Wool coverings with a sulfur-based dye comes immediately to mind, as does the replacement of particleboard with either of the two non-formaldehyde containing substitutes - but beware. All wood can and will liberate acetic acid, so even this step should be backed up further with barriers and coatings. We know enough at this point to treat, as equally dangerous, formaldehyde, acetaldehyde, formic and acetic acids.

Combinations of Various "Fixes"

As a qualitative insight then, Figure 10 shows a hypothetical display case and pollutant which have reached a steady-state equilibrium. In this figure, the display case has achieved a concentration of 800 parts per billion. (For the above mentioned four pollutants, concentrations this high were very rare in C. Druzik's surveys in the United States but common in Europe according to Norman Tennent (1991). However, it could equally be 8 ppb for acetic acid or 80 ppt for hydrogen sulfide.) Simply by doubling the air exchange rate, increasing internal reacting surfaces and effecting a reasonable reduction in emissions, we can reduce exposure concentration and possibly the rate of damage by a factor of twenty. This is even before any form of surface protection is given to a vulnerable material, i.e. B72 or Incralac on copper.

I hope to be able to convey the idea that, by combining a series of mechanical and chemical abatement techniques, independent of knowing any detail of what pollutants exist within a display case or storage area and in ignorance of which materials are sensitive, we can predict general trends in concentration reduction. And this is, the heart and soul of preventive conservation.

Words of Caution!

It should always be remembered that there is no such thing as a "threshold limit value" for objects. Artifacts don't heal; they have no tolerance beyond their own compositional vulnerability. Therefore, one cannot make any recommendations for acceptable lower limits. If you reduce the concentration by ten-fold you may or may not reduce the rate of deterioration in a similar manner, but, there is little or no credible literature indicating a point where deterioration stops. Corrosion of metals, identified as formates, has been observed even at low parts per billion levels. The conservation literature is resplendent with "suggested museum levels" and it's an easy way to get a fast publication, but ultimately the lowest attainable, economically-reasonable concentrations based upon our best models, applied by competent practitioners, and peer-reviewed, should be our guideline.

Conclusions and Recommendations

Within the last ten years we have learned a great deal about controlling pollutants within display cases and storage areas. If no problem exists; nothing needs to be done even under the banner of "preventive conservation.". *But if a degenerative condition can be pinpointed to indoor pollutants, there are a number of mechanical and semi-chemical/mechanical procedures that can be applied.* **Let us revisit our major corrective steps and add a few additional thoughts.**

(1) Sorbents and Sacrificial Surfaces Lining microenvironments wherever possible with a calcium carbonate-buffered paper or paperboard and the use of activated carbon, as an internal sorbent for pollution were largely speculative recommendations when Padfield made them in 1982. Since then numerous behaviors of these two materials have been quantified by Williams (1990) and Parmar (1991), respectively, and we believe Padfield's faith has been well founded. However, this area needs considerable future research because we know more about how display materials release pollutants than how they absorb them. Sabersky (1973) for example has done this for ozone's reactivity towards such materials as cotton, linen, plywood, nylon, etc. but more needs to be done. Reilly's work on photographic materials clearly identifies a large body of objects that are probably as sensitive to the pollutant as the protection.

(2) Increase Surface-to-Volume Ratios One other advantage not envisioned by Padfield with an acid-free tissue paper used for wrapping or padding purposes, is its effect in increasing the surface-to-volume ratio in tight spaces. This increases the "deposition velocity" of acidic pollutants, some of their precursors, and most oxidants, thereby increasing the loss to surfaces other than those provided by objects of cultural value. Regardless of the chemical mechanisms involved, the result is a drop in ambient concentrations.

(3) Coatings and Barriers Since Catherine Miles' article in Studies in Conservation on wood coatings for storage and display cases, nothing has replaced two-component epoxy or moisture-cure urethanes as sealants although metal/polymer laminate films still remain the most secure barriers to wood VOCs. Use the solvent swab test early on to determine if cured enamel coatings are cured well enough and monitor the environment anyway. There have been a few painful failures of these systems in the last few years where the manufacturer has denied responsibility. If one is considering purchasing enameled metal, explain your concerns and request or demand a "return policy" if, within a reasonable time period, these types of housings "turn on" their contents.

(4) Increase Air Exchange Rates - Display Cases Air exchange rates in sealed cases are important, but any attempt to seek standardization or find "recommended values" for safe storage, is probably a waste of time. Leakage rates of one air exchange per day have been independently measured by Thomson (1978), Ramer (1981) and Padfield (1982) and are considered average for commonly sealed display cases. While this is slow enough to dampen external environmental fluctuations, it is too slow to insure that internal pollutants won't damage susceptible contents. Nevertheless, pollutant release rates can never be generalized accurately enough to be trustworthy which is why a fixed recommendation for air exchanges is useless. Increasing air exchange rates from 1 day^{-1} to 1 hr^{-1} or even faster is however suggested to mitigate a problem when damage is known to be occurring or sampling has shown a probably cause for concern. Recently, interest in microenvironments with very low or trace leakages has grown (Preusser, 1989). The case developed for the Royal Mummies in the Cairo Museum for example has a 2-3 ppm day^{-1} leakage rate. These types of cases should not be considered without also considering how the designer intends to monitor their contents or make them self-cleaning.

Re-Evaluate Air Circulation - Storage Areas Reduced air exchanges in storage areas is often advocated because it has certain advantages in terms of energy conservation, fire suppression, keeping out outdoor-generated pollutants, and generally stabilizing climatic fluctuations in temperature and relative humidity. But reduced air circulation does nothing to improve air quality from the standpoint of indoor-generated pollutants, a phenomenon occasionally described as "sick building syndrome." If a building has activated carbon or permanganate/alumina filter media in the return air supply or is in a non-urban environment, it makes more sense to increase storage area air circulation rather than reduce it, thereby continuously suppressing pollutant levels.

In the event of active corrosion, doors on cabinets restrict air circulation and could be removed. Objects should also be spread out to use up available space. This may not reduce localized concentrations significantly, but even a slight reduction is better than no reduction at all. We inculcate the point that there is no such thing as a "threshold limit value" for objects. All damage is cumulative and therefore all reductions, even very minute ones lengthen the time for accumulated damages to be visible.

