

# Monitoring indoor air pollution in the stacks of the Swiss National Library

G. Di Pietro<sup>1</sup>, A. Blüher<sup>2</sup> and G. Grossenbacher<sup>2</sup>

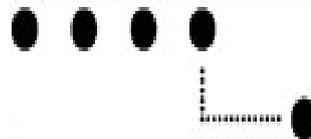
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Schweizerische Eidgenossenschaft  
Confédération suisse  
Confederazione Svizzera  
Confederaziun svizra

Eidgenössisches Departement des Innern EDI  
Bundesamt für Kultur BAK  
**Schweizerische Nationalbibliothek NB**



**Bern University of Applied Sciences**

## Aims of the project

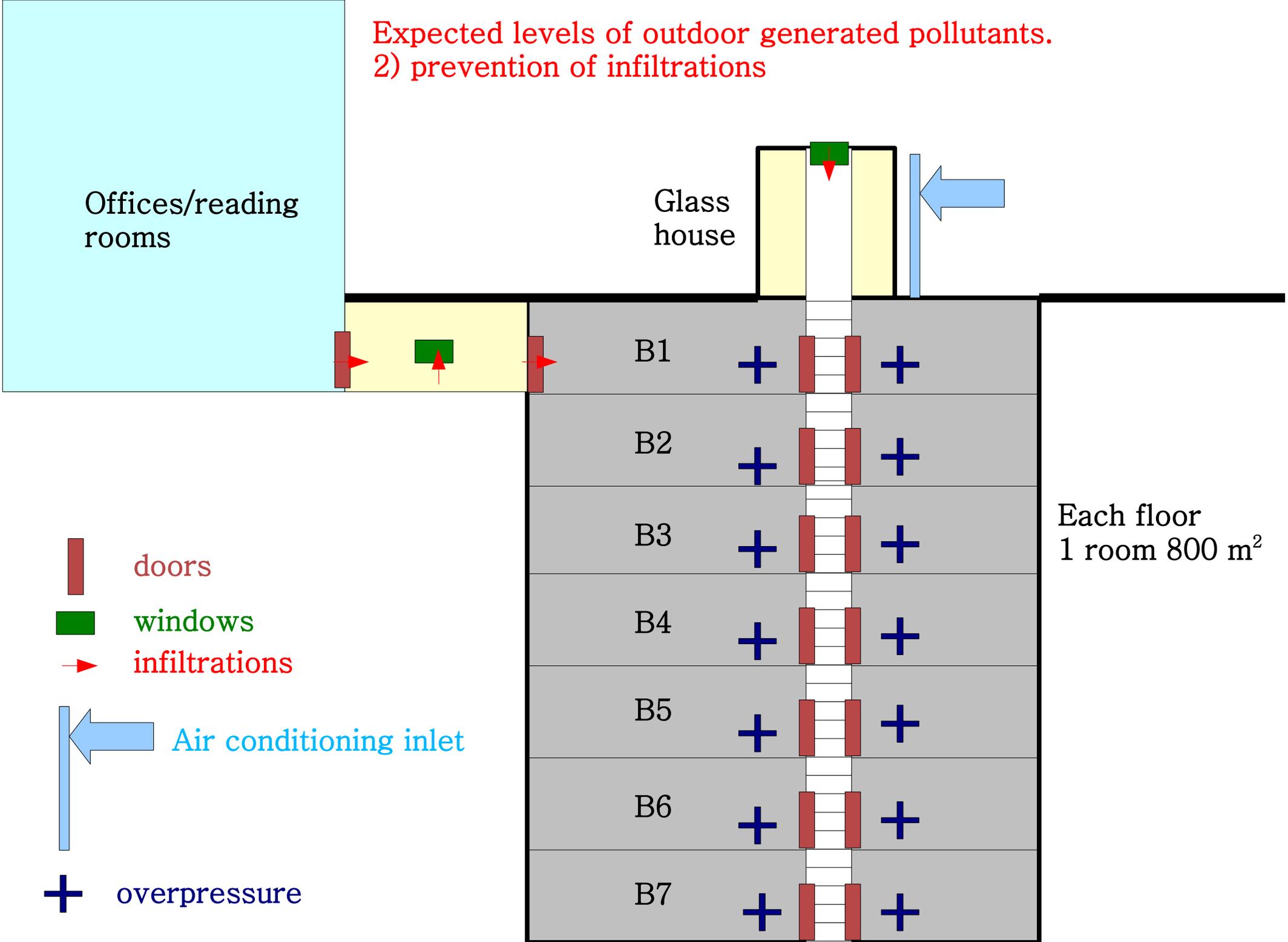
- Determine the predicted paper degradation due to air pollution in the library
- Determine the efficiency of control measures (filters): should the “filter policy” be changed ?
- Efficiency of monitoring device (OnGuard)



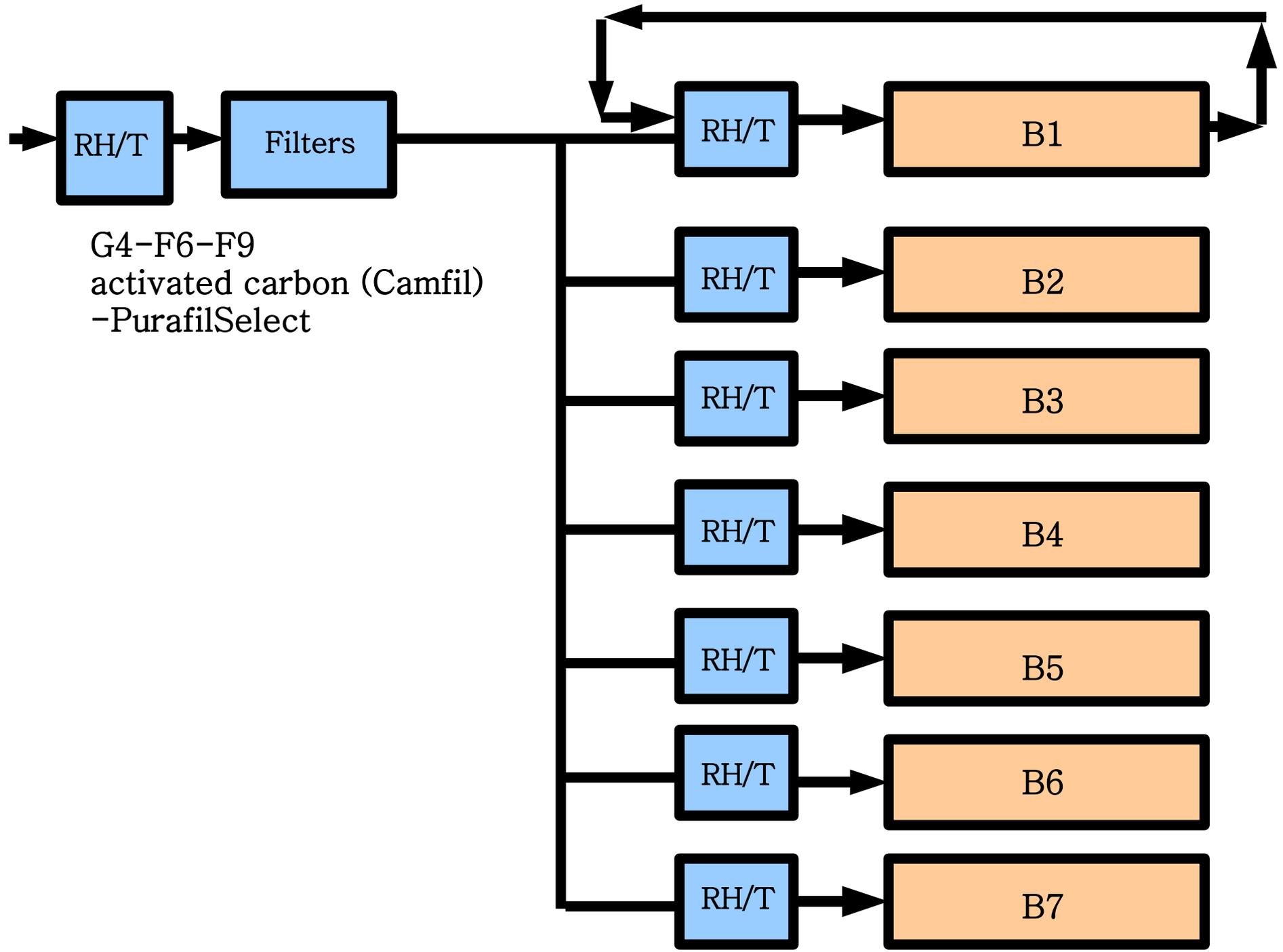
Expected levels of outdoor generated pollutants.  
1) low polluted area



Expected levels of outdoor generated pollutants.  
2) prevention of infiltrations



Expected levels of outdoor generated pollutants. 3) Filters in air conditioning system



