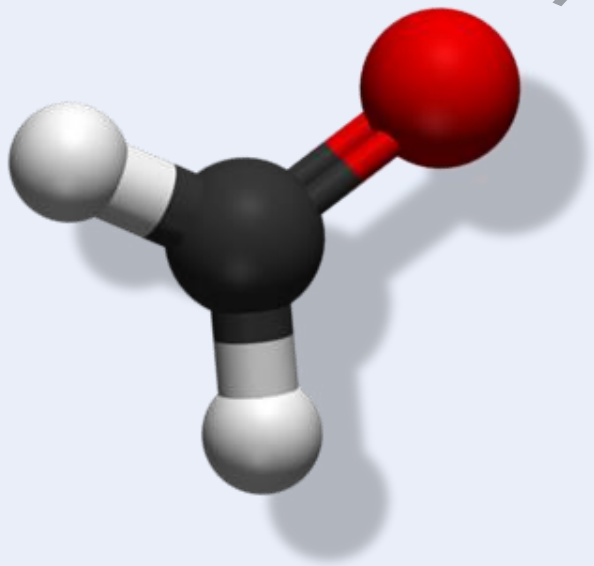
CRITICAL ASSESSMENT OF FORMALDEHYDE SOURCES AND CONCENTRATIONS IN AMBIENT AND INDOOR AIR



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Fraunhofer WKI scientific network

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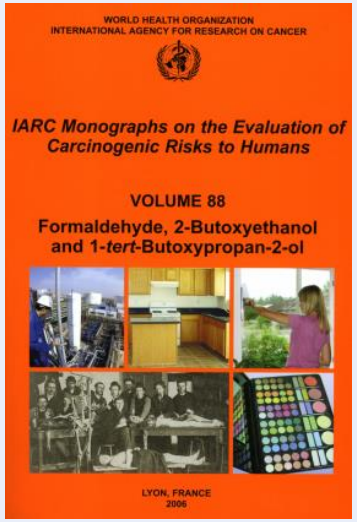
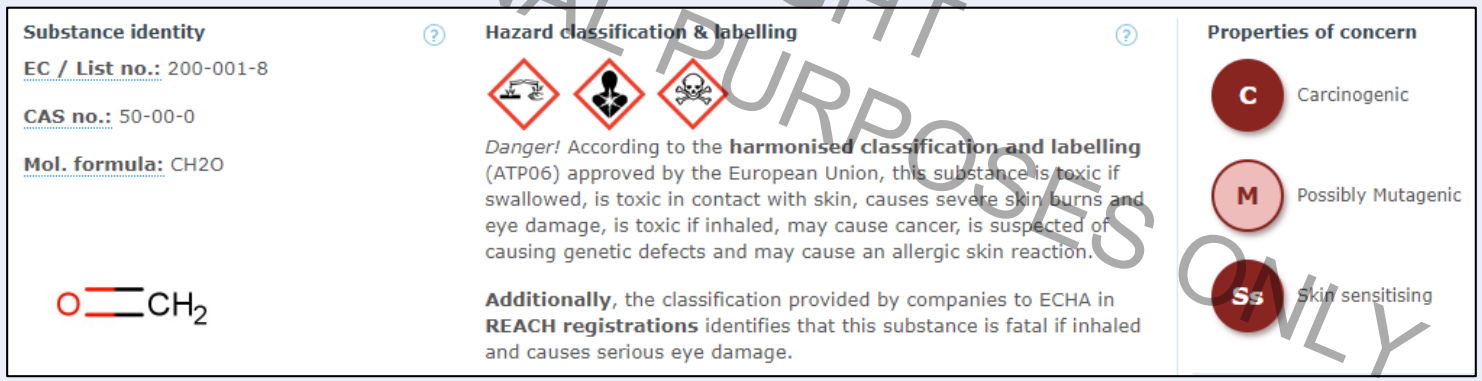
Toxicological classification of formaldehyde

Classification by IARC (2004): **Group 1 “Carcinogenic to humans“**



Classification by ECHA (2014): **Carcinogen 1B “presumed human carcinogen” and germ cell mutagen Category 2**



https://echa.europa.eu/de/substance-information/-/substanceinfo/100.000.002

Final Report

Information requirements on formaldehyde given in the ECHA decision letter "DECISION ON SUBSTANCE EVALUATION PURSUANT TO ARTICLE 46(1) OF REGULATION (EC) NO 1907/2006, for formaldehyde, CAS No 50-00-0 (EC No 200-001-8)"

Funding Organisation

ReachCentrum
on behalf of the REACH Consortium for Formaldehyde
Avenue E. van Nieuwenhuyse 6
1160 Brussels
Belgium

The statements made in this report are those of the author and are not necessarily in agreement with the views of governmental organizations, other research institutions or industry.

Publications on formaldehyde

2536 Chem. Rev. 2010, 110, 2536–2572

Formaldehyde in the Indoor Environment

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Angewandte Minireviews

T. Salthammer

Atmospheric Chemistry

DOI: 10.1002/anie.201205984

Formaldehyde in the Ambient Atmosphere: From an Indoor Pollutant to an Outdoor Pollutant?

*Tunga Salthammer**

International Journal of Hygiene and Environmental Health 218 (2015) 433–436

Contents lists available at ScienceDirect

International Journal of Hygiene and Environmental Health

journal homepage: www.elsevier.com/locate/ijheh

Commentary

The formaldehyde dilemma

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Building and Environment 150 (2019) 219–232

Contents lists available at ScienceDirect

Building and Environment

journal homepage: www.elsevier.com/locate/buildenv

Formaldehyde sources, formaldehyde concentrations and air exchange rates in European housings

Tunga Salthammer

Fraunhofer WKI, Department of Material Analysis and Indoor Chemistry, Bienroder Weg 54E, 38108, Braunschweig, Germany

Data in Brief 22 (2019) 400–435

Contents lists available at ScienceDirect

Data in Brief

journal homepage: www.elsevier.com/locate/dib

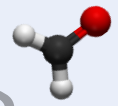
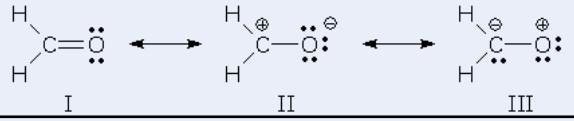
Data Article

Data on formaldehyde sources, formaldehyde concentrations and air exchange rates in European housings

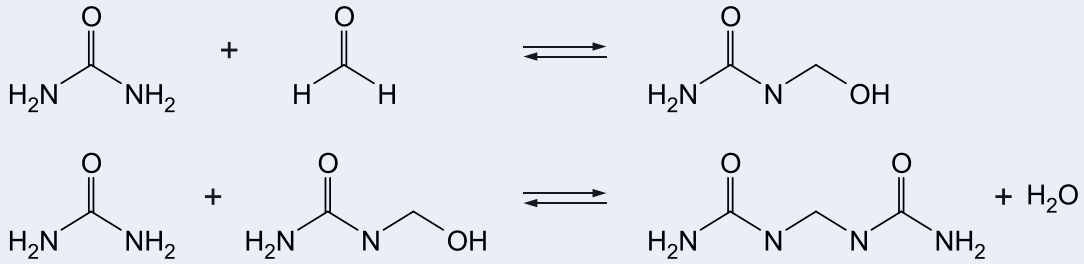
Tunga Salthammer

Fraunhofer WKI, Department of Material Analysis and Indoor Chemistry, Bienroder Weg 54 E, 38108 Braunschweig, Germany

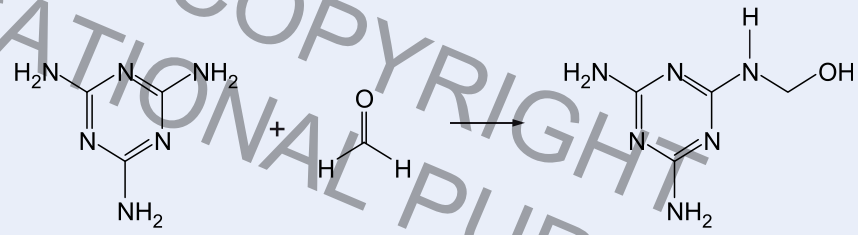
Formaldehyde: chemical properties and application as resin

Structure 	 I II III
CAS registry no.	50-00-0
Molecular formula	HCHO, CH_2O
Molecular weight	30.03 g/mol
Melting point [a]	-92 °C
Boiling point	-21 °C
Dipole moment	2.33 D
Solubility	soluble in water, ethanol, ether, acetone
Henry's law constant	$2.5 \cdot 10^3$ M/atm (25 °C)
$\log(K_{ow})$ [b]	-0.83
$k_{OH\cdot}$	$9.37 \cdot 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (298 K)
k_{O3}	$2.09 \cdot 10^{-24}$ cm^3 $molecule^{-1}$ s^{-1} (298 K)
k_{NO3}	$5.80 \cdot 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} (298 K)

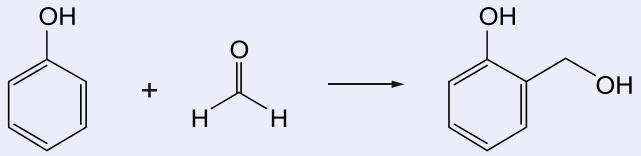
urea-formaldehyde-resin



melamine-formaldehyde-resin



phenol-formaldehyde-resin



Indoor related indoor formaldehyde guidelines

OEHHA[1)] REL (acute)	55 µg/m³
OEHHA[1)] REL (8 h)	9 µg/m³
OEEHA[1)] REL (chronic)	9 µg/m³
WHO indoor guideline[2)]	0.1 mg/m³
German indoor Guideline[3)]	0.1 mg/m³

1) California‘s Office of Environmental Health Hazard Assessment (OEHHA), *REL = Reference Exposure Limit.*
2) World Health Organisation, 2010. WHO guidelines for indoor air quality: selected pollutants. WHO Regional Office for Europe, Copenhagen.
3) Ausschuss für Innenraumrichtwerte, 2016. Richtwert für Formaldehyd in der Innenraumluft. Bundesgesundheitsblatt 59, 1040-1044.