(5) Adopt a Passive Monitor Program For both display and storage areas, active or passive monitoring is strongly suggested. Druzik (1991b) has demonstrated that the technologies for passive monitors either currently exists or is just awaiting validation for museum application, before being recommended for inexpensive sampling. The GMD Series Formaldehyde Dosimeter for example has an analytical detection limit of less than 1 part per billion. This is more than adequate for what is needed.

(7) Active Filtration Stulik (1990) has included a cartridge of activated carbon impregnated with catalyst (the same type used in respirator masks) into an air purification device for display cases. This small machine is currently being tested in museum field trials and should be able to "knock down" concentrations over 1 part per million.

(8) Stabilize Contents Regretably, we only think we know how to do this in a few instances.

(9) Know Your Materials Excellent background on dangerous materials and testing have been compiled by Padfield (1982), Hatchfield and Carpenter (1987) and Blackshaw (1979). In addition, compilations of materials testing like those maintained at the Canadian Conservation Institute (1986) or the Getty Conservation Institute (1989), regardless of their limitations, remain invaluable reference sources. Special attention should also be given to products that have evolved as a parallel response to indoor air pollution, such as particleboards that do not incorporate formaldehyde-containing resin systems. Incidentally, plastic bubble wraps should also be watched carefully since tarnishing from these had been previously reported in a regional conservation association newsletter (Chandler, 1982).

As a well-know television personality says, "Keep well informed, and fight back."

Products and Services

Passive Formaldehyde Monitors - GMD 570 Series Formaldehyde Dosimeter Badge
GMD Systems, Inc., Old Route 519, Hendersonville, PA 15339. (412) 746-3600

Charcoal Cloth - Charcoal Cloth Limited, East Wing, Bridgewater Lodge, 160 Bridge Road, Maidenhead, Berkshire, SL6 8DG, England. FAX (0628) 773380
Attention: Mrs. S. Scott, Product Manager

Barrier Films -
Film-O-Wrap 2175, 2176 and 7750, Bell Fibre Products Corporation, P.O. Box 1158, 1 Minden Road, Homer, LA 71040

Marvel Seal 360 and 1177, Ludlow Corporation, Laminating & Coating Division, Columbus, GE 31993

Plexiglas is a registered tradmark of Rohm & Haas

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Figure Captions

Figure 1	Building where the museum shell and the HVAC filtration provide the principal defense against pollutants
Figure 2	Building where the inside microenvironments provide the principal defense mechanisms against pollutants
Figure 3	Ozone concentrations inside the Montgomery Gallery as a function of air exchange rates (Cass, 1988)
Figure 4	Ozone concentrations inside microenvironments where the principal defense are the glass or Plexiglas walls (Cass, 1988)
Figure 5	Relationship between formaldehyde concentration, air exchange rate and increased incidence of corrosion (C. Druzik, 1991b)
Figure 6	Reduction of hydrogen sulfide in a Plexiglas case by including sacrificial surfaces (Parmar, 1991a,b)
Figure 7	Reduction of ozone concentrations by increasing the surface/ volume ratio of the microenvironment (Parmar, 1991a,b)
Figure 8	Effects of coatings on formaldehyde release from particleboard (after Hatchfield and Carpenter, 1987)
Figure 9	Effects of chemical sorbents on sulfur dioxide concentrations in microenvironments (Parmar, 1991a,b)
Figure 10	Effects of four additive steps in reducing the overall concentrations of a hypothetical pollutant in a microenvironment

