MORTEN RYHL-SVENDSEN
National Museum of Denmark
Department of Conservation
Lyngby, Denmark
morten.ryhl-svendsen@natmus.dk
http://www.natmus.dk

THE INFLUENCE OF URBAN AIR POLLUTION IN ARCHIVES

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ABSTRACT

The ingress of ambient pollutants will increase with ventilation. Therefore, pollution control for archival collections must be obtained either by the use of gaseous filtration within a ventilation system, or by keeping the building at a low air exchange rate, especially when located in an urban environment. While ozone has a direct impact on the materials it meets, nitrogen dioxide acts mainly as a precursor for nitric acid indoors. In an archival facility in central Copenhagen, the indoor concentration of nitrogen dioxide was 20 percent of ambient for a natural ventilated building, and 56 percent for a building with mechanical ventilation but without gaseous filtration. For both locations the ozone level was <10 percent. Based on measurements of nitrous acid in the air, the corresponding generation rate of nitric acid on surfaces was calculated to 4 mg m^{-2} annually for the highly ventilated building, and <0.1 mg m^{-2} annually for the low-ventilated building.

RÉSUMÉ

L'infiltration des polluants atmosphériques augmente en présence de ventilation. Par conséquent, le contrôle de la pollution pour les collections d'archives doit être garanti soit par l'emploi d'une filtration gazeuse dans le système de ventilation, soit en maintenant un faible taux de renouvellement de l'air dans le bâtiment, surtout lorsqu'il est situé dans un environnement urbain. Si l'ozone a un impact direct sur les matériaux qu'il rencontre, le dioxyde d'azote agit essentiellement comme précurseur de l'acide nitrique à l'intérieur. Dans des locaux d'archives au centre de Copenhague, la concentration de dioxyde d'azote à l'intérieur était de 20 pour cent de l'air ambiant dans un bâtiment à ven-

INTRODUCTION

Archival buildings located in urban areas are influenced not only by the ambient climate, but also by elevated levels of pollution, especially due to traffic. Different buildings can, however, vary a great deal in their performance in terms of the protection of the collections stored indoors against the ambient environment depending on construction design and climate control systems.

Air pollutants enter buildings through free air flow, e.g. via ventilation systems or open windows and doors. Ozone, which originates from natural photochemical reactions in the atmosphere, is known to be a strong oxidant, which deteriorates paper and other organic materials. Likewise nitrogen dioxide, a by-product of combustion, deteriorates paper, leather bindings and dyes by acid hydrolysis when turning into nitric acid via surface reactions involving water (for air pollution and paper degradation in general, see, e.g., Havermans 1995, Johansson 2000 or Strlič and Kolar 2005).

In this article, an estimate is made of the amount of nitric acid which may be generated on archival materials (paper and book bindings) housed inside an urban archive. The calculated accumulation rate is based on field measurements of the atmospheric content of air pollutants in Danish archival buildings.

CASE STUDY: DANISH STATE ARCHIVES

The Danish State Archives regional branch in the Jagtvej area of Copenhagen is housed in two neighboring buildings of approximately uniform size (about 5000 m^3 volume each). They are, however, fundamentally different in construction and age. The old building (1893) has no climate control system except for comfort heating by radiators. Next to this was built a new structure in 1966. This building is constantly ventilated by mechanical means and the indoor climate is controlled by conditioning the air (heating and dehumidification). The archives contain paper records, bound in books or housed in archival boxes. The archives are shown in Figure 1.

The two storage buildings are exposed to exactly the same ambient environment; however, the ventilation rate of the newest storage building (15 air changes per day) is about ten times higher than the natural air exchange rate of the old building. As the level of traffic has constantly

tilation naturelle, et de 56 pour cent dans un bâtiment doté d'une ventilation mécanique mais sans filtration gazeuse. Dans les deux endroits, le niveau d'ozone était < 10 pour cent. En fonction des mesures d'acide nitrique dans l'air, le taux respectif de génération d'acide nitrique sur les surfaces a été évalué à 4 mg m^{-2} par an pour le bâtiment très ventilé et < 0,1 mg m^{-2} par an pour le bâtiment peu ventilé.