G4-F6-F9  
activated carbon (Camfil)  
-PurafilSelect

RH/T

Filters

RH/T

B1

RH/T

B2

RH/T

B3

RH/T

B4

RH/T

B5

RH/T

B6

RH/T

B7

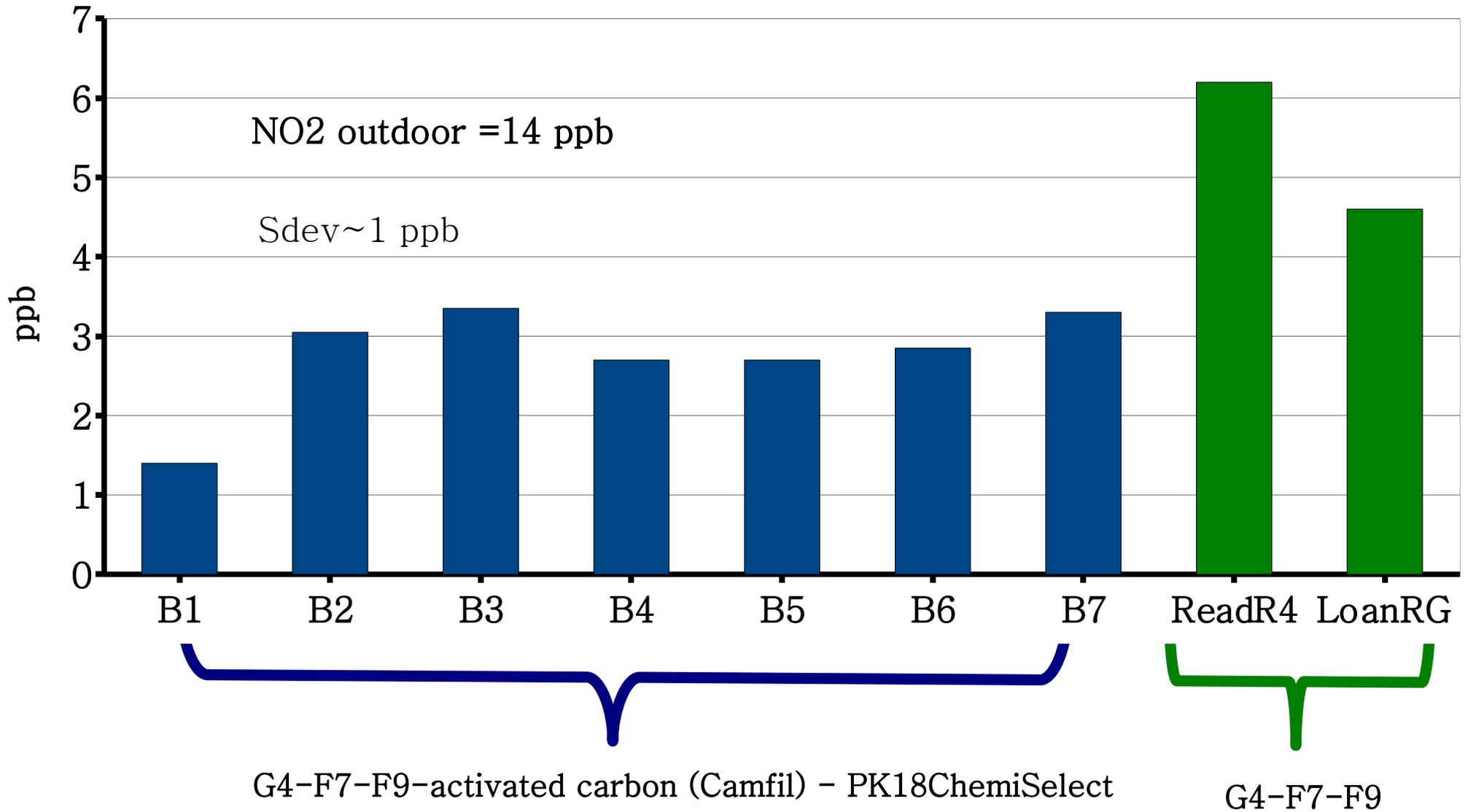
## Indoor air pollution monitoring campaign

- $\text{NO}_2$ ,  $\text{CH}_3\text{COOH}$ , alcohols,  $\text{O}_3$ , aldehydes
- passive samplers



# Results

NO<sub>2</sub> concentration in depot and reading rooms





## During storage and shipping, nitrogen oxides can cause rapid yellowing and degradation of pulp and paper products

By X. Zou

**Abstract:** Rapid yellowing and degradation of pulp and paper products have usually been associated with the effect of light or extreme heat. In this study, we found that exposure to  $\text{NO}_x$ , even at very low concentrations can cause rapid yellowing and degradation of pulp or paper. This result explains the rapid yellowing and degradation often observed during overseas shipping or short-term storage. To prevent this, it is recommended that  $\text{NO}_x$  concentration should be monitored and controlled, and/or paper should be properly wrapped during shipping and storage.

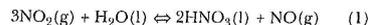
**R**APID YELLOWING and degradation of pulp and paper products are usually due to the effect of light or extreme heat [1,2]. However, rapid yellowing of mechanical pulps and newsprint, and significant degradation of market pulps have often been observed during short-term storage in warehouses or during overseas shipping. These phenomena cannot be explained by the effect of light or heat because it happens in the dark, and in some cases, even in a temperature and humidity controlled atmosphere.

Air pollutants (e.g.,  $\text{SO}_2$  and  $\text{NO}_x$ ) have always been a concern to long-term degradation of materials such as paper, film, plastics and metal [3]. Zinn et al. found that the air pollutants in storage atmospheres cause degradation of colour photographs [4]. Wan and Depew observed that lignin-containing paper suffers a very rapid yellowing and degradation when exposed to extremely high concentrations of  $\text{NO}_x$  [5]. A more recent study on the effect of air pollutants showed that at a low concentration of 10-20 ppm, air pollutants (mainly  $\text{NO}_x$ ) can cause significant degradation and reduction in brightness in lignin-containing paper [6-8]. These results may explain the yellowing and degradation of paper products without light and heat. The objective of this paper is to show that  $\text{NO}_x$  is indeed the culprit for rapid yellowing and degradation, even at low  $\text{NO}_x$  concentrations occurring in practical situations.

### CHEMISTRY ASPECT

$\text{NO}_2$  is the most stable nitrogen oxide in the exhaust from fuel burning at very high temperatures ( $>1,100^\circ\text{C}$ ). It is a strong oxidant and an acidic gas.  $\text{NO}_2$  can interact with paper in two ways:

**Acidification and acid-catalyzed hydrolysis:** Since paper usually contains a certain amount of moisture (5-10% of total paper weight),  $\text{NO}_2$  can readily react with the water to form acids according to the following overall reaction [4]:



For every 3 moles of  $\text{NO}_2$  that absorb and react, 1 mole of  $\text{NO}$  will be produced and absorbed, while 2 moles of  $\text{HNO}_3$  will accumulate in paper. No significant amounts of other nitrogen

oxides such as  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  are formed at room temperatures [9]. Since  $\text{NO}$  is always in equilibrium with  $\text{NO}_2$ , the total concentration of nitrogen oxides is the sum of the concentrations of  $\text{NO}_2$  and  $\text{NO}$  ( $[\text{NO}_x] = [\text{NO}_2] + [\text{NO}]$ ). The absorption of  $\text{NO}_2$  results in significant acidification of paper which, in turn, leads to acid-catalyzed hydrolysis of cellulose.

**Oxidation:** Both cellulose and lignin can be attacked directly by strong oxidants such as  $\text{NO}$  and  $\text{NO}_2$ . The attack on cellulose leads to depolymerization of cellulose and loss of mechanical strength while the attack on lignin can lead to yellowing.

### EXPERIMENTAL

#### Apparatus — environmental chamber

An automated environmental chamber was used to generate desired concentrations of  $\text{NO}_x$ , as previously described in details [7,8]. The temperature, relative humidity and concentration of  $\text{NO}_x$  in the chamber can be controlled.

#### Samples

Standard handsheets were made from lignin-containing pulps (TMP and BCTMP) and lignin-free pulp (cotton fibres). Handsheets of BCTMP and cotton were also made with the addition of 2% calcium carbonate. The initial properties of the above handsheets such as pH, degree of polymerization (DP), brightness and zero-span tensile strength, are summarized in Table I. More detailed information can be found in the literature [8].

#### Exposure and analysis

Paper samples were suspended in the environmental chamber and exposed to various concentrations of  $\text{NO}_x$  for different time periods at  $23^\circ\text{C}$  and 50% RH. After each exposure experiment, brightness, strength, and chemical properties of the exposed papers were measured. Details of the testing procedures can be found in previous publications [6-8].

### RESULTS

#### I. Effect of $\text{NO}_x$ exposure on yellowing

The effect of  $\text{NO}_x$  concentration on yellowing is shown in Fig. 1 for spruce BCTMP and in Fig. 2 for spruce TMP. As can be seen, increasing  $\text{NO}_x$  concentration significantly increases the reduc-



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## Effect of $\text{NO}_2$ on paper

Zou, X. (2004).