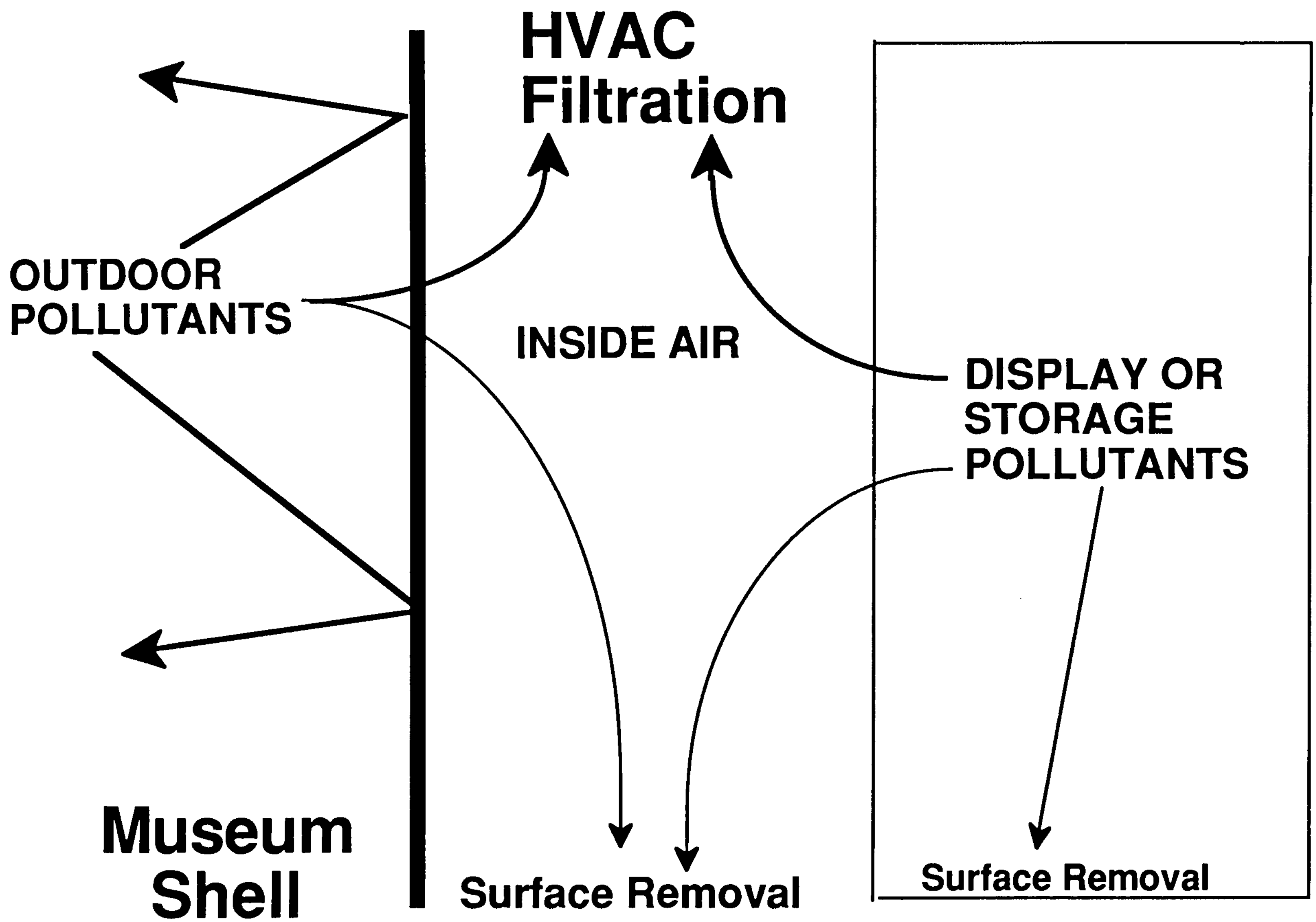

HVAC
Filtration
OUTDOOR
POLLUTANTS
INSIDE AIR
DISPLAY OR
STORAGE
POLLUTANTS
Museum
Shell
Surface Removal
Surface Removal

Fig.1.

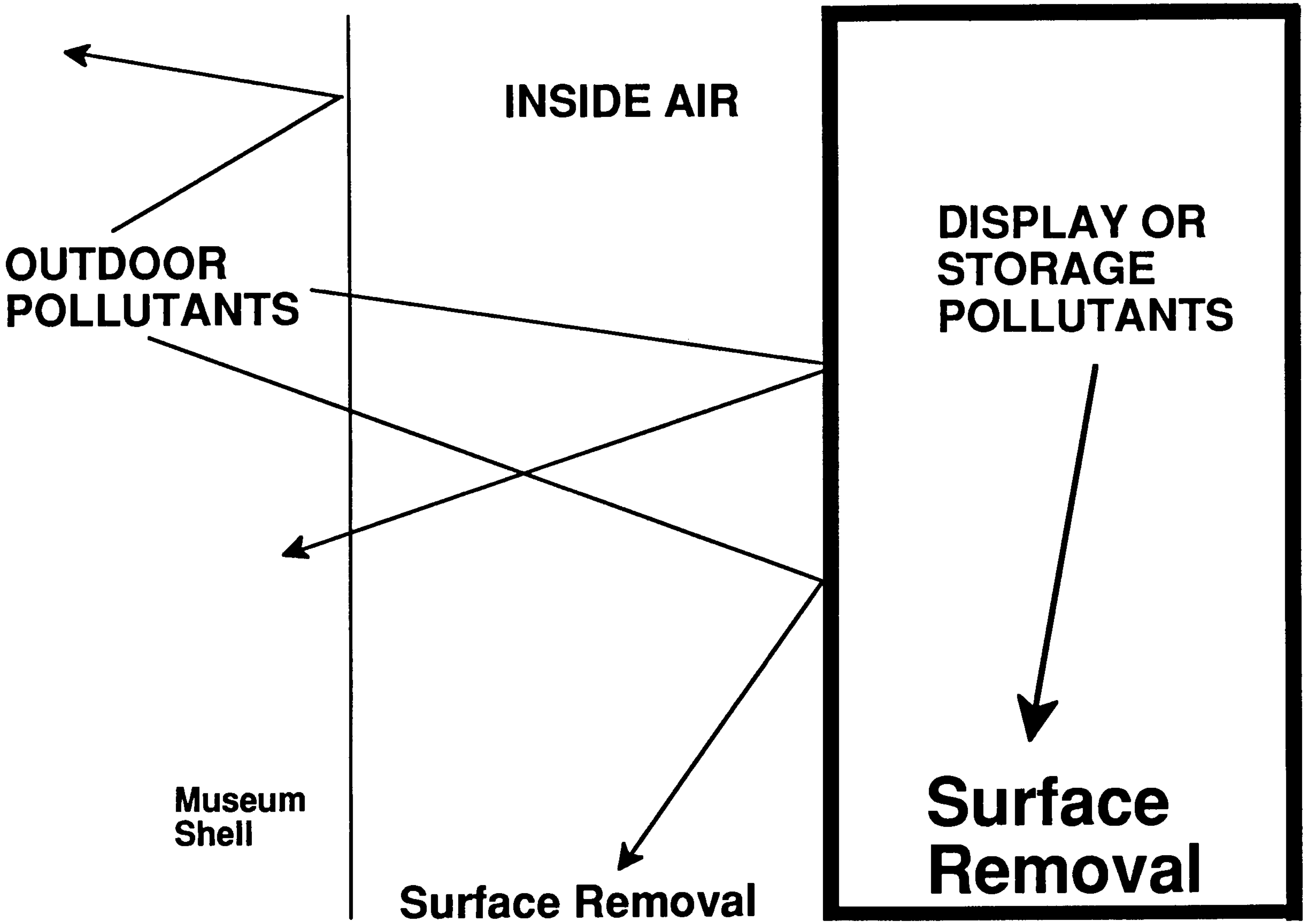

INSIDE AIR
OUTDOOR POLLUTANTS
DISPLAY OR STORAGE POLLUTANTS
Museum Shell
Surface Removal
Surface Removal

Fig.2.

