



# The generation of indoor air pollutants from surface reactions

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Morten Ryhl-Svensen  
National Museum of Denmark  
Department of Conservation





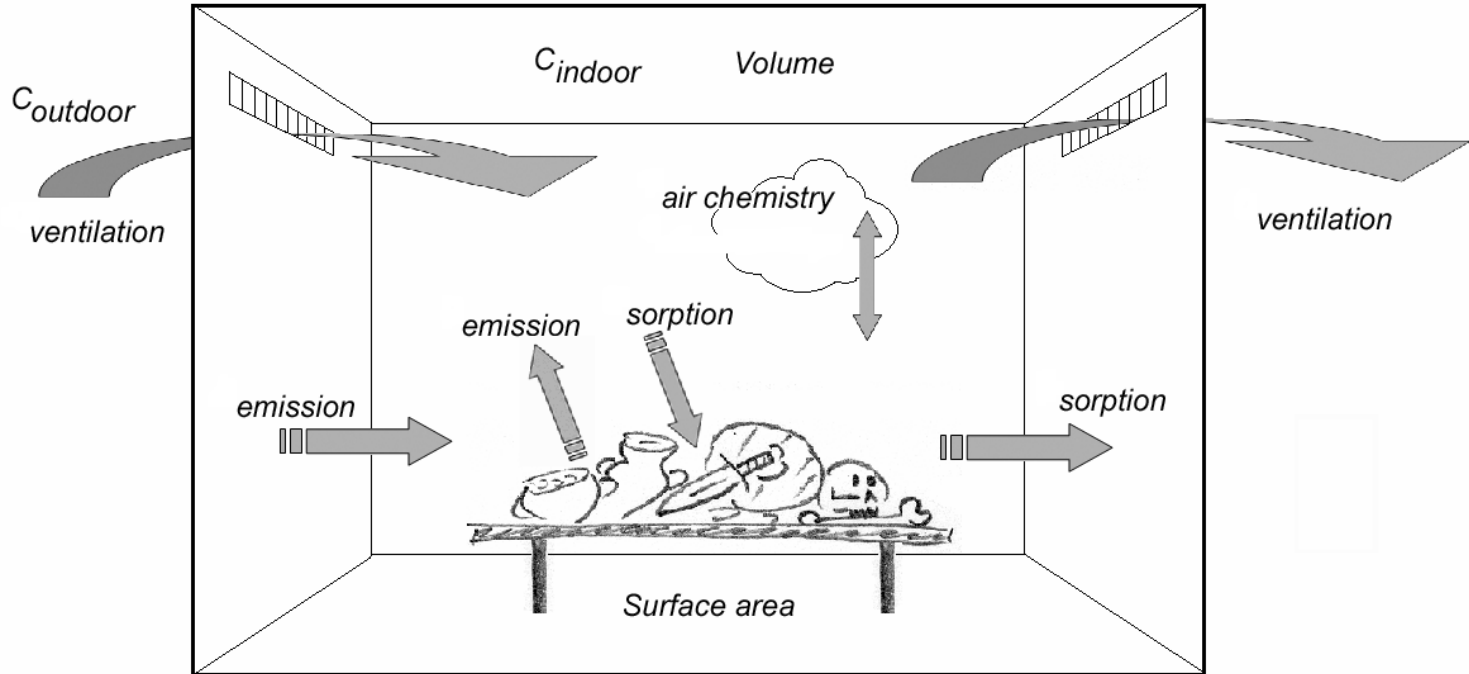
### Museum indoor environments

Pollutants move by free air flow from one zone to another, or are generated internally





# Pollution pathways



At steady-state:

$$C_I = \frac{(C_o \times n) + \left( \frac{G_s + G_g}{V} \right)}{n + K_s + K_g}$$

Ryhl-Svendsen, M., 'Indoor air pollution in museums: a review of prediction models and control strategies', *Reviews in Conservation* 7 (2006) 27-41.



# Mass balance: generation and removal rate

$$C_I = \frac{\left( \frac{G_s}{V} \right)}{n + K_s}$$

Surface removal rate

## Ozone:

- Office **1-4 h<sup>-1</sup>**
- Museum storage **2-3 h<sup>-1</sup>**
- Bedroom **>7 h<sup>-1</sup>**

*(Weschler, 2000)*

*(Ryhl-Svendsen & Clausen, 2009)*

*(Weschler, 2000)*

## Nitrogen dioxide:

- Museum gallery **0.4 h<sup>-1</sup>**
- Storage room **4.5 h<sup>-1</sup>**

*(Blades et al, 2000)*

## Organic acids:

- ?