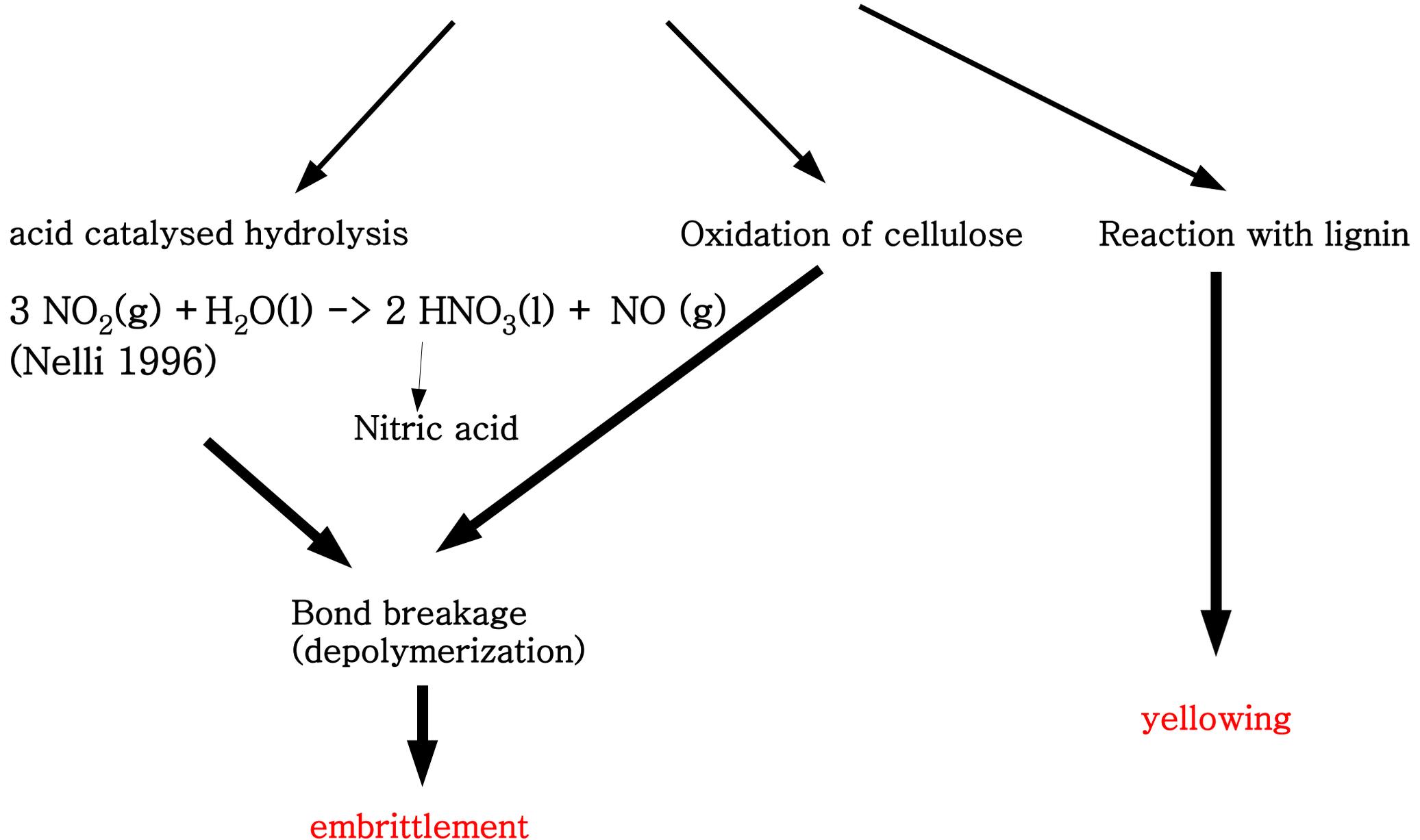
"During storage and shipping, nitrogen oxides can cause rapid yellowing and degradation of pulp and paper products."

Pulp & Paper-Canada 105(3): 51-54.

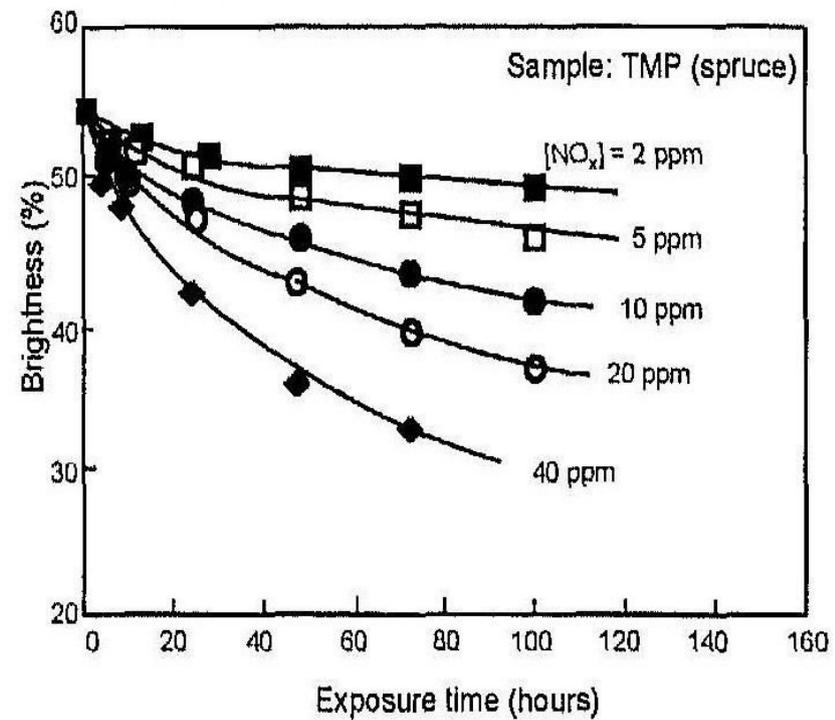
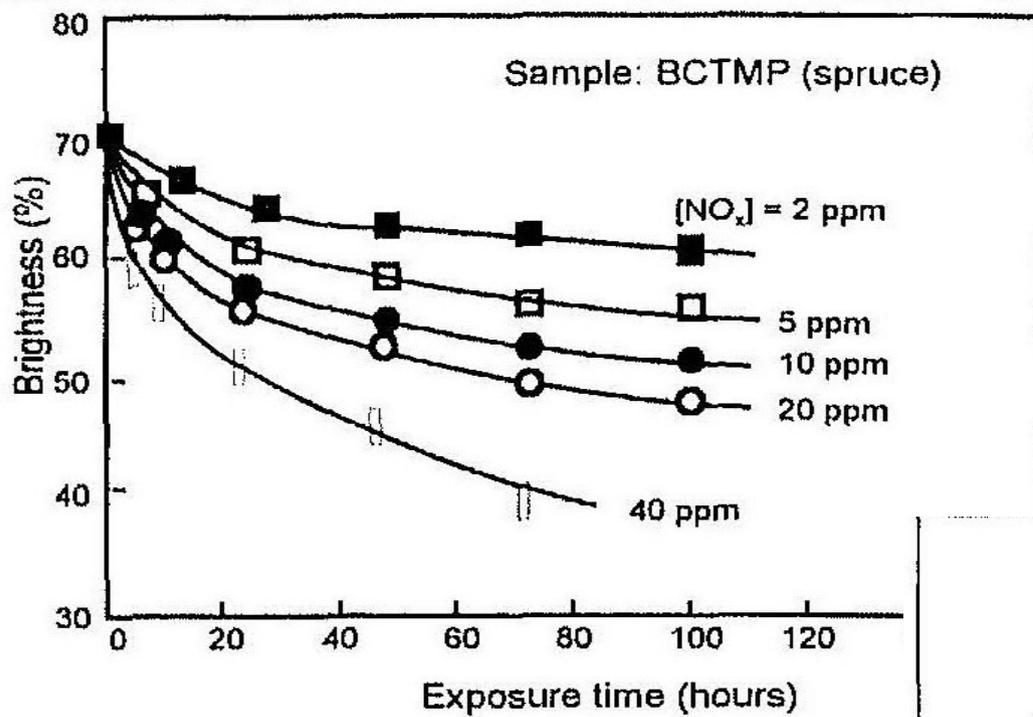
Paper samples exposed to  $\text{NO}_2$  in ventilated chambers. Color and DP measurements.

=>  $\text{NO}_2$  uptake is maximised => worst case

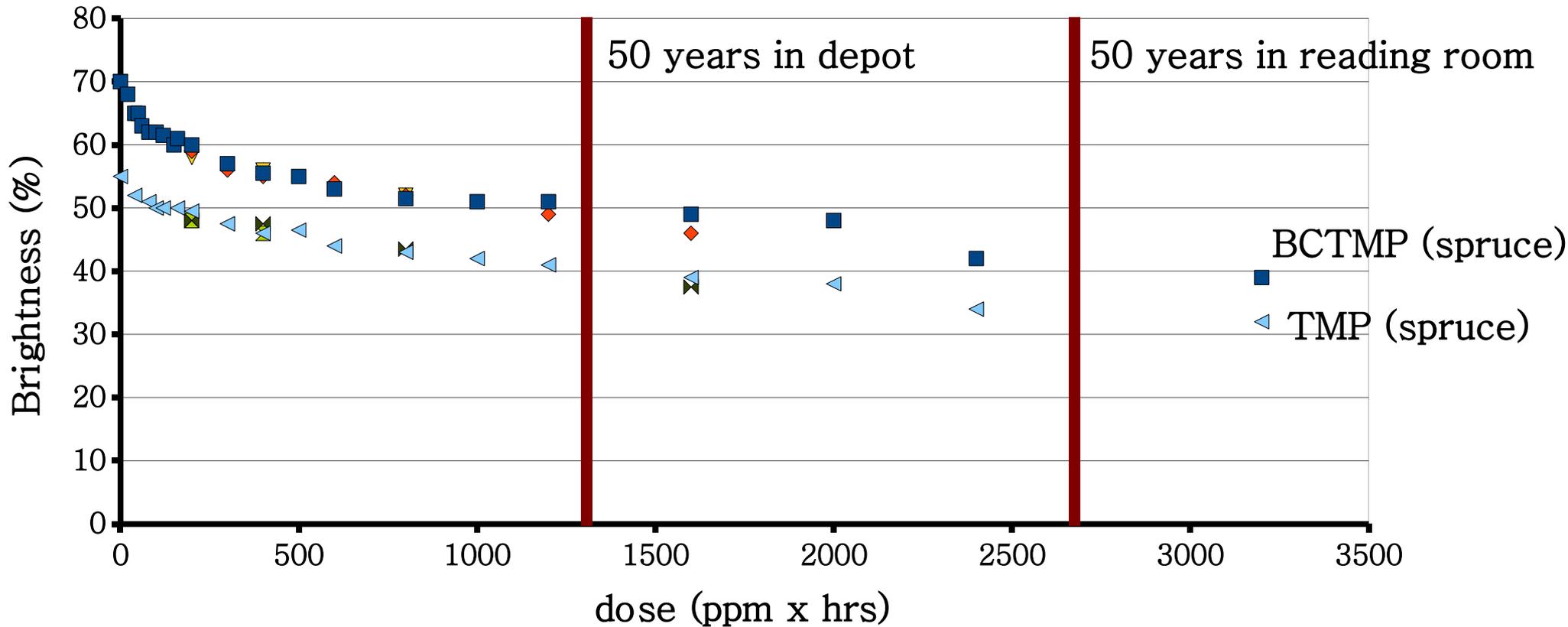
# Effect of NO<sub>2</sub> on paper Chemistry