RESUMEN

El ingreso de contaminantes ambientales aumenta con la ventilación. Por lo tanto, el control de la contaminación en las colecciones de archivo debe conseguirse ya sea por medio de filtración gaseosa dentro de un sistema de ventilación, o bien manteniendo una tasa baja de renovación del aire en el edificio, especialmente si éste se encuentra en un entorno urbano. Si bien el ozono tiene un impacto directo en los materiales con los que entra en contacto, el dióxido de nitrógeno actúa principalmente como precursor del ácido nítrico en el interior de los edificios. En las instalaciones de un archivo en el centro de Copenhague, la concentración de dióxido de nitrógeno en el interior era de 20% del ambiente en un edificio con ventilación natural, y de 56% en un edificio con ventilación mecánica pero sin filtración gaseosa. En ambos casos el nivel de ozono era inferior al 10%. Basándose en mediciones de ácido nítrico en el aire, se calculó que la tasa correspondiente a la generación de ácido nítrico en las superficies era de 4 mg m^{-2} al año en los edificios muy ventilados, e inferior a 0,1 mg m^{-2} al año en edificios con poca ventilación.

increased since the construction of the two buildings, they are today situated in a highly polluted environment not foreseen when the buildings and climate control systems were designed. The ventilation system in the 1966 building is equipped with particulate filtrations (bag filters), but does not have filtration for gaseous pollutants.

Figure 1
Left: the Regional State Archive building from 1966. Right: the old building from 1893. Photo collage by the author

The archival collections will actually move to a new facility within a few years, so in time the present air pollution problems will be solved. Nevertheless, as the buildings provide a perfect opportunity to investigate the climatic performance of different building designs in a highly polluted area, a survey of the indoor air quality was carried out in 2009.

For comparison purposes, a summary of monitoring results from four other cultural heritage storage facilities in the Copenhagen area are also reported. These are the National Museums' storage building in Brede, the Music Museums' storage facility in Søborg, the book storage of the Royal Library in Amager, and a private archive in Avedøre.

METHOD AND RESULTS

Measurements of air pollution inside and outside the two buildings were conducted during one winter month and one summer month (both in 2009) using passive diffusion samplers. The indoor samplers were located in approximately the centre of each building. The outdoor samplers were attached to a weather station located in a courtyard between the buildings. At each location, the ozone (O_3), nitrogen dioxide (NO_2), and nitrous acid (HNO_2) compounds were sampled and for each compound two samplers were used in parallel. The uncertainty of the method is expected to be ± 20%. The results are given in Table 1.

Table 1
State Archives buildings. The indoor level of nitrogen dioxide, ozone, and nitrous acid, given as a percentage of ambient concentration, and (in brackets) as concentration

Pollutant	NO_2	O_3	HNO_2
New building, winter	56% (14 ppb)	5% (2.2 ppb)	600% (4.2 ppb)
New building, summer	56% (9.0 ppb)	6% (3.7 ppb)	142% (5.1 ppb)
Old building, winter	20% (5.1 ppb)	<3% (<0.50 ppb)	250% (2.0 ppb)
Old building, summer	18% (2.9 ppb)	<3% (<0.50 ppb)	56% (1.8 ppb)

Pollution measurements (ozone and nitrogen dioxide only) from four other buildings are also reported; these data were collected during less intensive measurement campaigns but using the same methodology as for the State Archive study. These other measurements were also conducted by the author, except for the Royal Library, from which the data were provided by the library's conservation department. The buildings and their properties are listed in Table 2 and the results shown in Figure 2.