$$K_s = v_d \left( \frac{A}{V} \right)$$





# Archive for the Arnamagnaean Manuscript Collection, University of Copenhagen

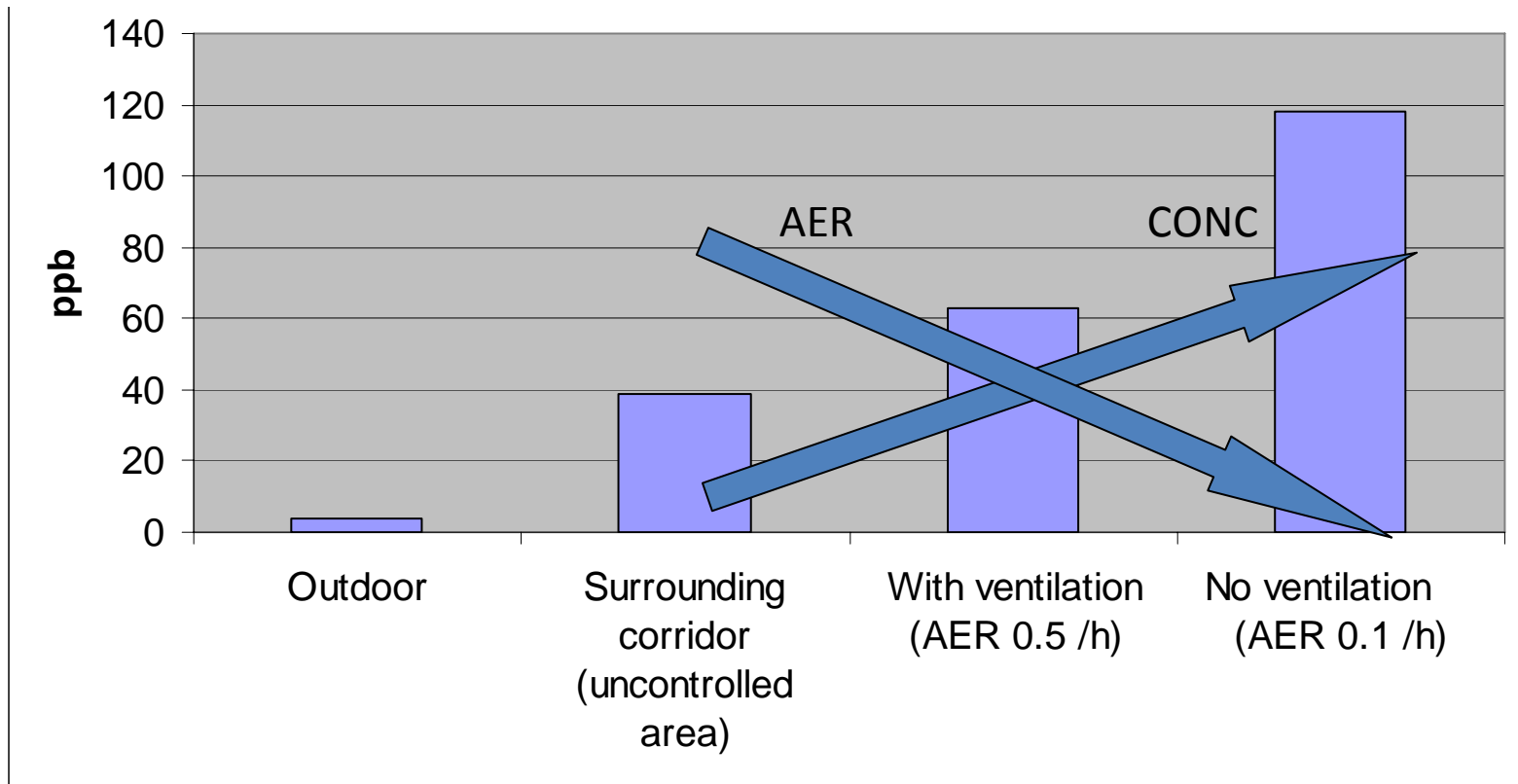




# Indoor generated pollutants

## Dilution by ventilation as expected

### ...But what is the deposition rate?





# Indoor generation mass balance: *organic acids*

For a 120 m<sup>3</sup> room:

- $n=0.14 \text{ h}^{-1}$  (118 ppb = 236  $\mu\text{gm}^{-3}$ )
- $n=0.49 \text{ h}^{-1}$  (63 ppb = 126  $\mu\text{gm}^{-3}$ )

$$C_I = \frac{\left(\frac{G_s}{V}\right)}{n + K_s}$$

Generation rate  $G_s$  (room): **11,200  $\mu\text{g h}^{-1}$**

Surface removal rate  $K_s$ : **0.26  $\text{h}^{-1}$**  (comparable to ventilation)