Minutes of the 49th Meeting of the Committee for Risk Assessment (RAC 49)
30 August 2019:

"RAC agreed on a weight of evidence approach considering human and animal data for the relevant precursor events deriving a ***chronic DNEL of 0.05 mg/m³ for the inhalation route*** *based on a study with monkeys (Rusch et al., 1983)".*

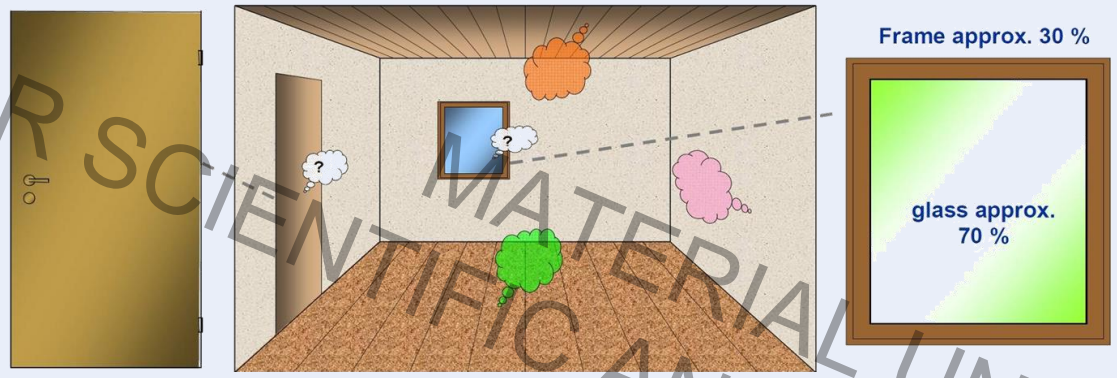
Note: the former DNEL was 0.1 mg/m³, which is in accordance with the WHO indoor guideline value.

DNEL = Derived No Effect Level

The revised German Chemicals Prohibition Ordinance for formaldehyde

Parameter	**EN 717-1**	**EN 16516**
Chamber size (m^3)	0.225, 1, >12	flexible
Temperature (°C)	23	23
Relative humidity (%)	45	50
Air exchange rate h^{-1})	1.0	0.5
Loading rate (m^2/m^3)	1.0	1.8
Edges/surface (m/m^2)	1.5	1.5
Testing time (days)	until steady state	28
Formaldehyde analysis	Acetyl acetone	DNPH
Limit value (ppm)	0.1	0.1
Value for evaluation	**2 x** Chamber concentration	Chamber concentration

The European Reference Room (EN 16516)



Parameter	Dimension	Loading
Chamber volume	30 m³	
Chamber dimension	4 m x 3 m x 2.5 m	
Surface walls	31.4 m²	1.0 m²/m³ (rounded)
Surface floor or ceiling	12 m²	0.4 m²/m³
Surface window	2 m²	0.05 m²/m³ (rounded)
Surface door (0.8 m x 2 m)	1.6 m²	0.05 m²/m³ (rounded)
Sealing	0.2 m²	0.007 m²/m³

Picture: WKI

Calculation of Reference Room concentrations from area sprecific emission rates (SER_A)

$$SER_A = c_{Ch} \cdot ACH_{Ch} / L_{Ch}$$

$$c_{Ref} = SER_A \cdot L_{Ref} / ACH_{Ref}$$

Small scale

Large scale (30 m³)

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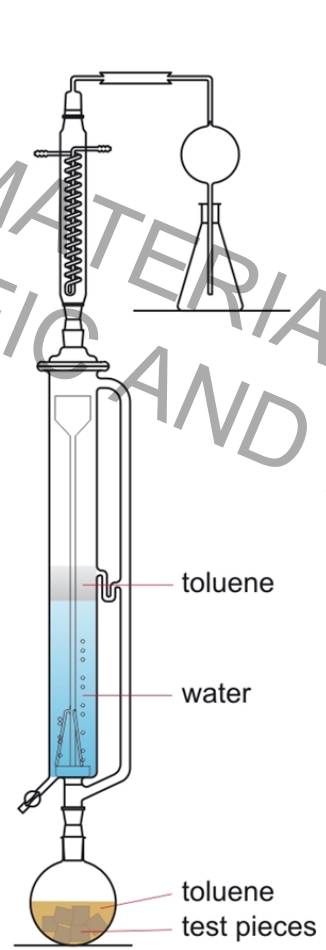
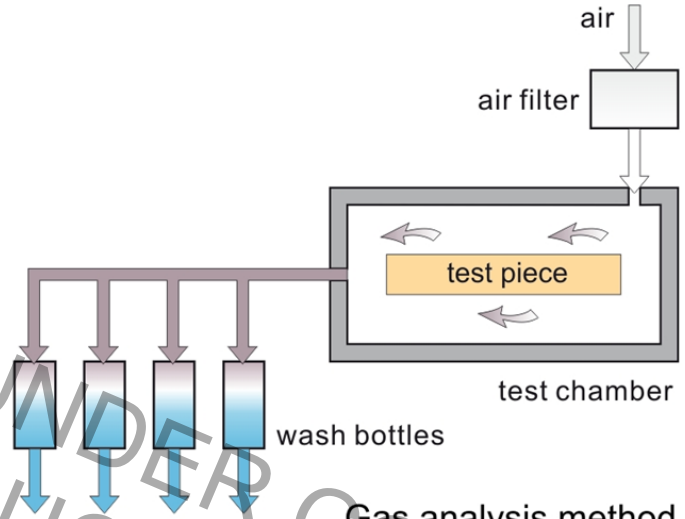
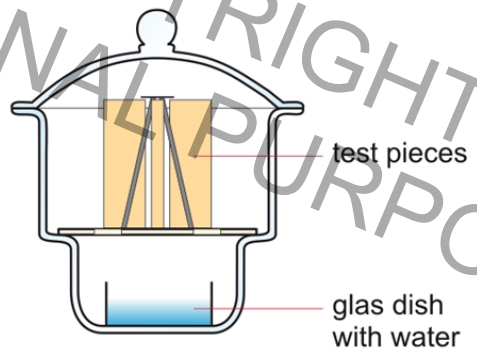
Derived methods for the emission testing of formaldehyde



(EN 120 / EN ISO 12460-5) Perforator method



Gas analysis method (EN 717-2 / EN ISO 12460-3)



Desiccator method (JIS A 1460)

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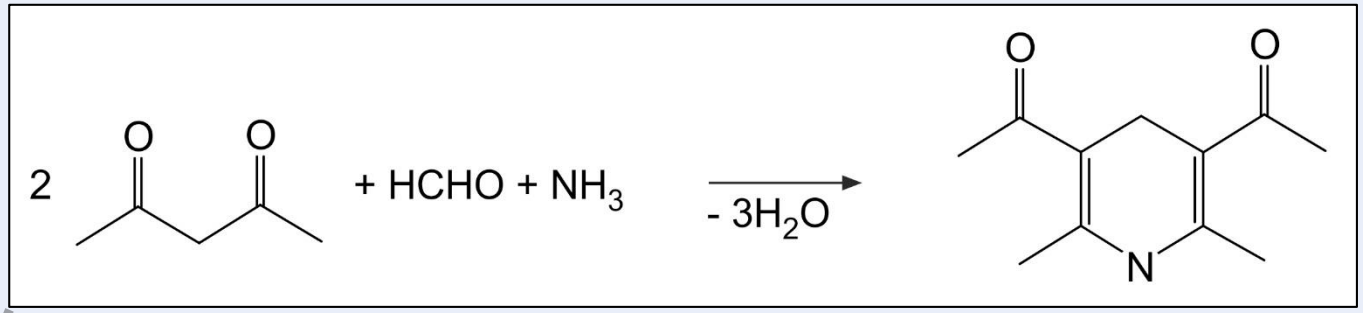
Analytical methods for the detection of formaldehyde in air