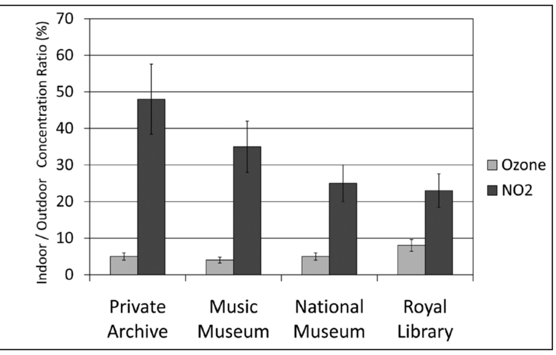

Figure 2
The I/O concentration ratio for ozone and nitrogen dioxide for four cultural heritage storage facilities in the Copenhagen area

Table 2
Properties of four storage facilities (museums, libraries or archives) from the Copenhagen area, with regard to air handling systems and pollution control

Building	Royal Library Storage (Amager)	Music Museum Storage (Søborg)	National Museum Storage (Brede)	Private archive (Avedøre)
Type of collection	Books	Wooden musical instruments	Mixed collection	Paper records
Type of climate control	HVAC	Conservation heating, natural ventilation	HVAC	HVAC
Air filtration	Particulate and gaseous filters	None, but low air exchange rate	Particulate and gaseous filters	Particulate filters only
Annual energy consumption (kWh m^{-3})	30 *	5 **	15 **	15 **

HVAC: mechanical heating, ventilation and air-conditioning system
*: measured value (Ryhl-Svendsen *et al*, 2010)
**: estimated value

DATA TREATMENT

For each pollutant, the indoor/outdoor concentration ratio (I/O) was calculated, as this ratio reflects the mass balance between the infiltration, and the indoor removal rate, of an ambient pollutant. Expressed as $I/O = n/(n+S)$, where n is the air exchange rate in room volumes of air per unit time, and S is the surface removal rate, also in room volumes per unit time, this balance was originally suggested for modeling ozone indoors (Weschler et al. 1989). It has since been applied to other pollutants as well, e.g. nitrogen dioxide (Blades *et al*, 2002), which is valid as long as the main indoor fate for a compound is surface reaction, as the model ignores reactions in air (see also Ryhl-Svendsen 2006).

The model by Weschler et al. is not readily applicable for compounds generated inside the building; however, if the I/O concentration ratio is above 100 percent, then the compound has an indoor source, in addition to what may infiltrate from outside.

While nitrogen dioxide can be monitored outdoors and indoors readily, and from this the indoor loss estimated, it is from a conservation point of view the amount of nitric acid (HNO_3) formed on the archival records which is important. Reactions between nitrogen dioxide and surface moisture film on materials will produce nitrous acid and nitric acid in molar equivalent amounts (Febo and Perrino 1991, Katsano et al. 1999):

$2NO_2 + H_2O/surface \rightarrow HNO_2 + (H^+ + NO_3^-)$

Nitrous acid will remain almost totally gaseous, while the nitric acid will exist mainly as ions in surface water film. And while nitrous acid in itself poses little threat to materials, its concentration in air indicates the concurrent production of the more harmful nitric acid on surfaces. From this rationale, nitrous acid was monitored in the air of the archives rather than nitric acid.

DISCUSSION

The effect of ventilation

The results from the State Archives show how strongly a building's air exchange rate influences the indoor environment, if at the same time the ambient environment is highly polluted. While the low-ventilated old building had approximately 20% of the outdoor nitrogen dioxide level, the newer building with a forced and ten-times-higher air exchange rate maintained an indoor level of 56 percent of the outdoor level.

For the private archive (Avedøre), which is also ventilated mechanically but without gaseous filtration, the I/O ratio (48 percent for nitrogen dioxide) was quite similar to the performance of the State Archives new building.

Maintaining a low air exchange rate is beneficial in terms of pollution control as it slows the entrance of pollutants from the outside environment. As reactive compounds such as ozone or nitrogen dioxide will react with any surface they meet, they are constantly being removed from the air as it enters a building. The slower the air flow rate, and the more tortuous the route, the higher the removal rate. As observed in this study, ozone in particular reacts very rapidly; in general the indoor level will rarely exceed 10 percent of the ambient level.

For the two buildings equipped with gaseous filtration (National Museum Storage and Royal Library Storage), the performance of the filters indeed ensured better indoor air quality (lower infiltration rate) than for the buildings with forced but non-filtered ventilation. But it was still within the same range of what was achievable with the low-ventilated buildings.