# Yellowing (Zou, 2004)



Loss of Brightness of paper  
after exposure to NO<sub>2</sub>  
(from Zou, 2004)

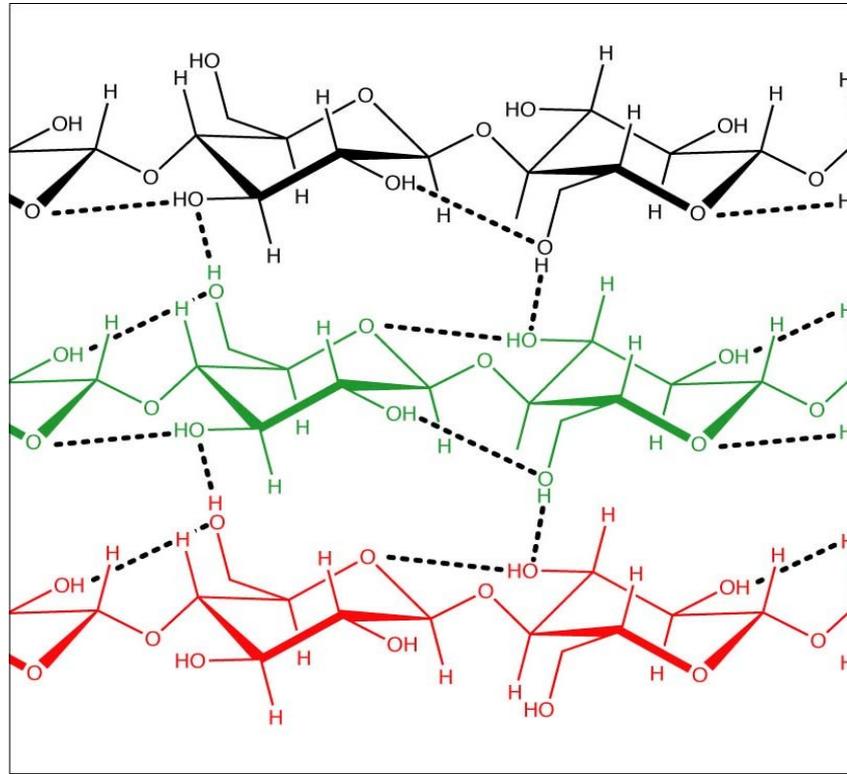


Dose absorbed in 50 years

Depot 1300 ppm x hrs => 15 -20% brightness reduction

Reading room 2600 ppm x hrs => 25-30% brightness reduction

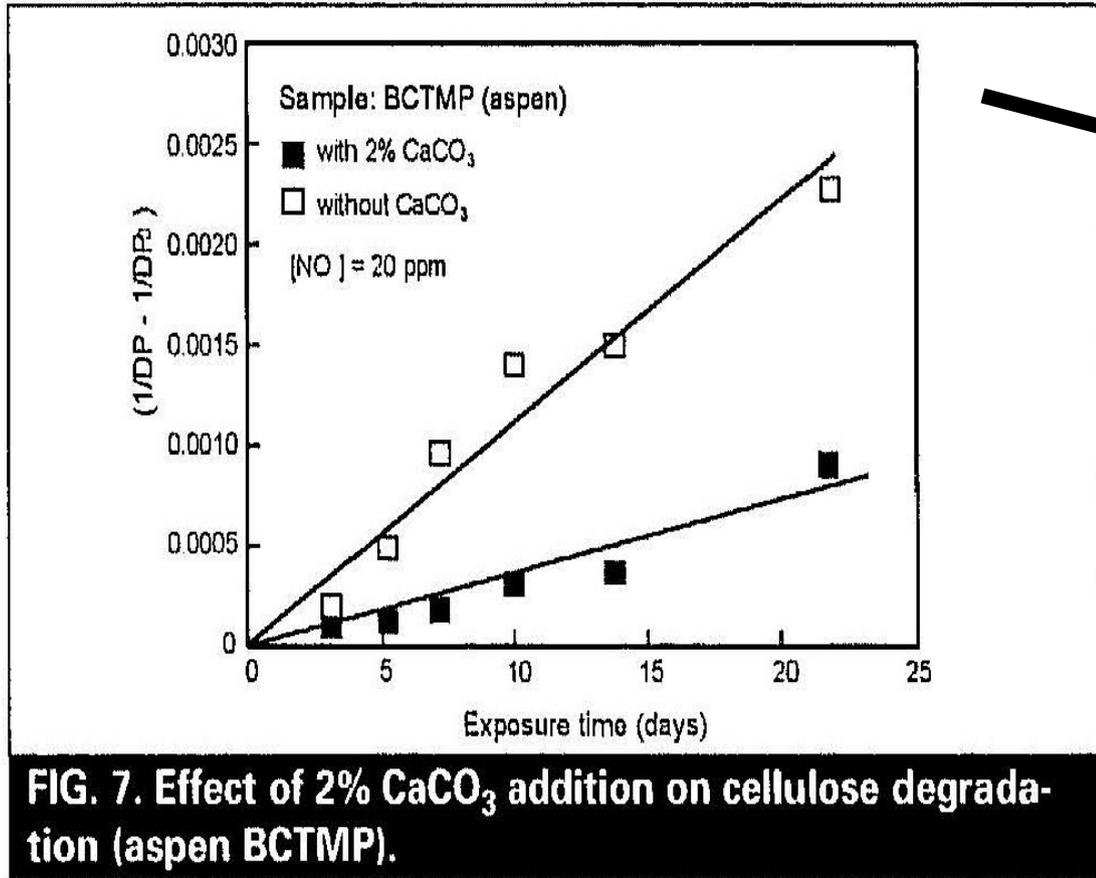
# Bond Breakage (Depolymerization) (Zou, 2004)



$k$  = rate of bond breakage = how many bonds between two glucosid units are broken per unit time is related to the change of Degree of Polymerization  $DP$

Ekamstam equation

$$\frac{1}{DP(t)} - \frac{1}{DP(0)} = k \times t$$



BCTMP (aspen), 20 ppm NO<sub>2</sub>, 23 C, 50% RH



k constant

$$\frac{1}{DP(t)} - \frac{1}{DP(0)} = k \times t$$

$$k = 1.6 \times 10^{-6} \text{ hr}^{-1}$$

1) calculate k for NO<sub>2</sub> = 3 ppb and 6 ppb

2) compare with k for depolymerization without external pollutants

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Zou, X., T. Uesaka, et al. (1996). "Prediction of paper permanence by accelerated aging 1. Kinetic analysis of the aging process." Cellulose 3(4): 243-267.