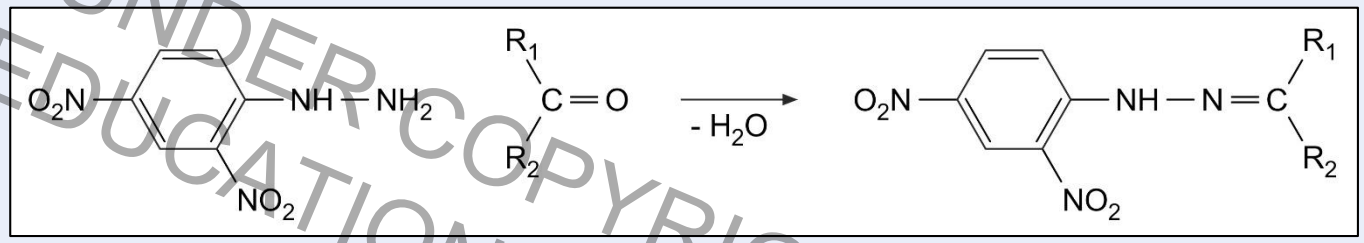
Acetyl acetone (Hantzsch) method

selective with fluorescence detection



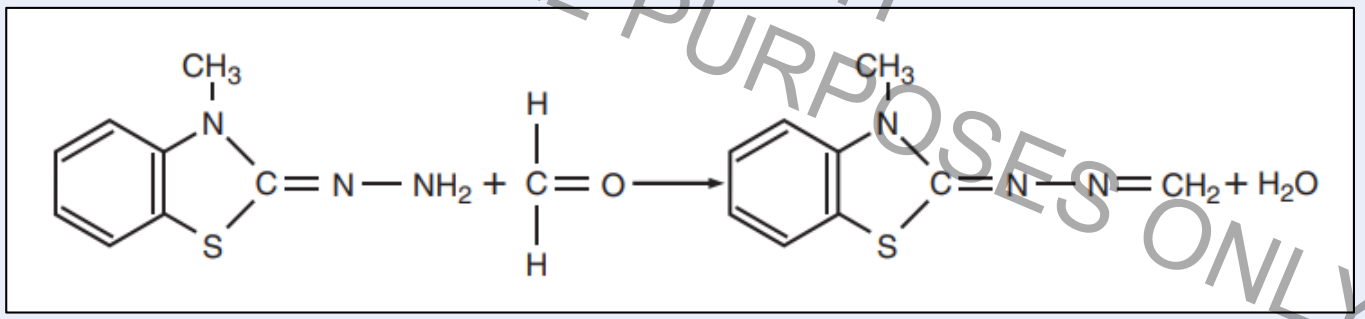
DNPH method

selective with HPLC/UV



MBTH method

not selective for formaldehyde !!!



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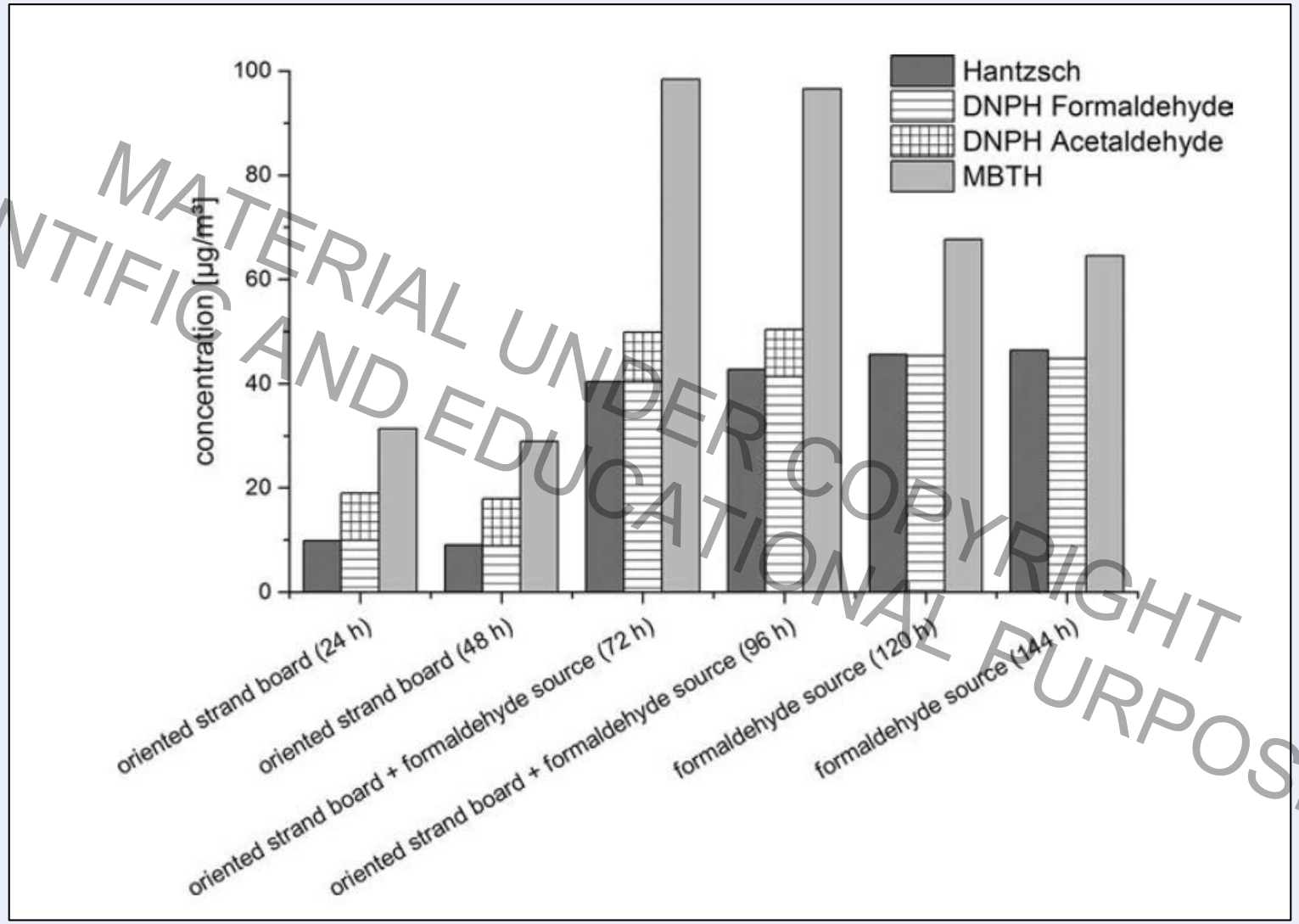
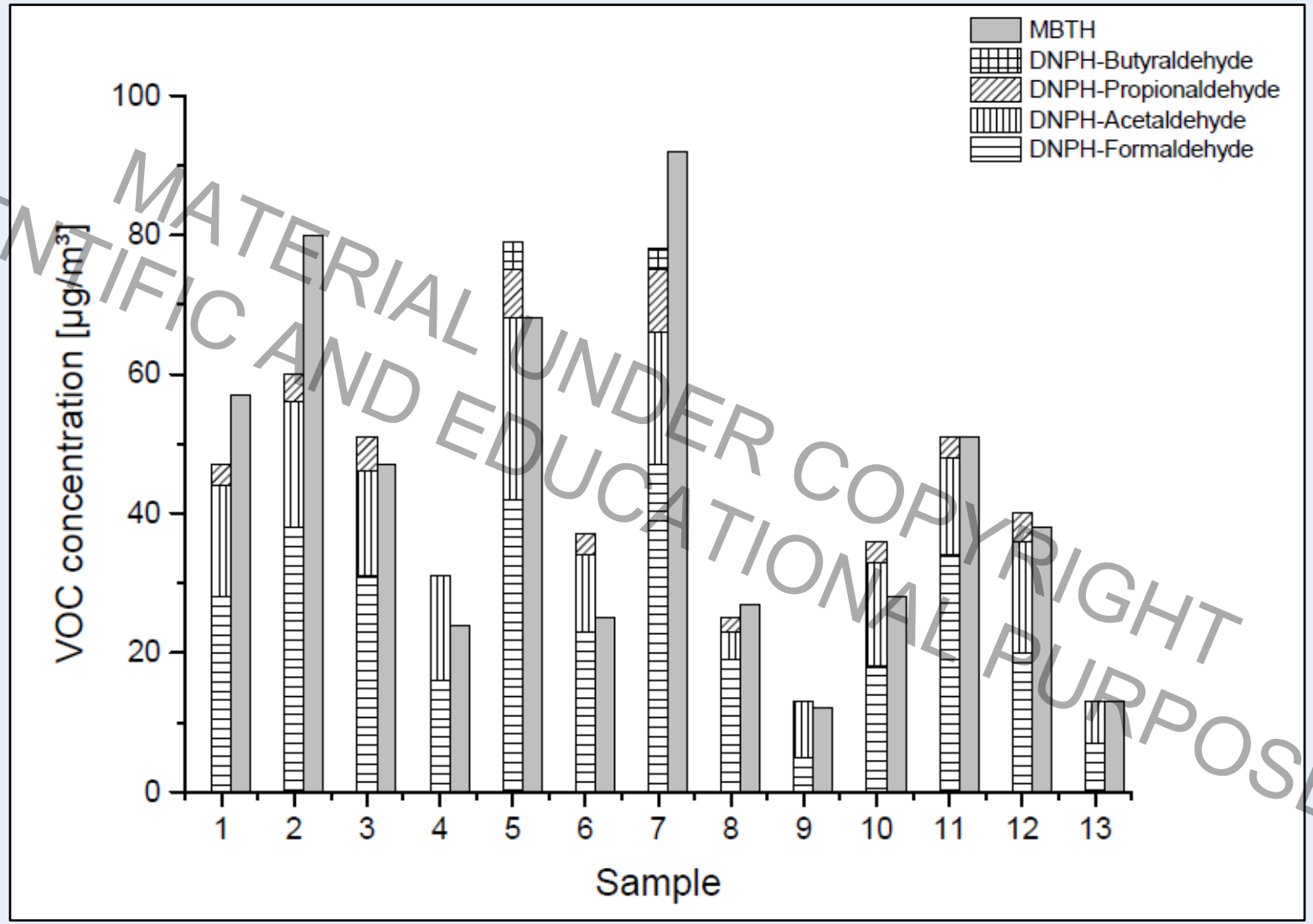
Analysis of wood-based materials by use of the Hantzsch (acetyl acetone), DNPH and MBTH method