As the I/O ratios of the low-ventilated buildings of this study suggest, the use of pollution-sorption on walls may be an efficient control method, even though it was not originally a deliberate part of the design of these buildings. There may be many reasons to use mechanical air-conditioning, mainly from a desire for strict climate control, but it comes at a cost (Table 2). The high cost of climate control in the Royal Library is mainly due to the use of cooling in summer. The moderate energy consumption of the National Museum and the private archive is due to winter heating and summer dehumidification. The State Archives' new buildings have similar energy consumption per cubic meter of storage space.

Although experience shows that it is indeed possible to reach a very high level of pollution control for buildings with forced ventilation, the quality of this depends crucially on a constantly well-functioning filter system. Any failure, such as exhausted filter media, or filter leaks, will instantly cause an increased ingress of pollutants due to the high air intake rate. And filtration itself consumes energy too, via the ventilation fan needed to drag the air through the filter matrix. As a rule of thumb, when ventilating at 1 cubic meter of air per second, there is an annual cost of about 15 kWh for each 1 Pa pressure drop caused by air resistance in the filters.

The dosage and effect of nitrogen dioxide

The measurements of nitrous acid inside and outside the new State Archives building showed an indoor/outdoor concentration ratio of up to 600% in winter. Although some nitrous acid was present in the ambient air, and therefore infiltrating the building by ventilation, the I/O ratio still reflects a high indoor generation rate. When taking the ambient concentration, ventilation rate, and the volume of the room into account, the additional indoor generation of nitrous acid was calculated to be up to 3500 µg $hour^{-1}$ for the full room (in winter). This is molar equivalent to ca. 4700 µg $hour^{-1}$ of nitric acid, which will form on and be left to react with hygroscopic surfaces, including those of books and other archival objects present in the room.

Assuming the area-to-surface ratio inside a typical archive to be about 3 m^2/m^3, of which about half represents the building interior and the other half represents the items in the collection, the area-specific formation rate of nitric acid in the new building varied between 0.64 µg m^{-2} $hour^{-1}$ in winter and 0.28 µg m^{-2} $hour^{-1}$ in summer. On a yearly basis, this accumulated to about 4 mg m^{-2}.

The reason why the production of indoor nitrous and nitric acid was higher in winter is mainly due to a higher ambient nitrogen dioxide level because of the increased combustion from the heating of buildings in the city. This causes a higher flux of pollutants into the archives, even though the I/O ratio was maintained constant.

For the old State Archives building, the nitric acid formation rate was much lower. This is reflected in the lower I/O ratio of nitrous acid (sometimes <100%), but primarily it is a consequence of the infiltration rate of nitrogen dioxide which is ten times lower. The area-specific surface formation of nitric acid was < 0.1 mg m^{-2} annually.

For both State Archives buildings, the surface removal rate (derived from the Weschler et al. model) was in the order of 8-10 room volumes per hour for ozone and 0.4-0.5 room volumes per hour for nitrogen dioxide. However, due to the ten-times-higher ventilation rate of the new archive, the absolute flux of pollutants into this building (and the subsequent deposition rate) was also higher, which is reflected in the higher area-specific values for nitric acid formation.

Ozone is a strong oxidant which engages in direct oxidation of paper and other archival materials, e.g. by breaking double bonds in the molecular structure of the material. Nitric acid is a strong acid (pKa = -1.5) and will cause acid hydrolysis of the organic materials in archival records, as well as corrosion on metal surfaces. A well-known phenomenon is the yellowing and weakening of paper, e.g. on the edges of a book, which is due to the impact of air pollution. The high level of air pollutants, which may flow into archives in urban settings, will contribute significantly to the environmental impact on the stored materials, unless retarded by ventilation filters or a low air exchange rate.

CONCLUSION

As shown by the calculations obtained from the monitoring at the State Archives buildings, in an urban setting nitric acid will be formed in high amounts on indoor surfaces when the ventilation rate is high. This is due to a high ingress of nitrogen dioxide from ambient air. Although the actual state of the stored paper records was not investigated in this study, a yearly accumulation of up to 4 mg m^{-2} of nitric acid must be considered to be a significant deterioration factor, taking the acid dissociation constant (pKa=-1.5) of nitric acid into account.

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