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V)  $k = k_0 + k_1$

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V)  $k = k_0 + k_1$

VI)  $k_1 = D \times [NO_2](g)$

$k(20 \text{ ppm}) = 1.6 \times 10^{-6} \text{ hr}^{-1}$  

$k_1(3 \text{ ppb}) = 2.4 \times 10^{-10} \text{ hr}^{-1}$

$k_1(6 \text{ ppb}) = 4.8 \times 10^{-10} \text{ hr}^{-1}$

## 2) compare with k for depolymerization without external pollutants

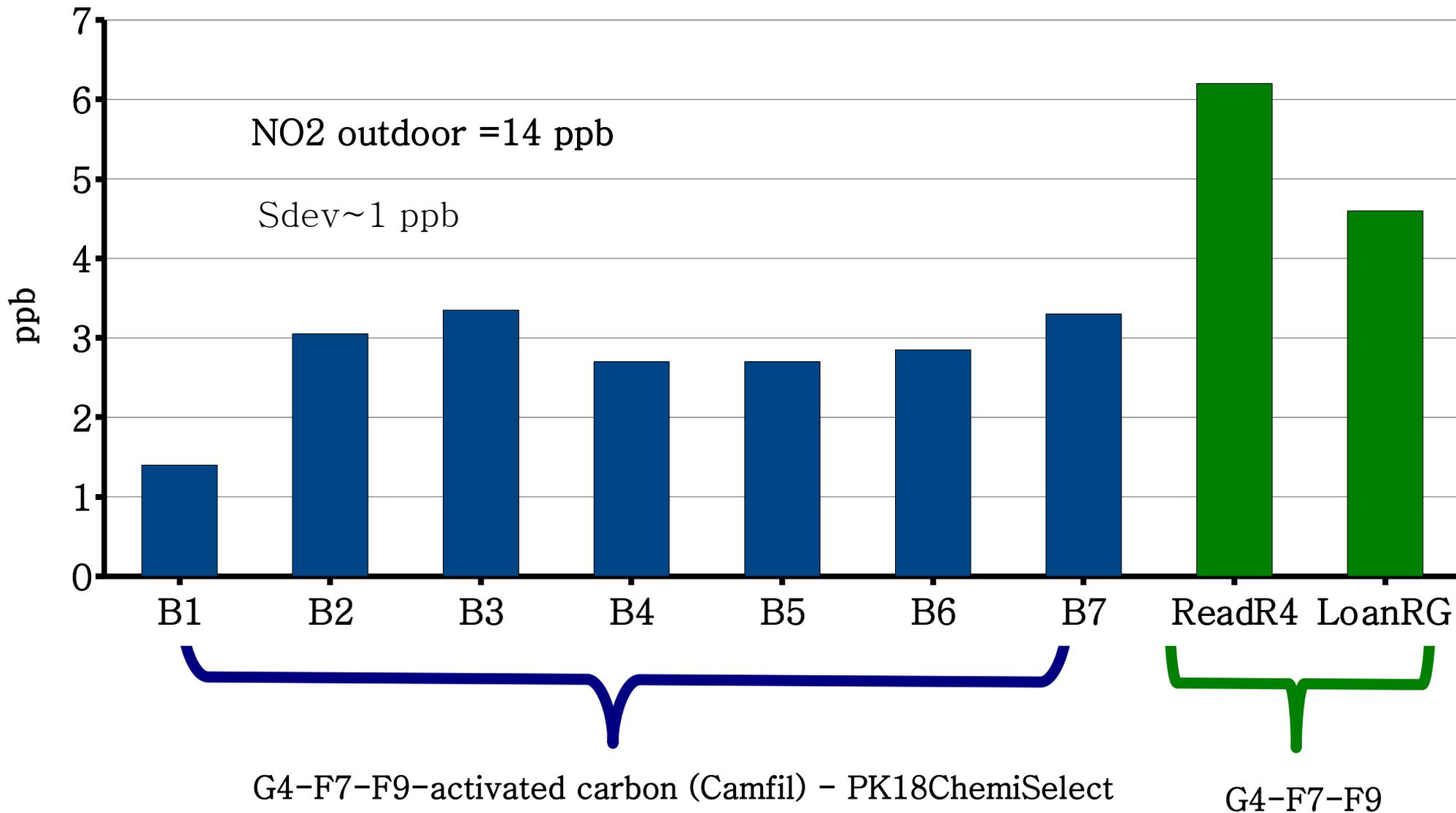
- No data for BCTMP at 50% RH
- Data for chemical pulps at 75% RH (Zou 1996)

chemical pulps at 75% RH, 23 C no pollutants	BCTMP pulp at 50% RH, 23 C 3 ppb and 6 ppb NO <sub>2</sub>
$k_0 = 1.2-1.9 \times 10^{-9} \text{ hr}^{-1}$	$k_1 = 2.4-4.8 \times 10^{-10} \text{ hr}^{-1}$

Degradation rates are comparable!

# Results

NO<sub>2</sub> concentration in depot and reading rooms



# How to explain the moderate NO<sub>2</sub> reduction in filtered areas?

Simulation with IMPACT model

<http://www.ucl.ac.uk/sustainableheritage/impact/>

Calculation of inside concentration as a function of:

- Outside concentration
- Air Exchange Rate
- **Filter efficiency E**
- Volume
- Surface of absorbing materials

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E=50%

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Filters 1 year old at time of measurement.

Direct measurements of filter “remaining life” (Purafil) confirms need of filter exchange.

Based on filter capacity, total mass of medium, external NO<sub>2</sub> level and AER filters should last 7 years.

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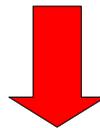


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**Capacity/efficiency of filters smaller than stated (especially at low levels)**

## Filter costs

installation

euro 8000

regular change (1/year)

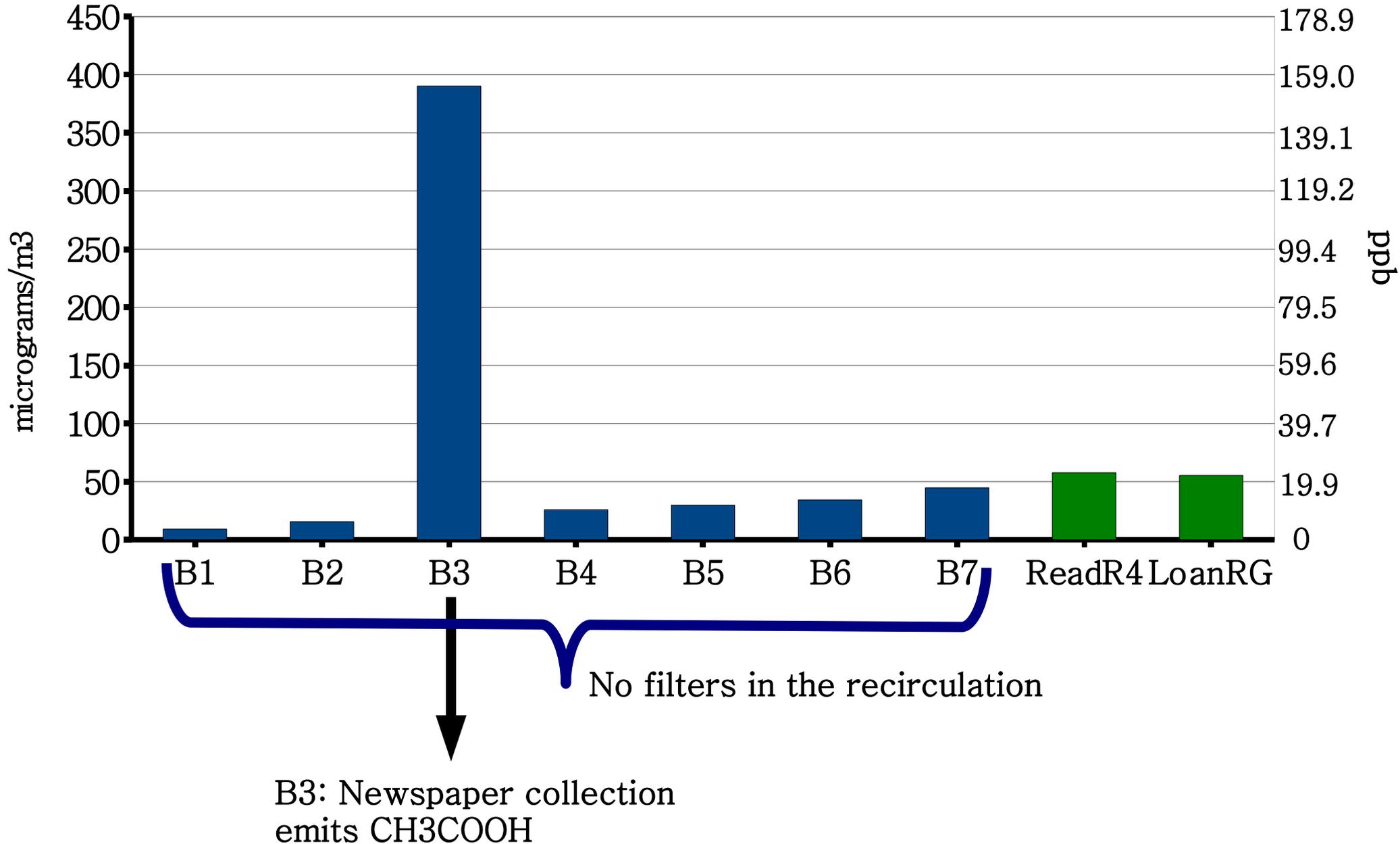
euro 1800/year

energy consumption

euro 400 /year

# Results

CH<sub>3</sub>COOH concentration in depot and reading rooms

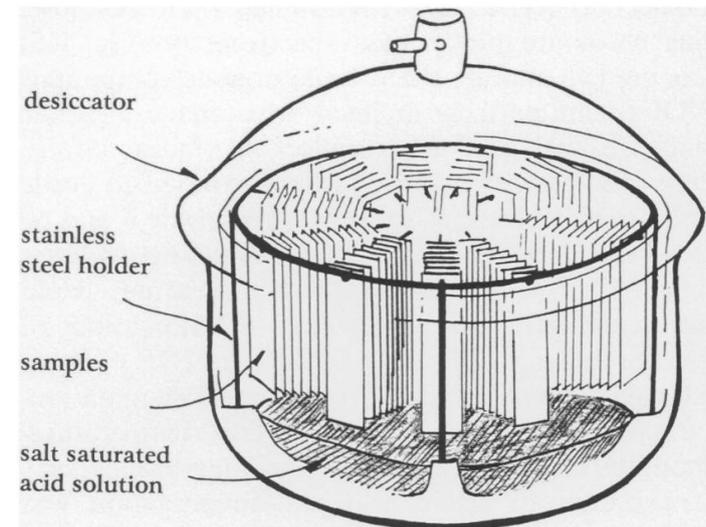


# Effect of CH<sub>3</sub>COOH on neutral paper

Dupont, A. L. and J. Tetreault (2000). "Cellulose degradation in an acetic acid environment." *Studies in Conservation* 45(3): 201–210)

Whatmsn n.1 paper samples exposed to CH<sub>3</sub>COOH in not ventilated dessiccators. pH and DP measurements.