Giesen et al. (2016) Analytical Letters

Fraunhofer WKI

The MBTH method may overestimate formaldehyde concentrations



Giesen et al. (2016) Analytical Letters

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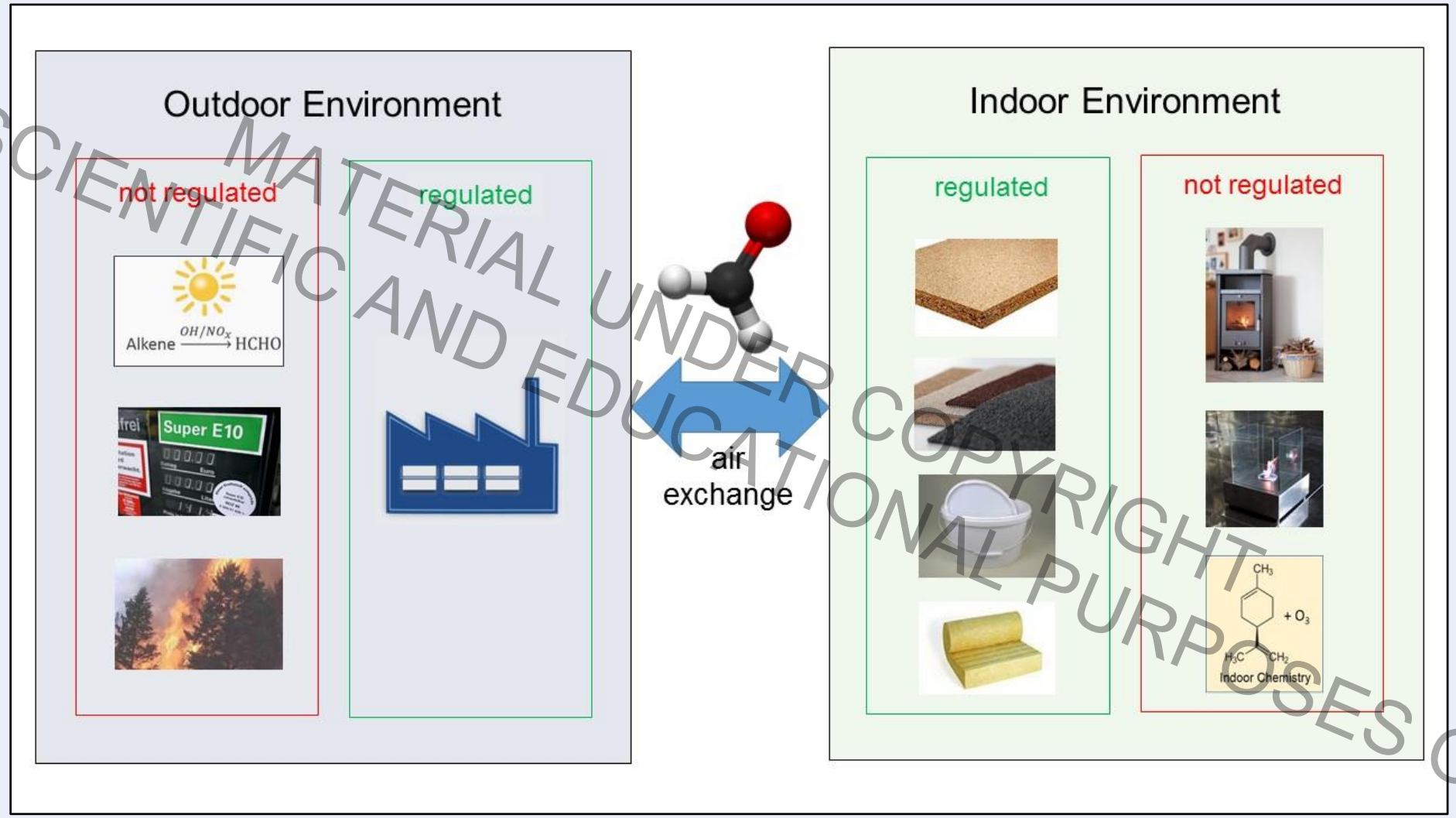
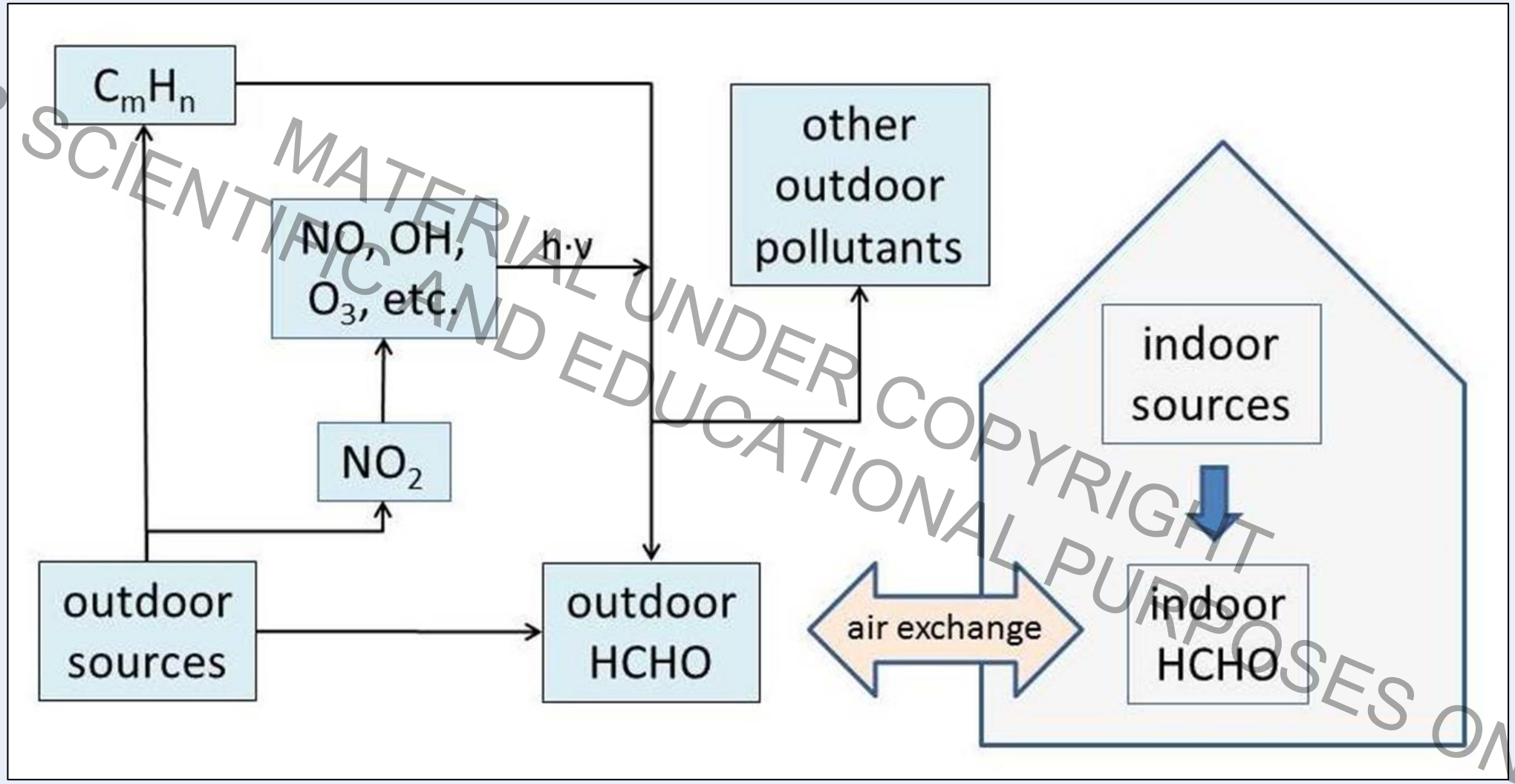
Formaldehyde in the indoor and outdoor environment