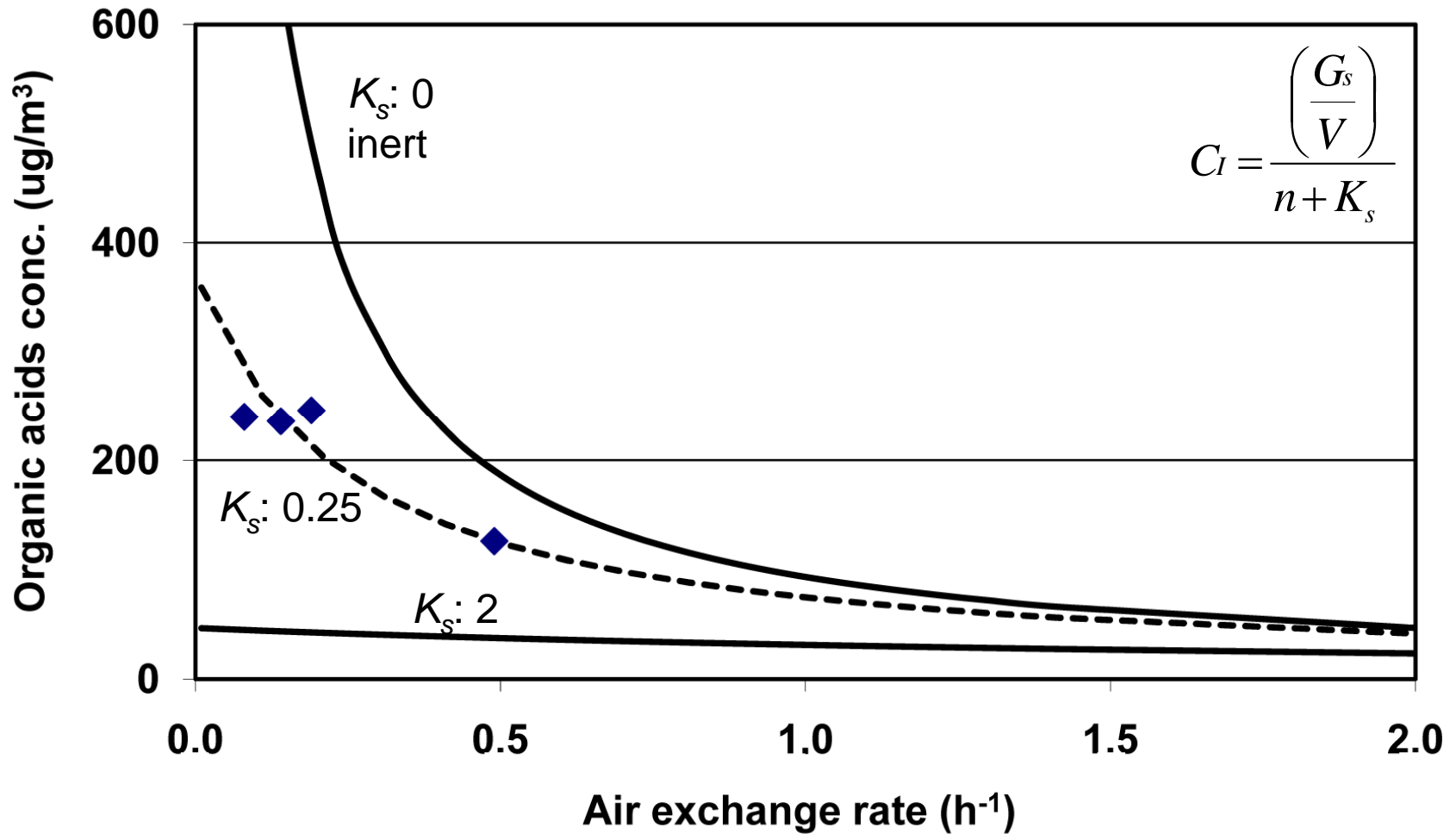
Deposition velocity  $v_d$  (average): **0.07  $\text{m h}^{-1}$**

(assuming surface-to-volume ratio = 4  $\text{m}^2/\text{m}^3$ )

$$K_s = v_d \left(\frac{A}{V}\right)$$



# Control by ventilation – or by passive sorption







# Danish State Archive Regional Branch - Copenhagen





# The building

- Located in central Copenhagen, urban air pollution dominated by traffic (NO<sub>x</sub>)
- Five floors of archival space, each 1600 m<sup>3</sup>
- Air exchange rate about 0.6 per hour
- Mechanical ventilation system, but only dust filtration (no chemical filtration)