=> CH<sub>3</sub>COOH uptake is slow



## CELLULOSE DEGRADATION IN AN ACETIC ACID ENVIRONMENT

A.-L. Dupont and J. T treault

**Summary**—Gas chromatography-mass spectrometry was used to analyse off-gassing from three archival boxes that had an acidic smell. A number of volatile organic compounds were found, including acetic (ethanoic) acid, likely to be generated by Jade 403, a poly(vinyl acetate/ethylene) adhesive that had been used in the boxes. The aim of this study was to assess the effect of acetic acid vapour on pure cellulose paper using cold extraction pH and viscometric determination of the average degree of polymerization ( $\overline{DP}_v$ ) of cellulose dissolved in cadoxen. Whatman No. 1 paper samples were exposed to 200, 20 and  $3\text{mgm}^{-3}$  of acetic acid vapour for 40 and 80 days. The degree of degradation both immediately after exposure and following artificial aging at  $80^\circ\text{C}$  and 65% RH for 30 and 60 days was significant in all samples except those exposed for 80 days at  $3\text{mgm}^{-3}$ . The results suggest that the effect of acetic acid on paper most likely occurs over the long term after the exposure. Concerns about acid-emitting materials being in contact with or in the vicinity of paper-based materials in museums and archives are discussed, based on these results, and preventive measures are recommended.

### Introduction

Paper-based cultural heritage is often exposed to indoor organic pollutants. Wood products, coatings, silicone-based sealants and poly(vinyl acetate) adhesives—materials that are commonly used in the fabrication of books, frames, display cases or storage containers—all emit acetic (ethanoic) acid [1–3]. Although the effect of acetic acid environments on metals [4–6], calcium-based materials [7–9] and acetate-based films [10] has been studied in recent years, little research has been done on paper-based materials. Acetic acid likely causes hydrolysis of cellulose polymers, but the action of weak acids on cellulose has not been investigated to the same extent as that of strong acids.

The purpose of this study was to quantify the impact of acetic acid environments on cellulose. Gas chromatography-mass spectrometry (GC-MS) was used to analyze the volatile organic compounds (VOCs) emitted from archival boxes made of acidic materials that gave off a noticeable vinegar odour. Pure cellulose paper samples were exposed to acetic acid at concentrations of approximately 1, 6 and 60 times the levels detected in the boxes. The acid was generated by an acid-water-salt mixture. Cold extraction pH and viscometric determination of average degree of polymerization ( $\overline{DP}_v$ ) using cadoxen solvent were used to measure degradation. Samples were aged in controlled temperature-humidity chambers to assess the long-term effects of exposure to acetic acid. An investigation was made to see if there was a correlation between  $\overline{DP}_v$  and pH values in the hope that pH measurements

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*Studies in Conservation* 45 (2000) 201–210

can provide an alternative to the labour-intensive  $\overline{DP}_v$  measurements.

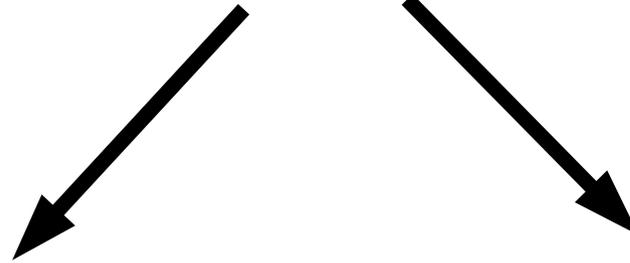
### Experimental

#### Description of the archival boxes and analyses of VOCs

The archival boxes (Solanger) were made of Davey Red Label 'Acid Phree' binder's board (an acid-free board), acrylic-coated buckram cloth (65% polyester and 35% cotton) and Mohawk Superfine lining paper. Jade 403 (a vinyl acetate/ethylene copolymer emulsion) was used to glue the buckram cloth and lining paper on the board. After fabrication, the archival boxes were kept open for three months, at which time they still gave off a strong odour. Three boxes of different dimensions were analyzed: box 1,  $41.2 \times 31.3 \times 9.9\text{cm}$ ; box 2,  $73.5 \times 61.0 \times 6.0\text{cm}$ ; and box 3,  $83.5 \times 68.5 \times 6.0\text{cm}$ . A hole (7mm diameter) was made in each box to allow air sampling. Boxes were kept closed for four days before the first sampling. Between sampling operations, the hole was covered with adhesive tape.

Fifty millilitres of air were sampled from each box and quantitative analyses of VOCs were performed using thermal desorption (Dynatherm Analytical Instruments Inc., model 890) and GC-MS (Hewlett Packard model 5890 with a DBWax-30X capillary column and Hewlett Packard mass spectrometer model 5970). The method is described elsewhere [2]. Four replicates were done per box.

# Effect of $\text{CH}_3\text{COOH}$ on paper Chemistry



acid catalysed hydrolysis  
(of not acid paper)

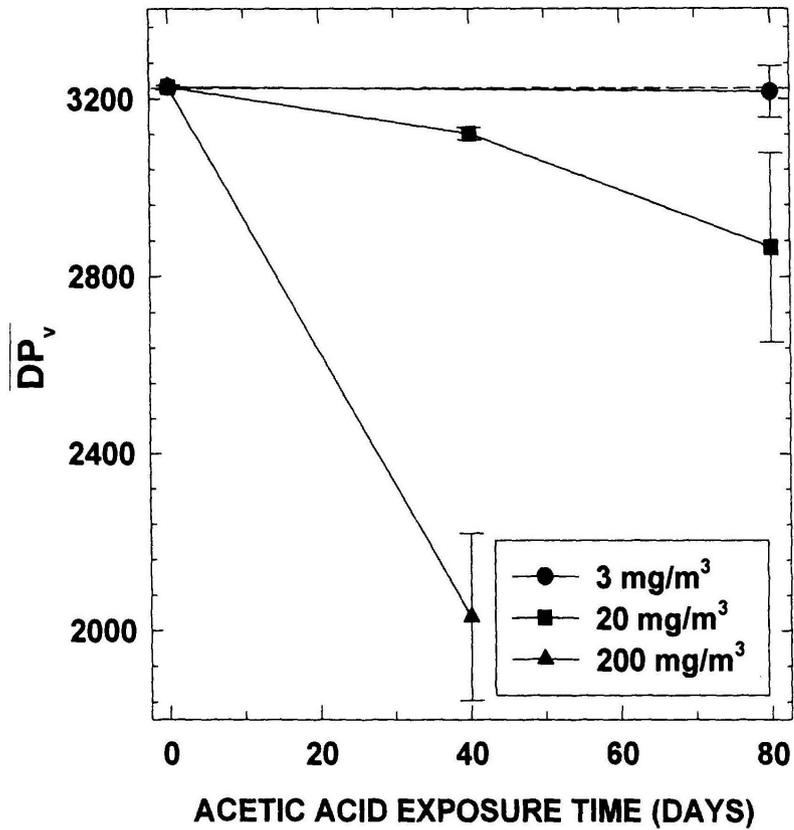
minor yellowing



Bond breakage  
(depolymerization)

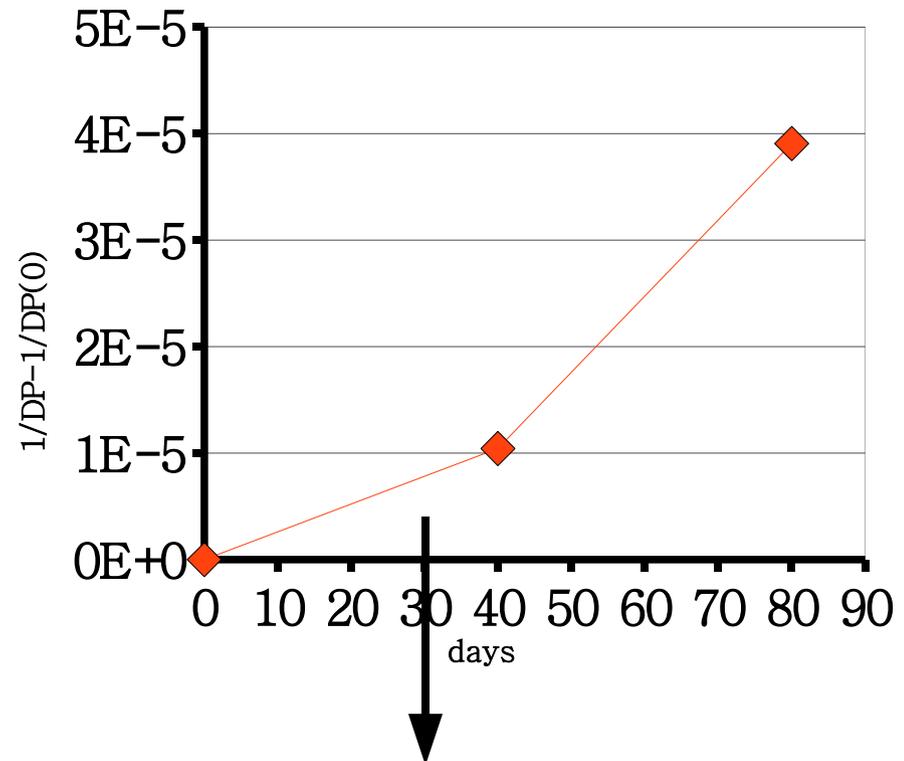
embrittlement

# Whatman n.1 paper



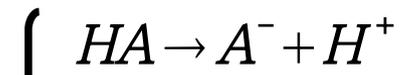
# Effect of 20mg/m<sup>3</sup> CH<sub>3</sub>COOH

## Whatman n.1 paper



**Problem: k is not constant!**

## Slow uptake of acetic acid by paper (F. Ligterink 2010)



Dissociation of acetic acid

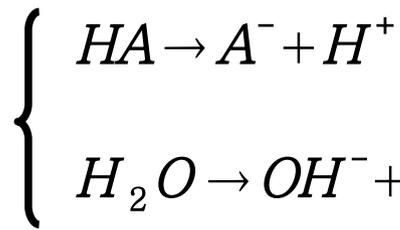
$$K_A = \frac{[A^-] \times [H^+]}{[HA]}$$