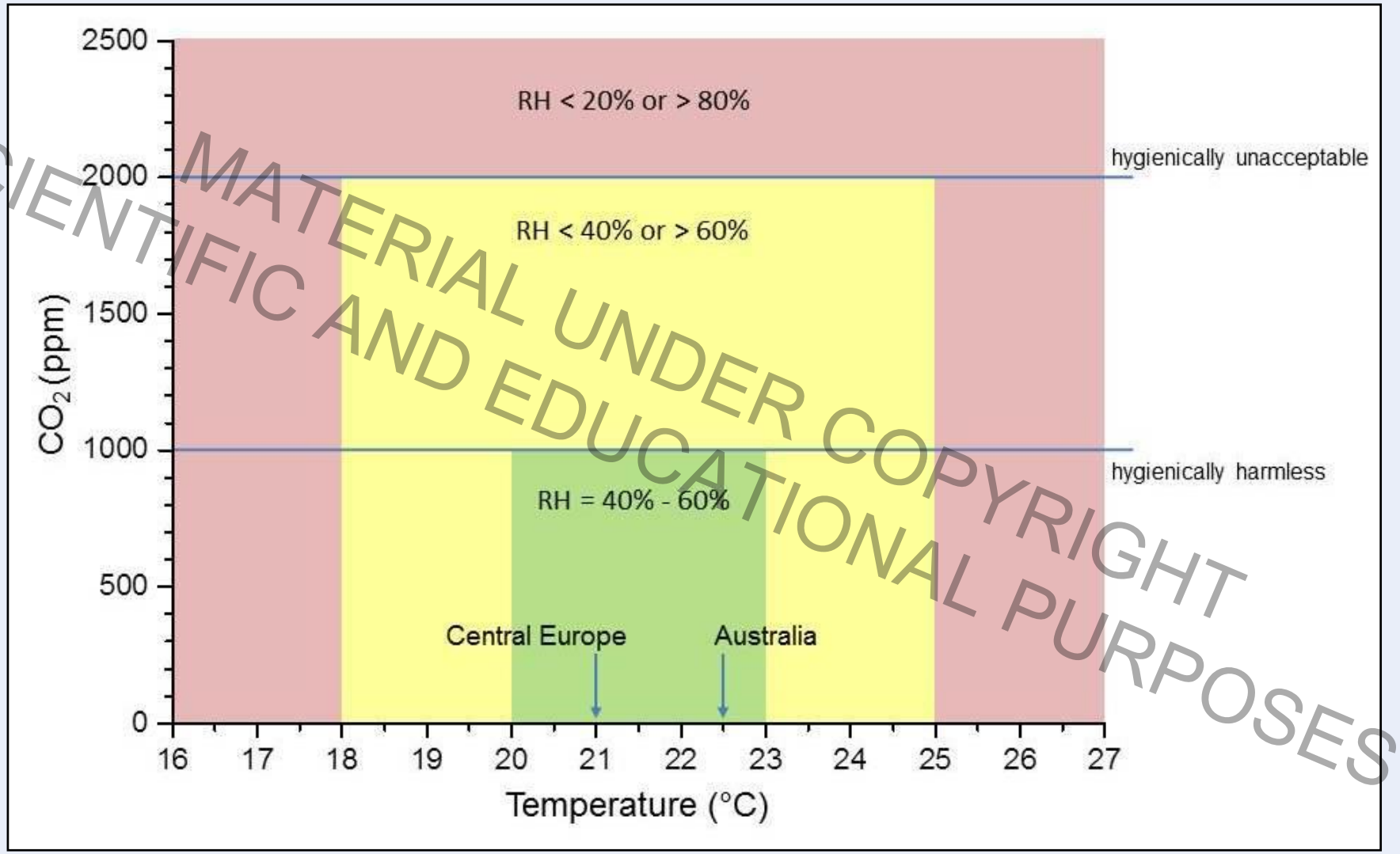
Exchange of formaldehyde between indoor and outdoor air



Salthammer (2013) Angewandte Chemie Int. Ed.

Fraunhofer WKI

Indoor climate: carbon dioxide and hygienic levels



Salthammer et al. (2016) Environment International

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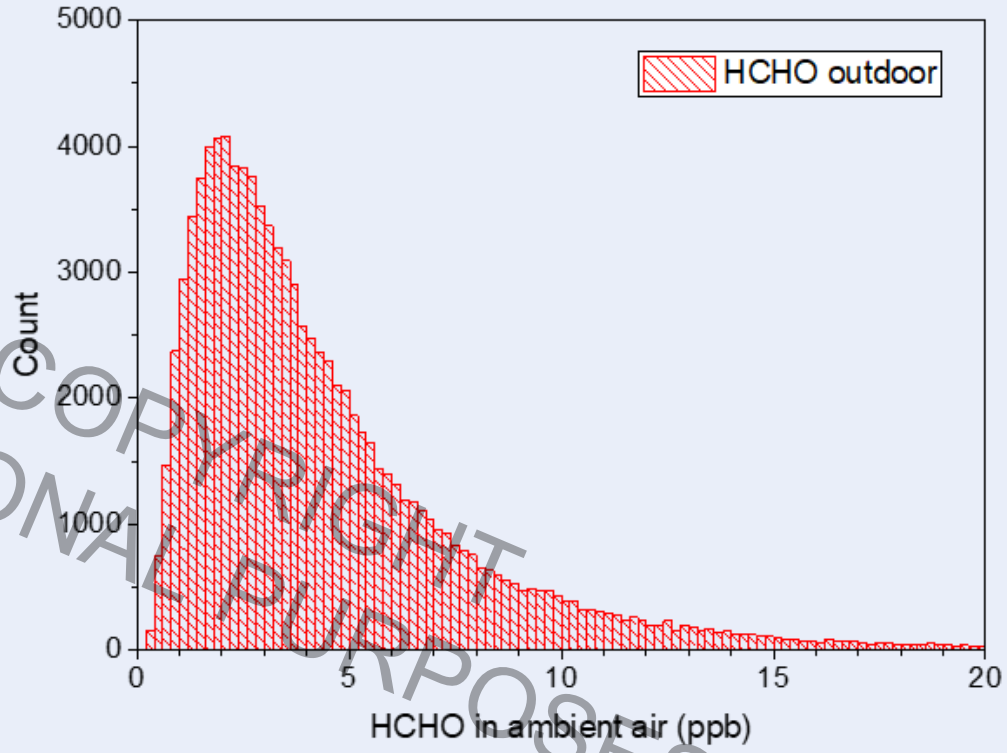
Formaldehyde in ambient air (Europe)

Location	C_{HCHO} (ppb)	Comments	Reference
Rural European sites	0.4 - 5.5	Range	(Solberg et al., 2001)
Kuopio, Finland	35/55 1.0 2.2	Maximum Background	(Solberg et al., 2001)
Uppsala, Sweden	1.1	GM	(Sakai et al., 2004)
Milan, Italy	1.5 - 13	Range	(Hak et al., 2005)
Rome, Italy	1.0 - 5.7 2.0	Range Median	(Santarsiero and Fuselli, 2008)
Athens, Greece	0.04 - 31.6 12.9	Range Median	(Bakeas et al., 2003)
Barcelona, Spain	3.1 - 4.1	Range	(Gallego et al., 2016)
European cities	0.3 - 4.0	Range	(Bruinen de Bruin et al., 2008)

Calculated distribution:



Note: 100 ppb = 124 µg/m

High formaldehyde concentrations are possible in ambient air (world, in ppb)