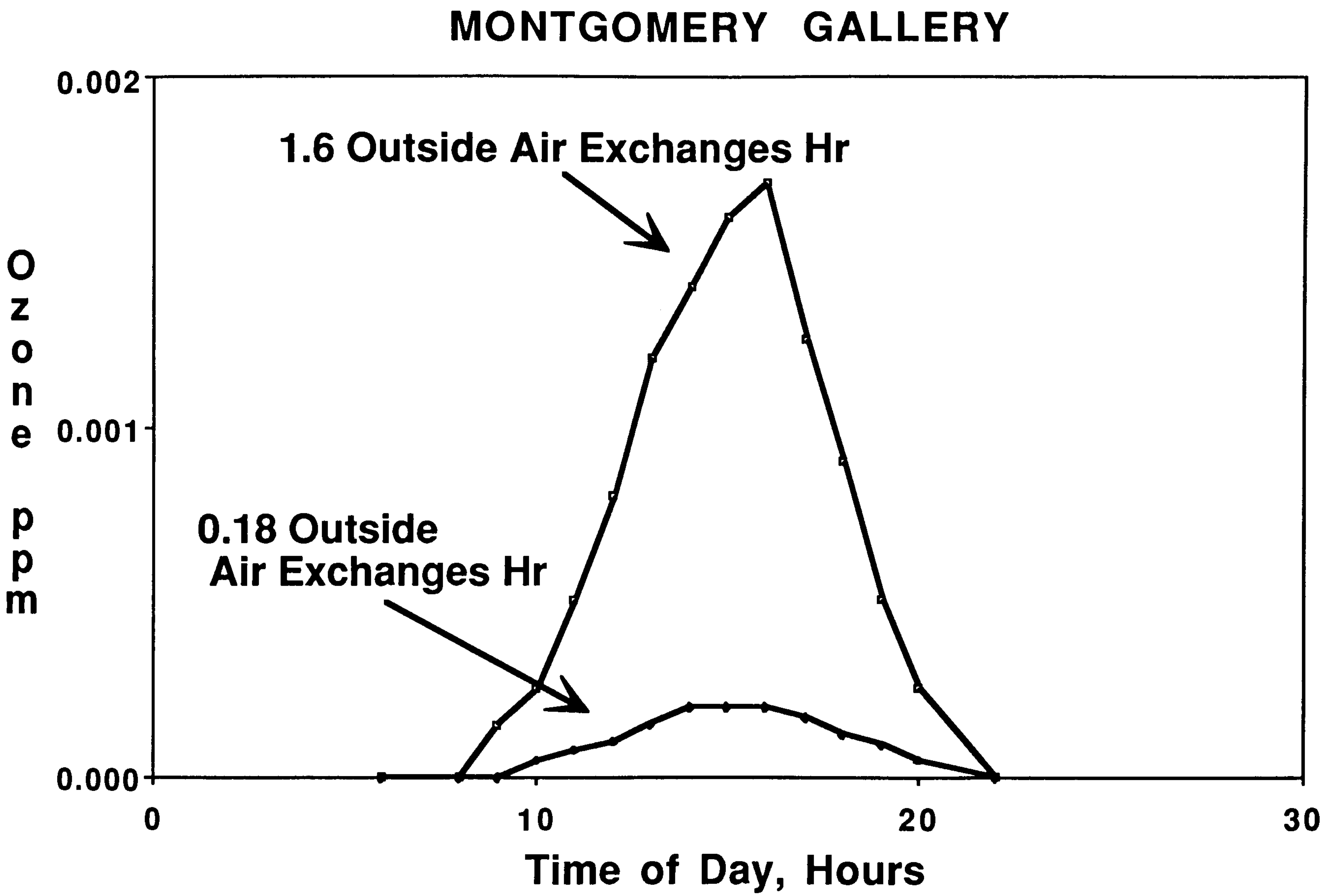

MONTGOMERY GALLERY
1.6 Outside Air Exchanges Hr
0.18 Outside
Air Exchanges Hr
Ozone ppm
0.002
0.001
0.000
0
10
20
30
Time of Day, Hours

Fig.3.

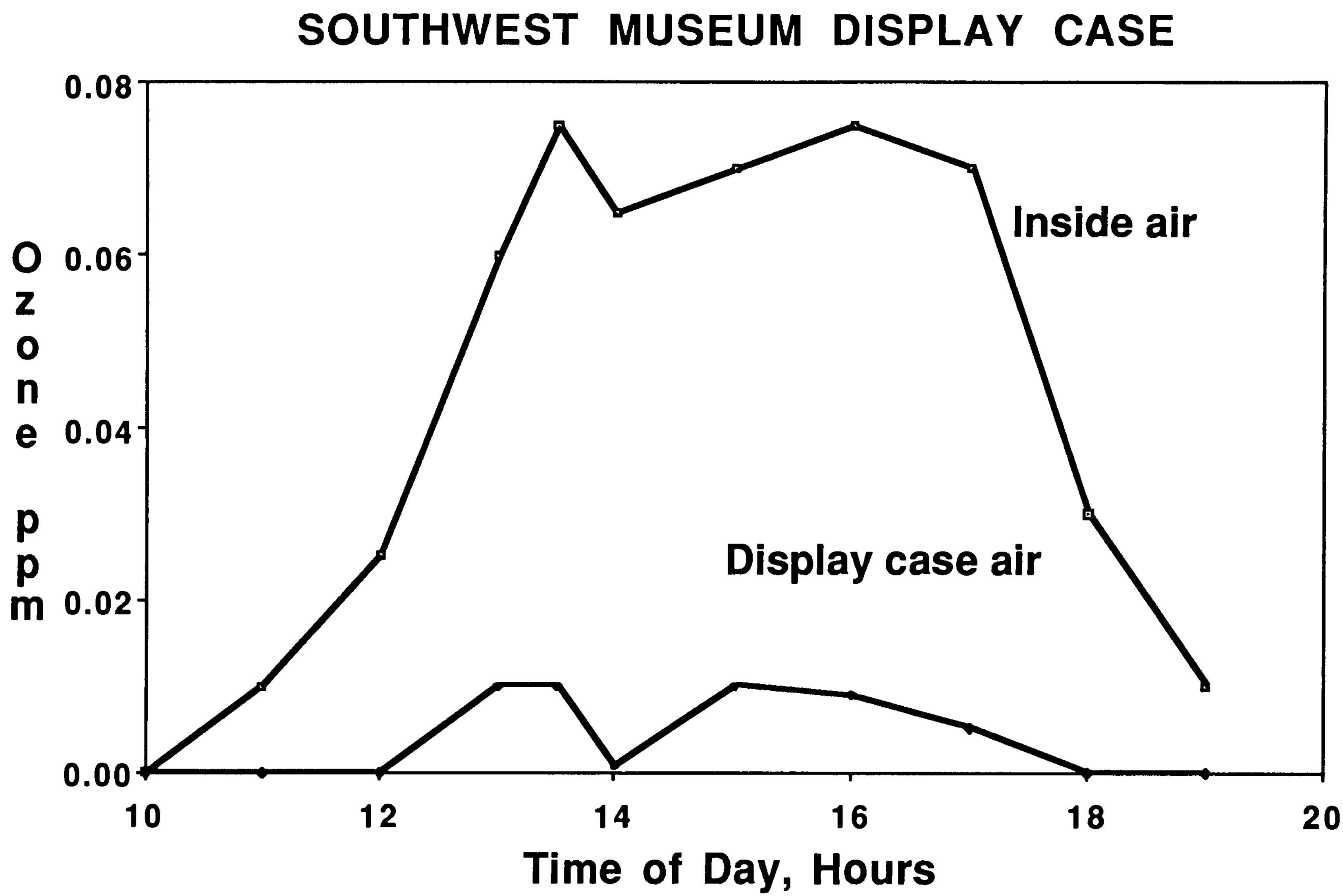

SOUTHWEST MUSEUM DISPLAY CASE
Ozone ppm
0.08
0.06
0.04
0.02
0.00
Inside air
Display case air
10
12
14
16
18
20
Time of Day, Hours

Fig.4.