Dissociation of water

$$K_W = [OH^-] \times [H^+]$$

## Slow uptake of acetic acid by paper (F. Ligterink 2010)



Dissociation of acetic acid

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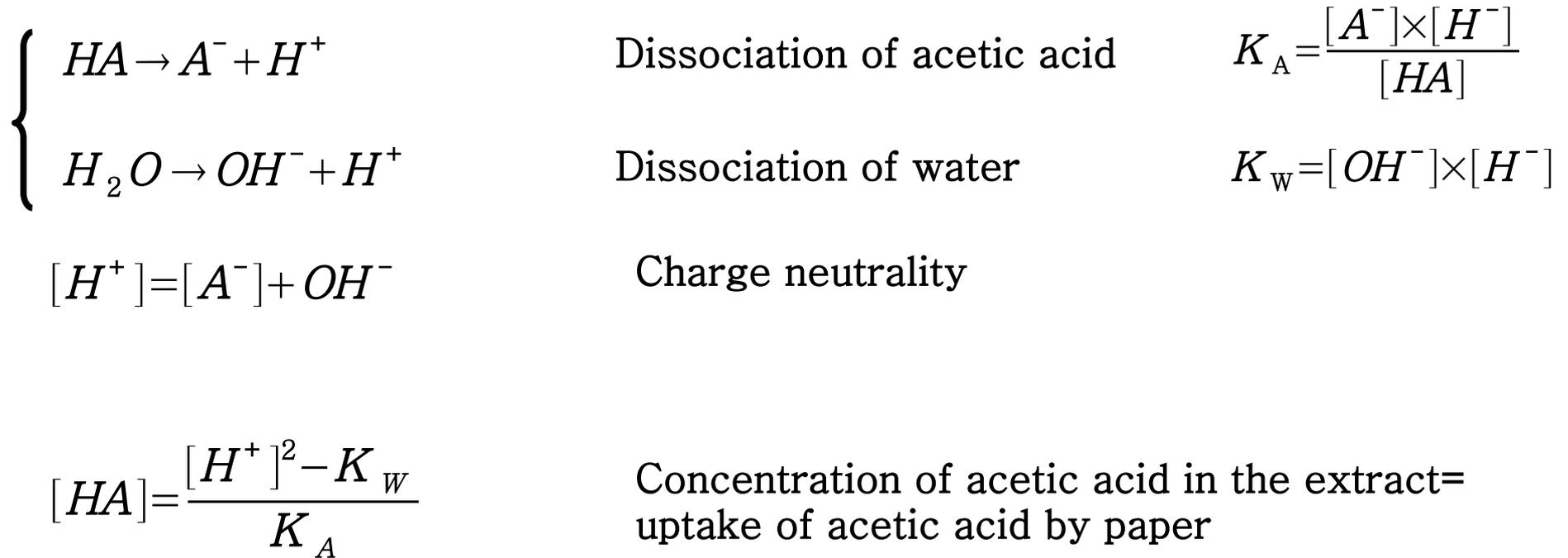
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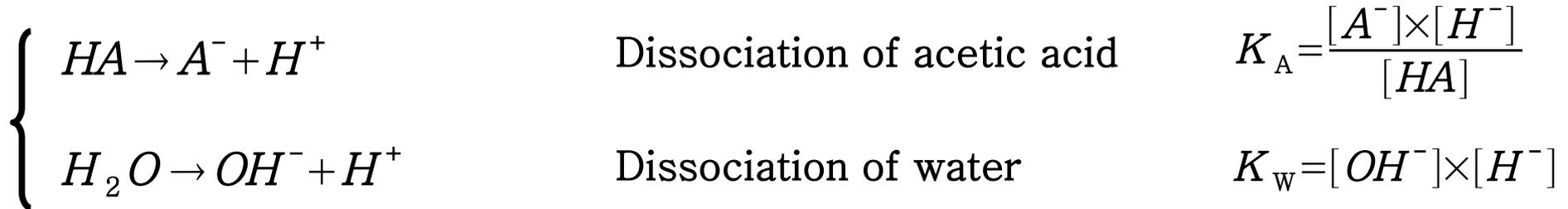
$$[H^+] = [A^-] + [OH^-]$$

Charge neutrality

## Slow uptake of acetic acid by paper (F. Ligterink 2010)



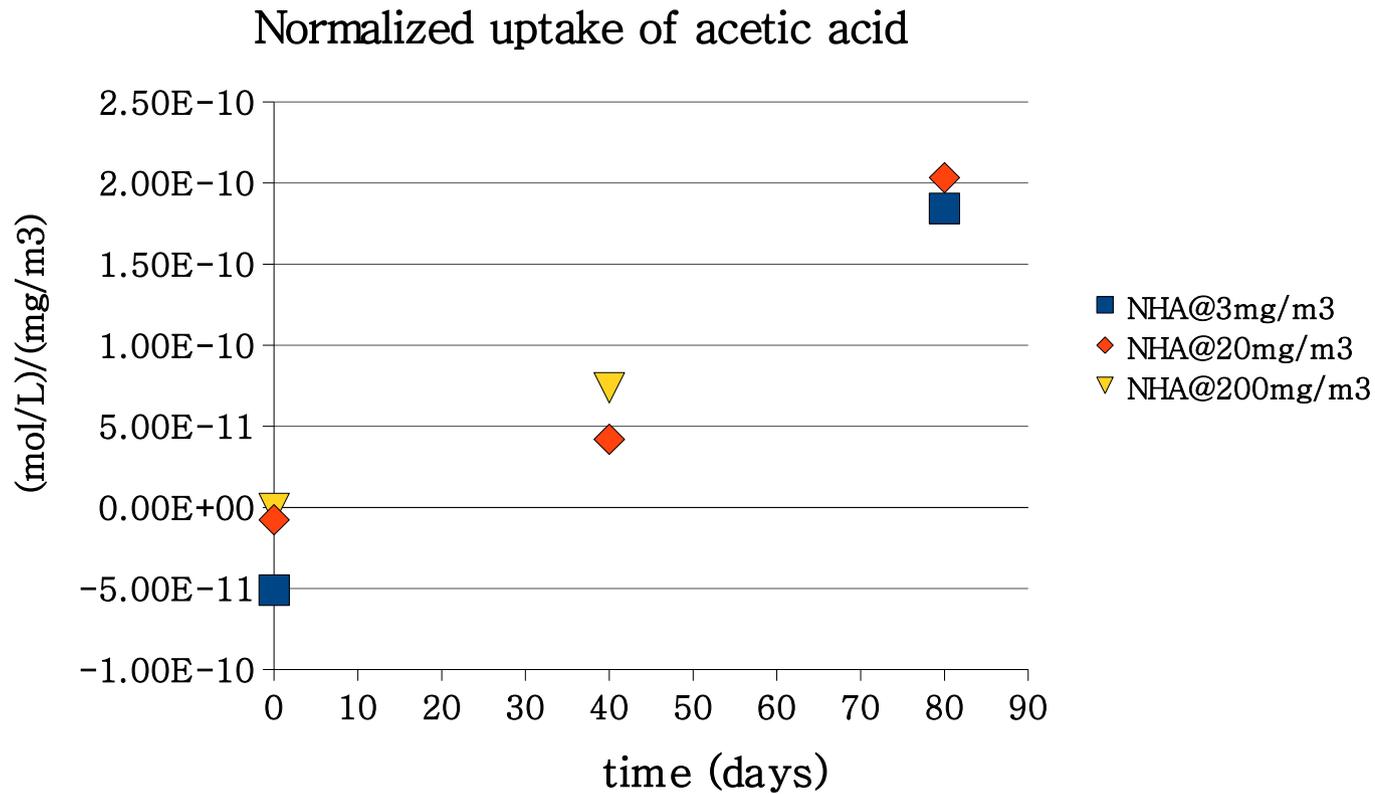
## Slow uptake of acetic acid by paper (F. Ligterink 2010)



$$[H^+] = [A^-] + [OH^-] \quad \text{Charge neutrality}$$

$$[HA] = \frac{[H^+]^2 - K_W}{K_A} \quad \text{Concentration of acetic acid in the extract = uptake of acetic acid by paper}$$

$$\frac{[HA]}{\text{concentration in air}} \quad \text{Normalized uptake of acetic acid by paper}$$



1) all data on a line  $\Rightarrow$  uptake  $\propto$  concentration in air

2) uptake increases with time,  $\text{CH}_3\text{CCOH}$  in paper not in equilibrium  $\rightarrow$   $k$  is not constant