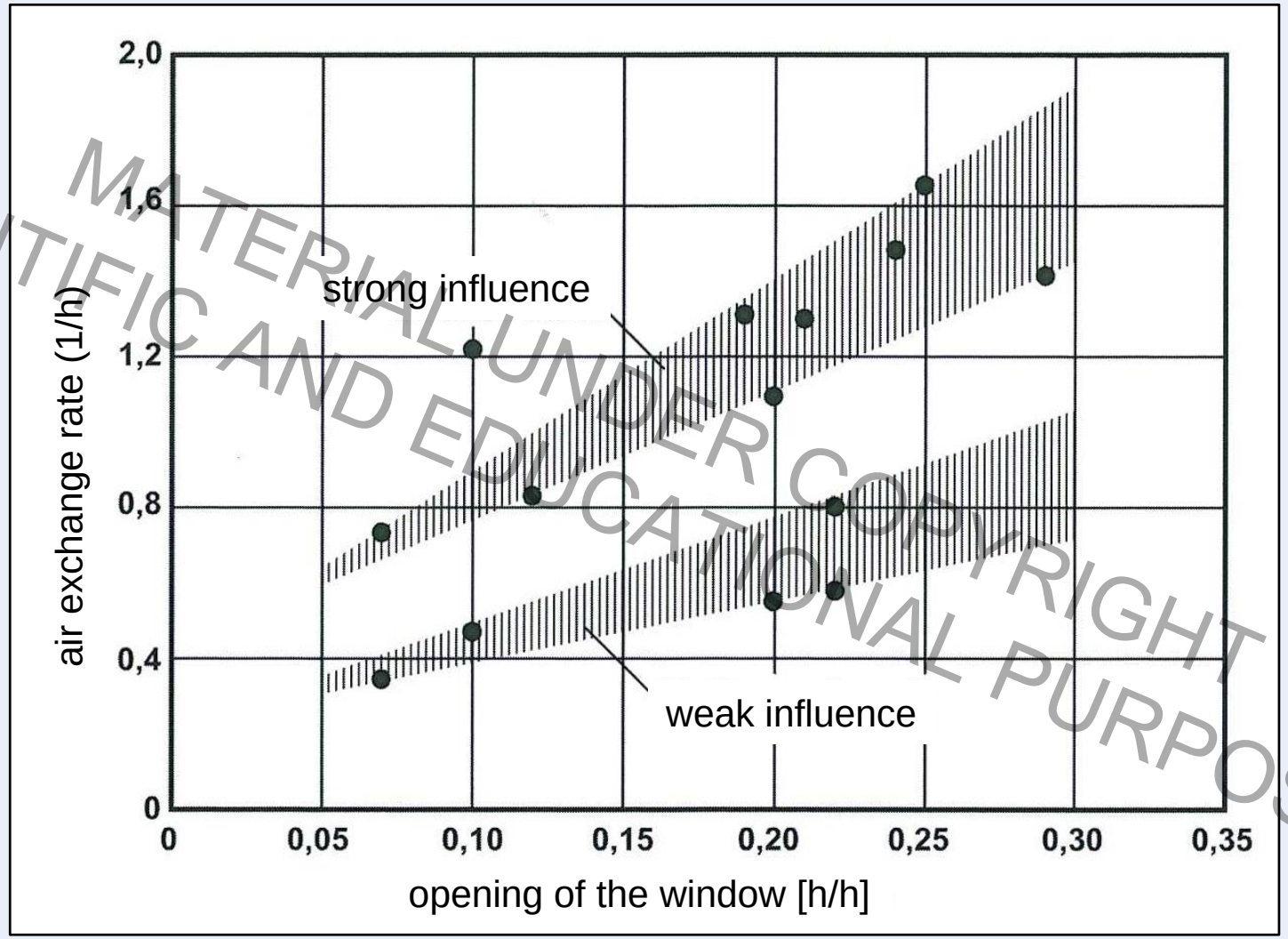
Salthammer (2013) Angewandte Chemie Int. Ed.

Fraunhofer WKI

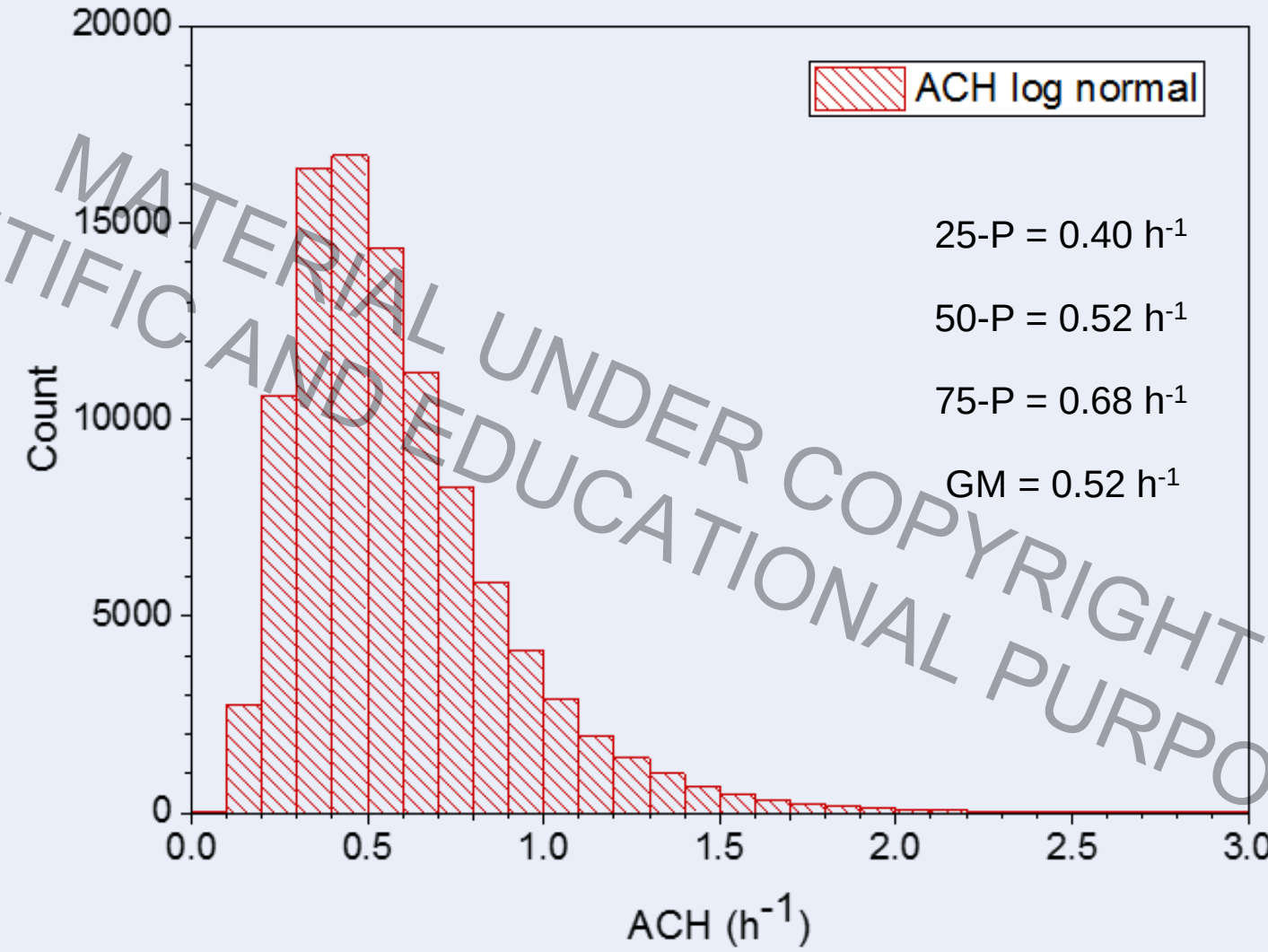
Air exchange rates in European housings under living conditions

ACH [h^{-1}]	Statistics	Condition	Reference
0.60	median	Conventional houses (Sweden)	Langer et al. (2015)
0.68	median	Passive houses (Sweden)	Langer et al. (2015)
0.44	median	Dwellings (France)	Langer et al. (2016)
0.35	median	Residences (U.S.)	Du et al. (2015)
1.15	median	Residences, basement (U.S.)	Du et al. (2015)
0.08 – 0.69	range	Low energy buildings (Lithuania)	Kauneliene et al. (2016)
0.43	median	Renovated	Földváry et al. (2017)
0.45	median	Renovated	Földváry et al. (2017)
0.4	median	Night-time, heating season	Derbez et al. (2018)
0.5	media	Night-time, non heating season	Derbez et al. (2018)