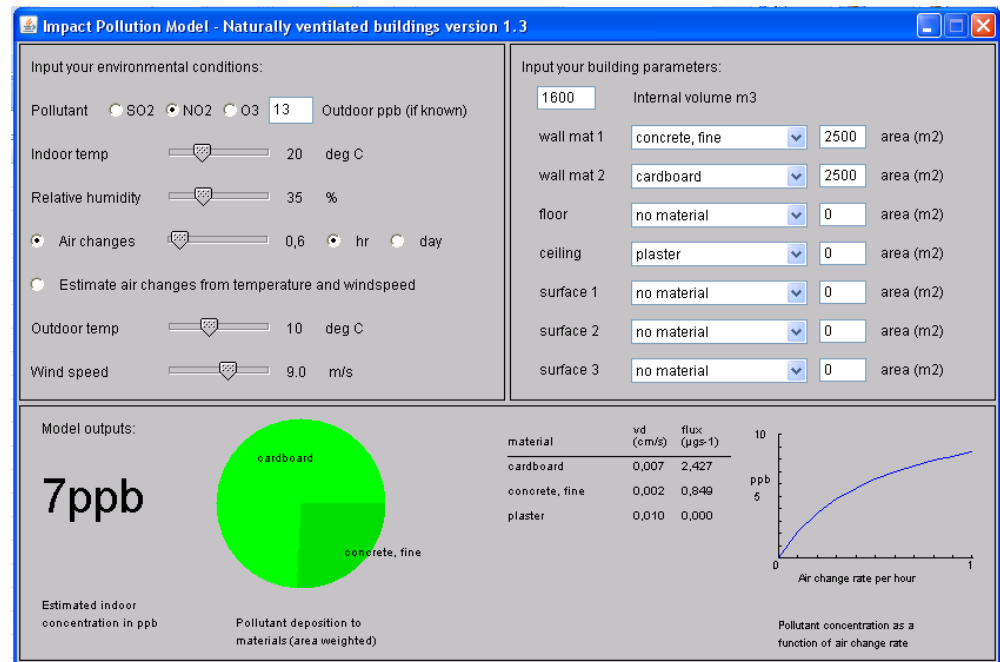


# Infiltration

The NO<sub>2</sub> indoor/outdoor ratio (measured):  
(14,2  $\mu\text{g m}^{-3}$  / 25,5  $\mu\text{g m}^{-3}$ ) = **0.56**

*The Impact model seems to agree 😊*

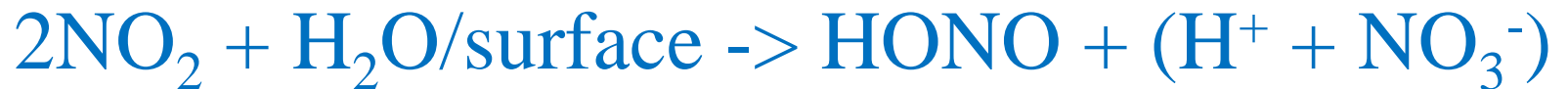
Some - but not all –  
of indoor's NO<sub>2</sub> will  
be converted to  
nitric acid (HNO<sub>3</sub>)





## So...

- It is generally assumed that HONO and HNO<sub>3</sub> will be produced by NO<sub>2</sub> and surface moisture in molar equivalent amounts:



- HONO remains mainly in gas phase
- HNO<sub>3</sub> remains as ions in surface moisture film





# Estimating $\text{HNO}_3$ production from HONO concentration

- HONO was measured by passive samplers (Analyst): The (indoor/outdoor) concentration ratio was **6**.
- The excess HONO generation rate (room):  
 **$G=3500 \mu\text{g h}^{-1}$**
- Which is molar equivalent to a generation of about  **$4700 \mu\text{g h}^{-1}$  of  $\text{HNO}_3$**
- Area-specific generation rate:  
 **$5 \text{ mg/m}^2$  per year** (assuming surface-to-volume ratio =  $5 \text{ m}^2/\text{m}^3$ )



# Conclusion

- Organic acids generation and deposition rates are little known, however, on a room scale the surface deposition can easily be comparable to ventilation removal rates
- Indoor generation of HONO and HNO<sub>3</sub> must be assumed to be part of the fate of NO<sub>2</sub> in air (I/O ratio of HONO = 6)
- In that case the indoor generation of HNO<sub>3</sub> can easily be few mg per m<sup>2</sup> per year – also on museum objects or archival records



# Acknowledgements

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*The IAQ organizers and all of you who made it to  
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Wish I could be with you!