Experimental geometry determines uptake

## Decisions on filters and costs

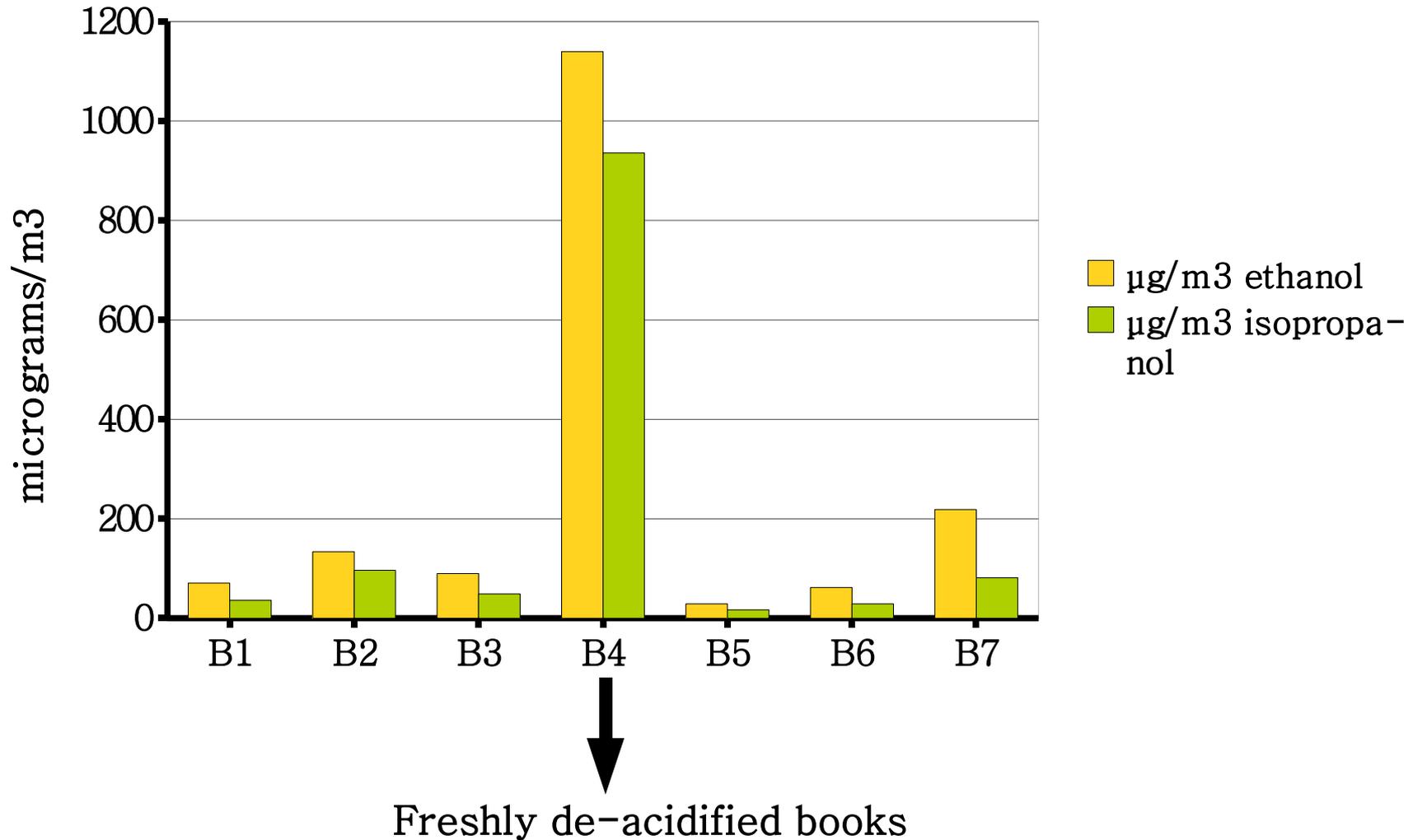
New underground depot:

- main HVAC unit: activated carbon filter (Camfil) + Purafil Select filter
- recirculation on floor with newspapers: Purafil Select CP Blend

	<b>Depot West</b>	<b>Depot East</b>
<b>Main HVAC</b>		
Installation	9000 €	8000 €
Filter change/year	6370 €	1800 €
Energy consumption/year	426 €	400 €
<b>Recirculation</b>		
Installation	14500 €	
Filter change/year	5880 €	
Energy consumption/year	311 €	
<b>TOTAL</b>	<b>36487 €</b>	<b>9800 €</b>
<b>TOTAL/year</b>	<b>12987 €</b>	<b>2200 €</b>
<b>TOTAL</b>	<b>46287 €</b>	
<b>TOTAL/year</b>	<b>14787 €</b>	

# Results

Ethanol and Isopropanol concentration in Depot



- Ethanol and isopropanol used in the de-acidification process (Papersave swiss process)

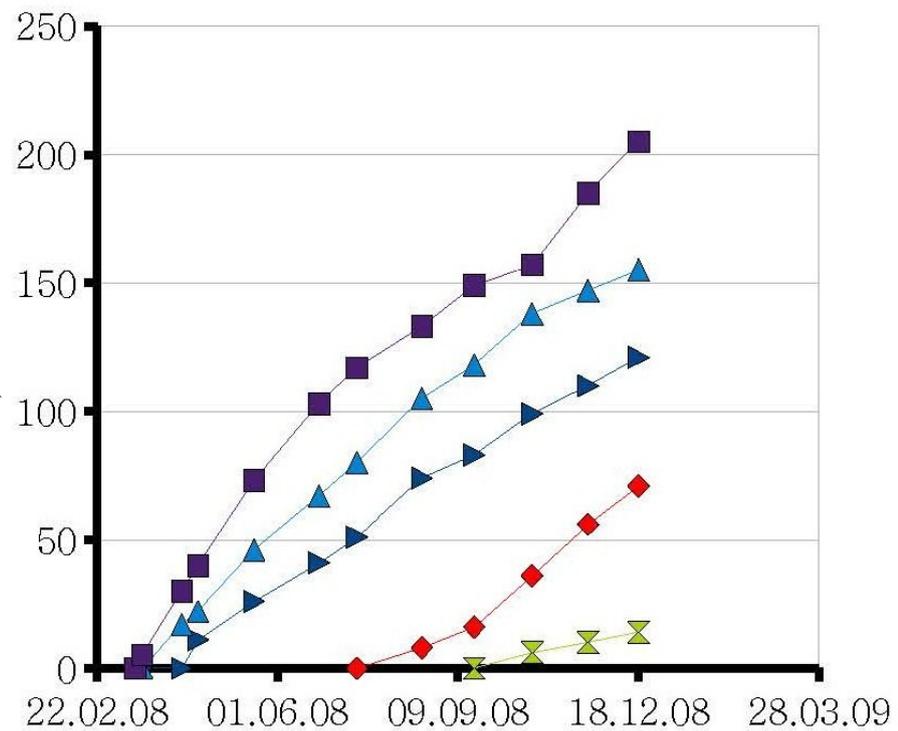
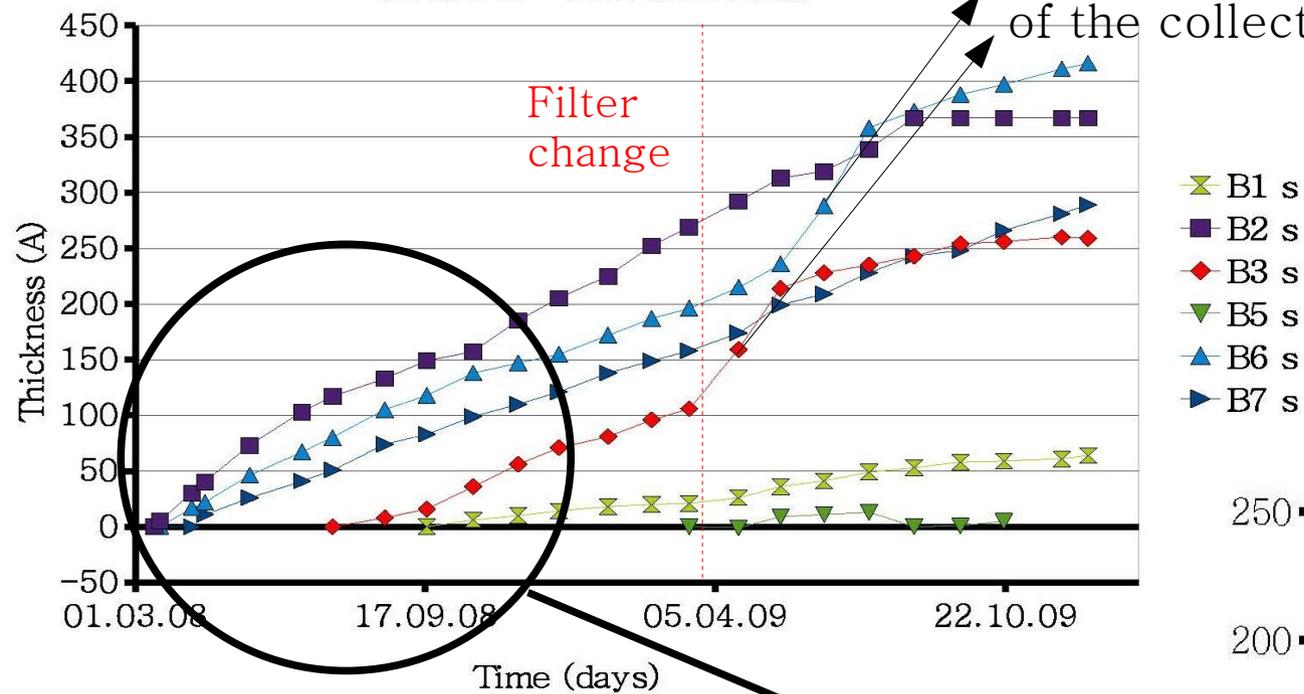
- In B7 no books were de-acidified -> **despite overpressure air mixing among floors through doors and staircase** (during working hours each minute 1 door open)

# Results for On-Guards



Increase of corrosion layer  
on silver- OnGuard 2000

Relocation  
of the collection



- generally very small corrosion increase
- corrosion increases during major events
- no correlation with  $\text{CH}_3\text{COOH}$  concentration
- no correlation with filter change

## Conclusions

- concentration outdoor generated gases ( $\text{NO}_2$ ) small both in filtered and not filtered areas (factor 2 difference)
- effect of this  $\text{NO}_2$  concentration on the paper degradation rate comparable with “natural” degradation ?
- $\text{CH}_3\text{COOH}$  concentration high in room containing the newspaper collection
- corrosion of metals (On Guard) very small and not correlated to  $\text{CH}_3\text{COOH}$  concentration or filter change
- overpressure does not prevent air mixing among rooms