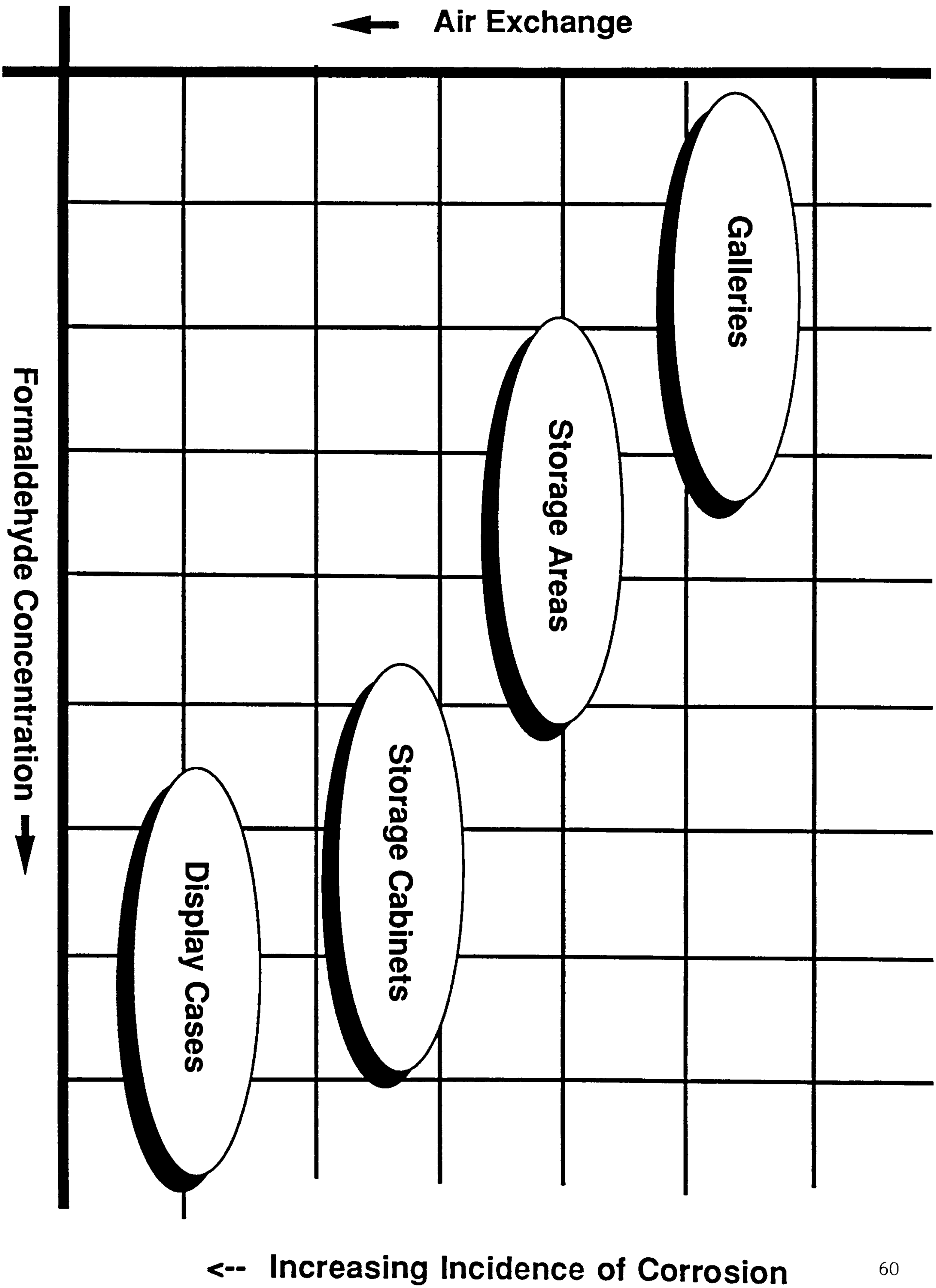
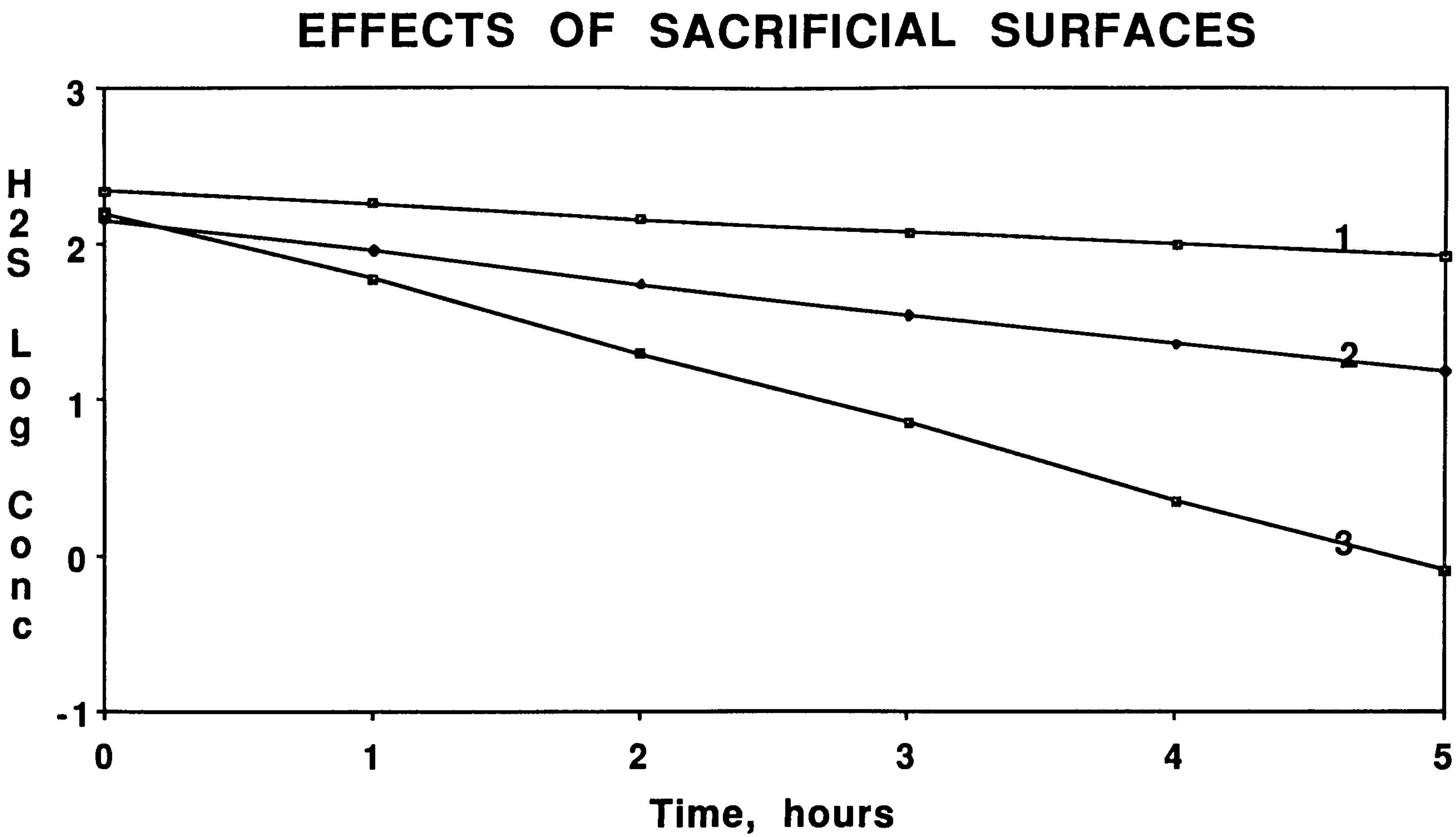