Influence of window opening on the air exchange rate



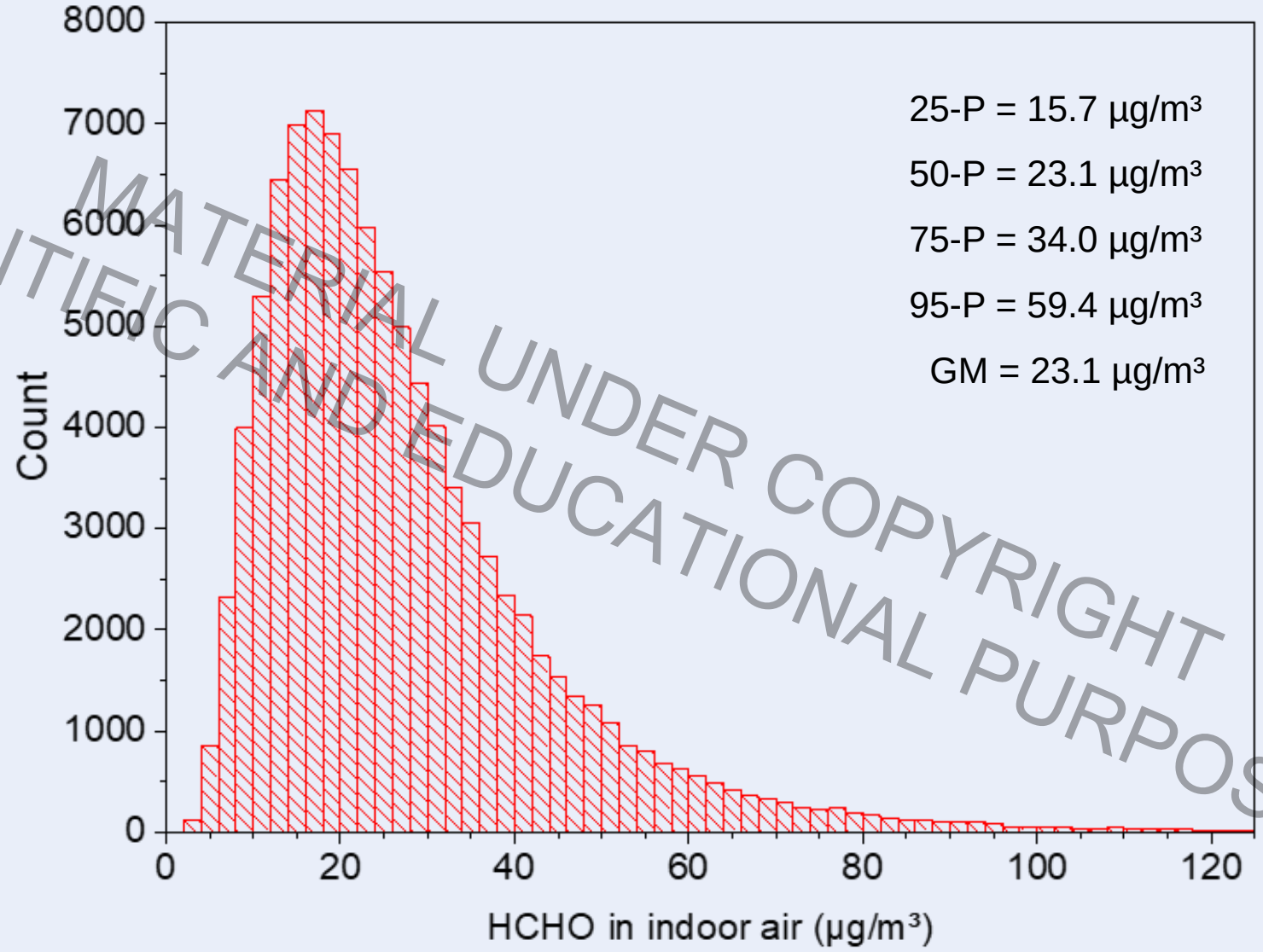
Probability distribution of air exchange rates under living conditions



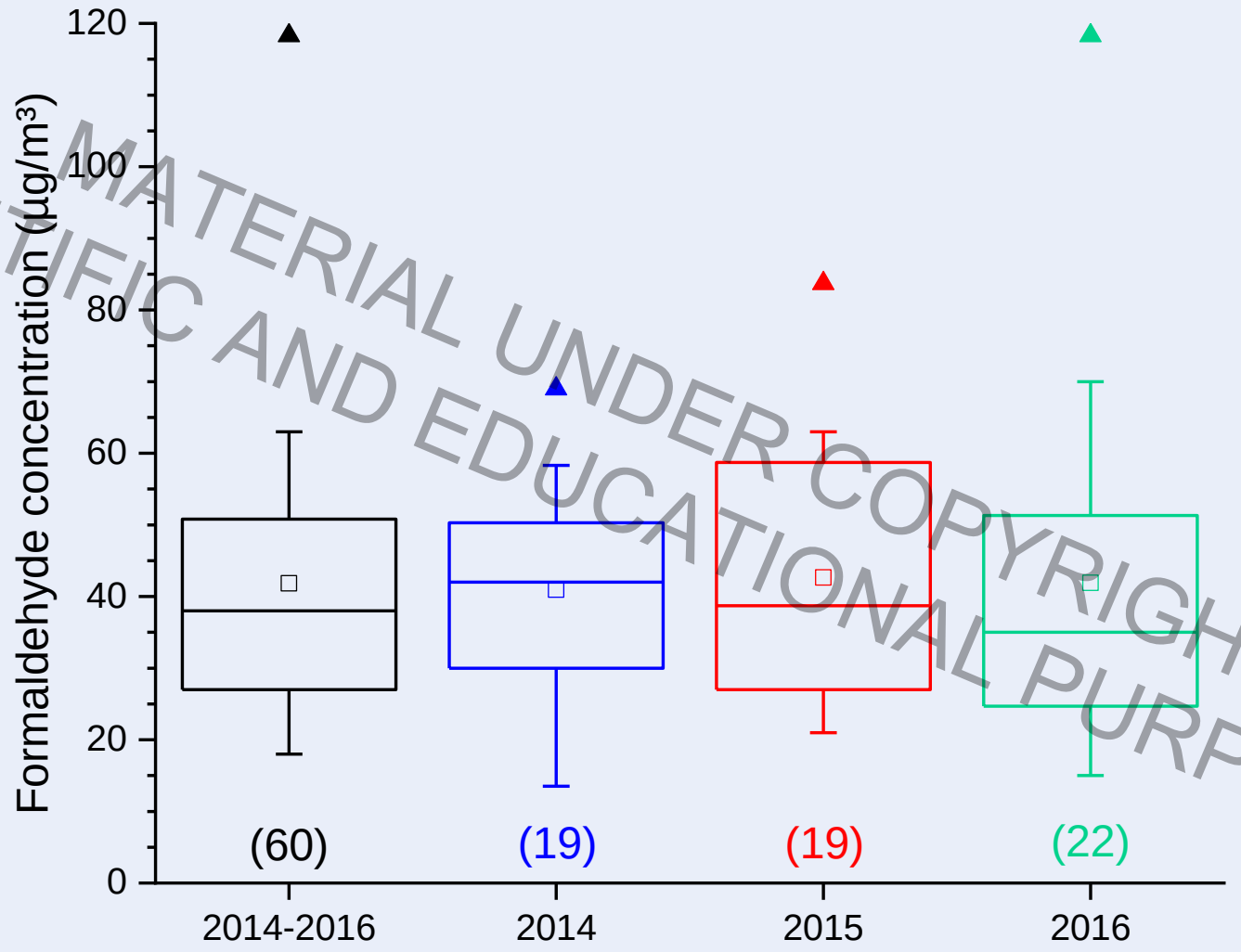
Formaldehyde in indoor air under living conditions (Europe)

Country	N	GM [µg/m³]	50-P [µg/m³]	75-P [µg/m³]	95-P [µg/m³]	Reference
Germany	586	23.3	23.5		47.7	(Umweltbundesamt, 2008)
France	143		26.7			(Marchand et al., 2008)
France	143		30.9			(Marchand et al., 2008)
France	554	19.5	19.7	29		(Langer et al., 2016)
Sweden	20		11.1			(Langer et al., 2015)
Sweden	21		15.7			(Langer et al., 2015)
Sweden	294	16.0	17.0			(Langer and Bekö, 2013)
England	876	22.2	24.0	35.2	61.2	(Raw et al., 2004)
Spain	10		22.5	*(31)*		(Rovira et al., 2016)
Spain	10		27.3	*(38)*		(Rovira et al., 2016)
Italy	40		10.6			(Santarsiero and Fuselli, 2008)
Italy	59		14.2			(Lovreglio et al., 2009)
Lithuania	11		30.8	40.5		(Kauneliené et al., 2016)
Denmark	20		40			(Kolarik et al., 2012)
Slovakia	20	30	30			Földváry et al. (2017)
Slovakia	20	41	42			Földváry et al. (2017)
France	65		13.8	19.1		Derbez et al. (2018)
France	65		19.4	25.4		Derbez et al. (2018)

Calulated distribution of formaldehyde in indoor air under living conditions



Formaldehyde in newly built prefabricated houses in Germany (steady state conditions)



Data by Courtesy of Bundesverband Deutscher Fertigbau e. V. (2017)