Air Exchange
Formaldehyde Concentration
Galleries
Storage Areas
Storage Cabinets
Display Cases
<-- Increasing Incidence of Corrosion

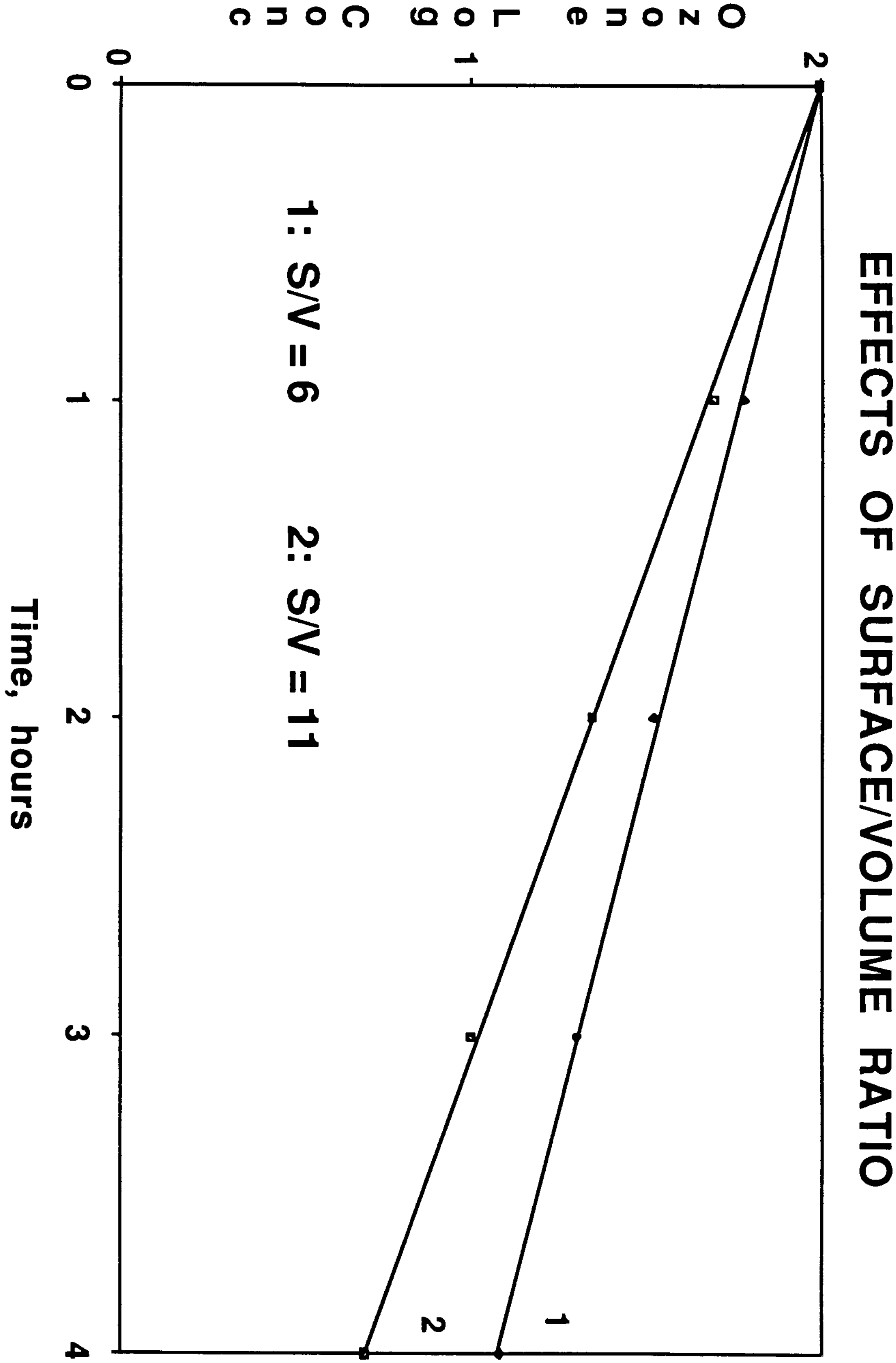
Fig.5.



1: Silver Object 2: Silver Object:Other Ag (1:3) 3: 20 gm Carbon

Half-lifes: 6.8 1.8 0.9

Fig.6.



EFFECTS OF SURFACE/VOLUME RATIO
Ozone Log Conc
Time, hours
1: S/V = 6
2: S/V = 11
0
1
2
3
4
0
1
2
1
2

Fig.7.

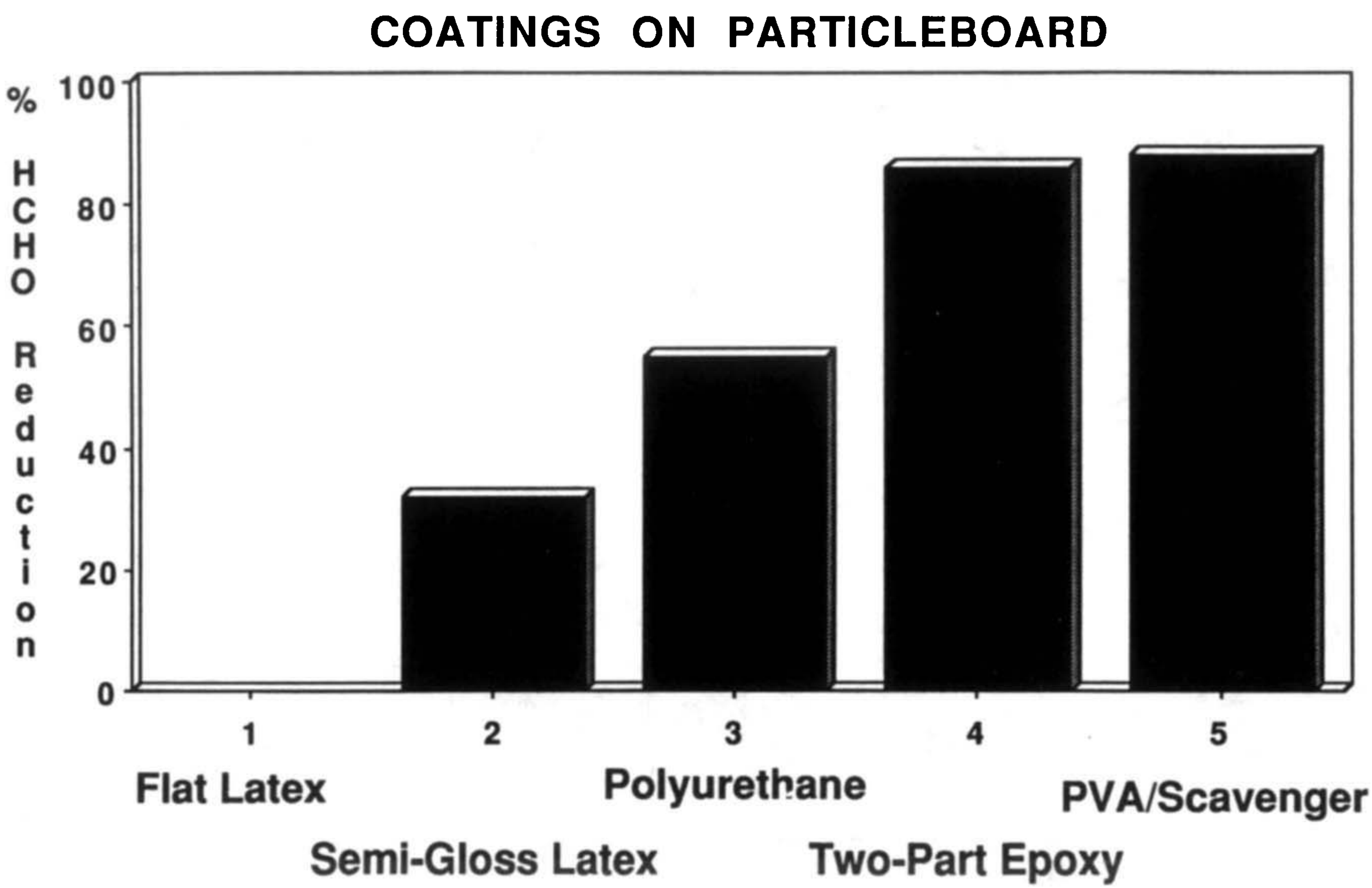

COATINGS ON PARTICLEBOARD
% HCHO Reduction
100
80
60
40
20
0
1
2
3
4
5
Flat Latex
Semi-Gloss Latex
Polyurethane
Two-Part Epoxy
PVA/Scavenger

Fig.8.

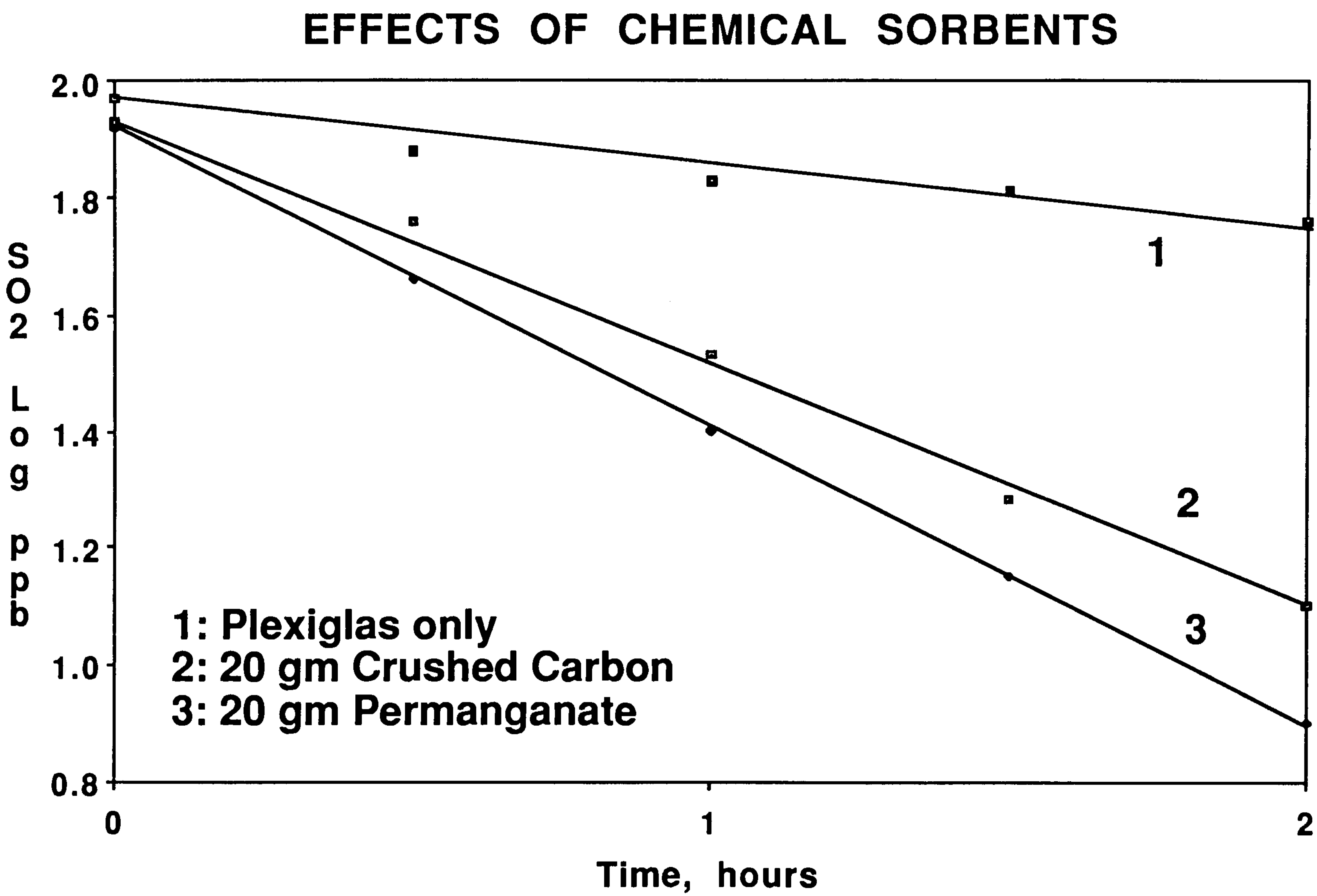

EFFECTS OF CHEMICAL SORBENTS
SO2 Log ppb
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
1
2
Time, hours
1
2
3
1: Plexiglas only
2: 20 gm Crushed Carbon
3: 20 gm Permanganate

Fig.9.

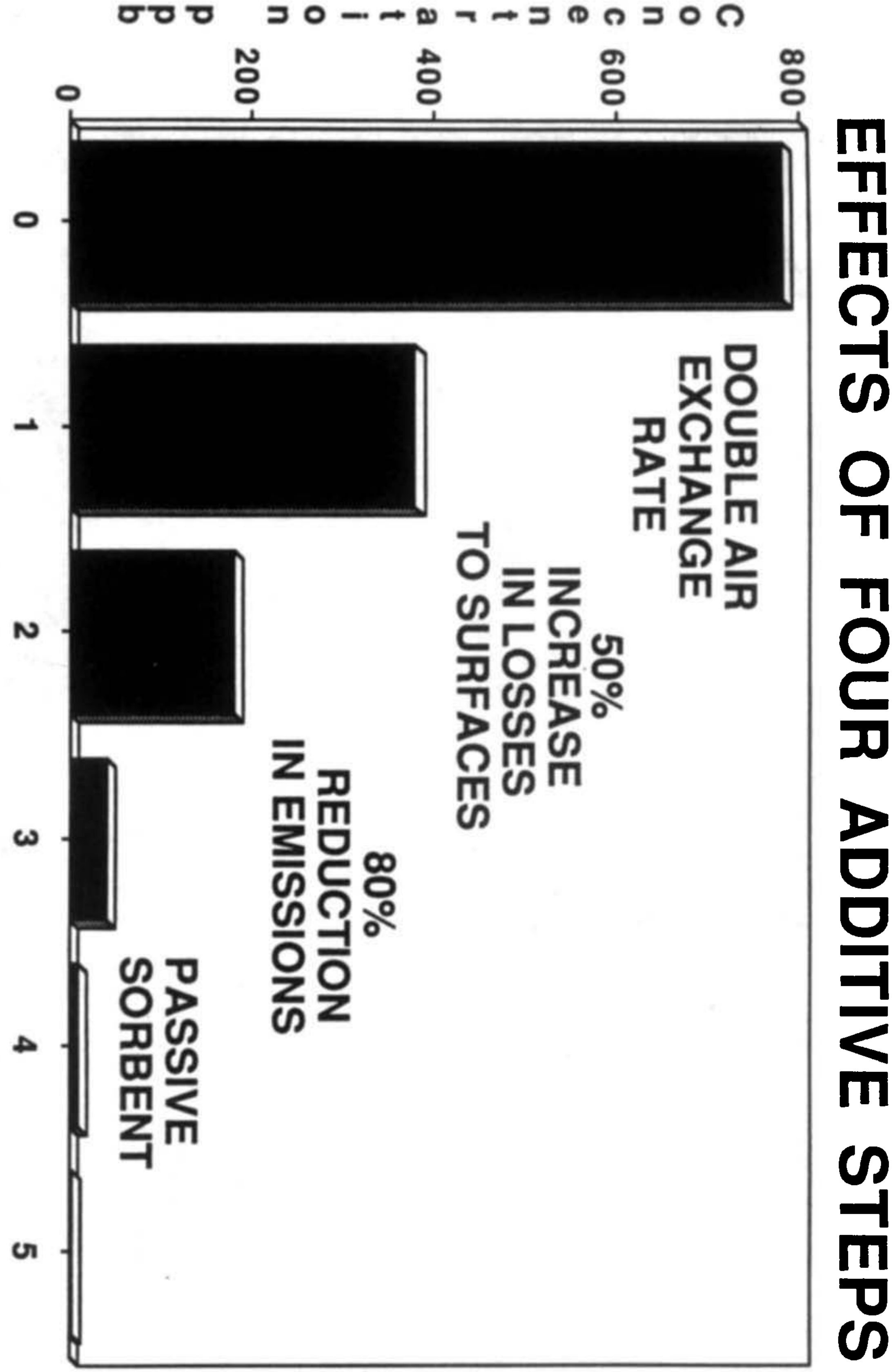

EFFECTS OF FOUR ADDITIVE STEPS
Concentration ppb
800
600
400
200
0
DOUBLE AIR EXCHANGE RATE
50% INCREASE IN LOSSES TO SURFACES
80% REDUCTION IN EMISSIONS
PASSIVE SORBENT
0
1
2
3
4
5

Fig. 10.

Fig. 10.