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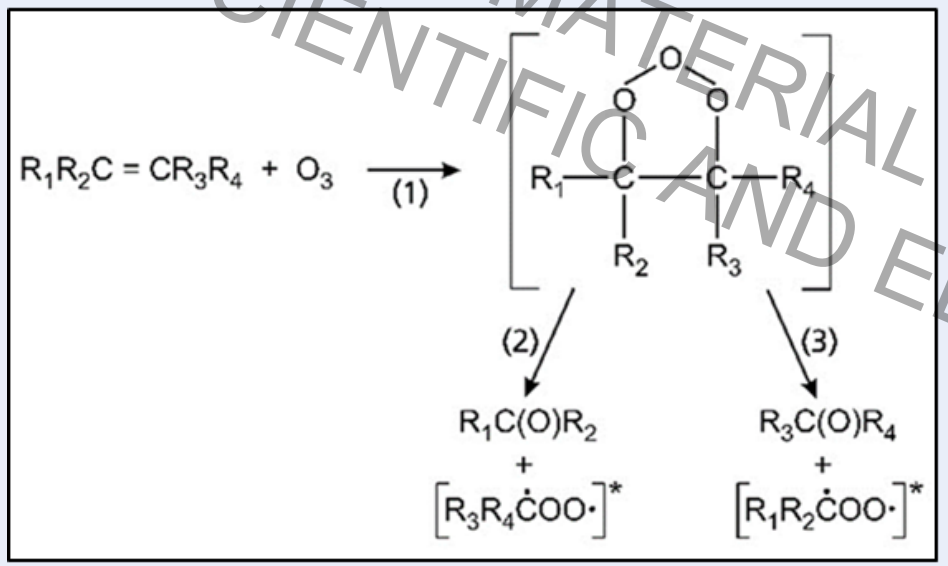
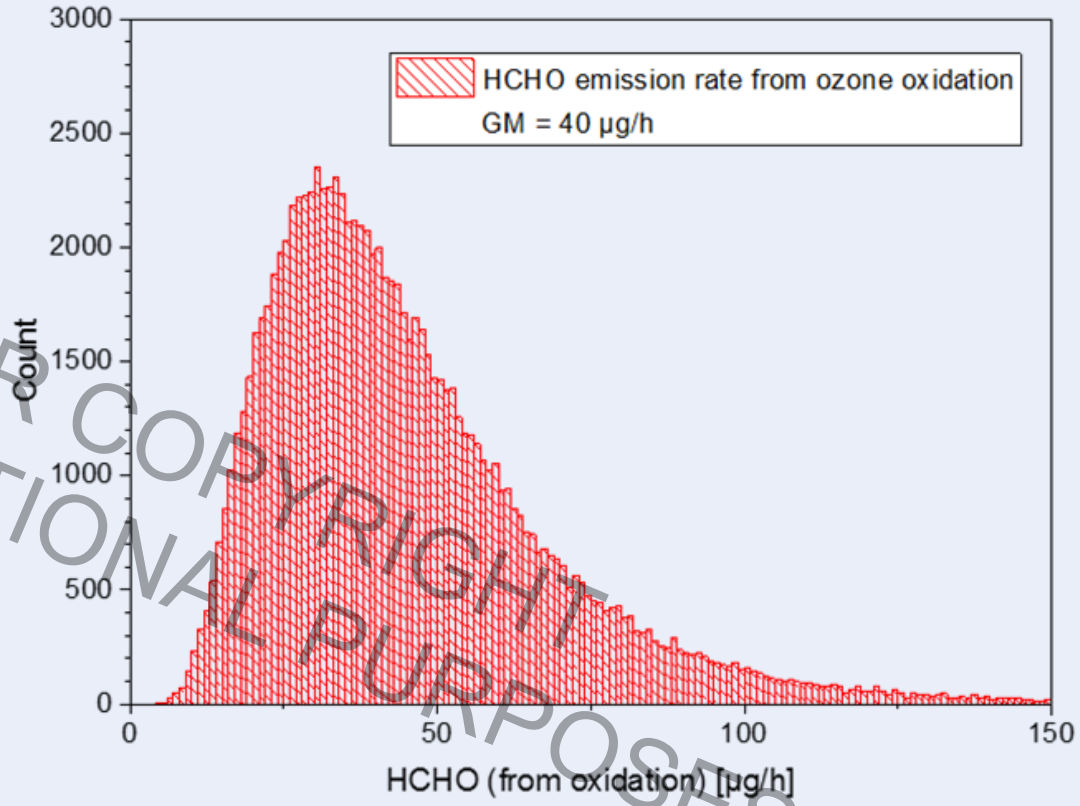
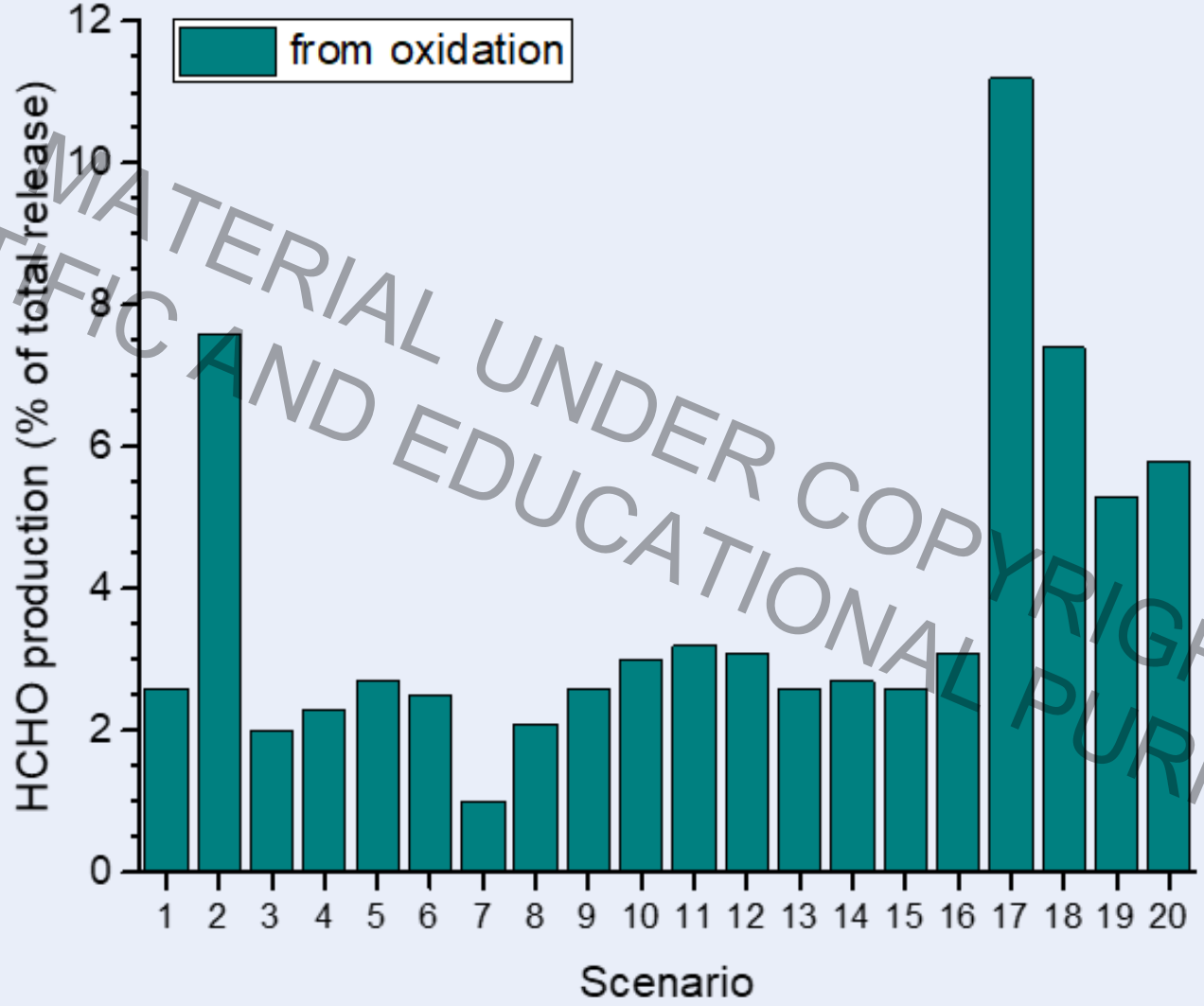
Probability distribution: indoor chemistry, isoprene/terpene oxidation by ozone



Criegee mechanism



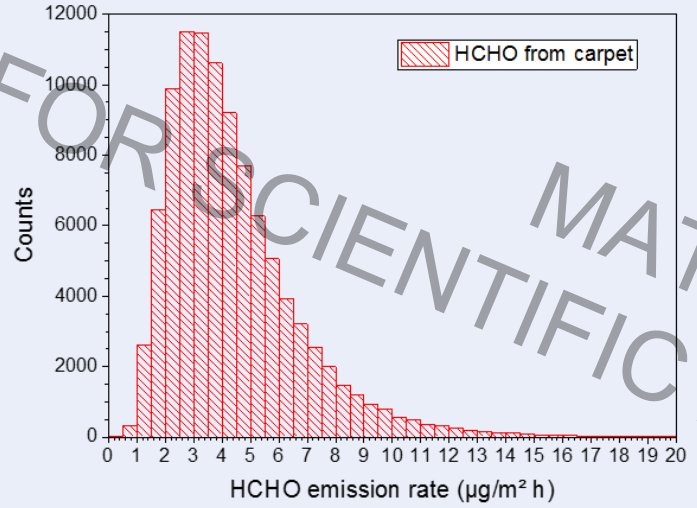
Contribution of indoor chemistry to indoor formaldehyde

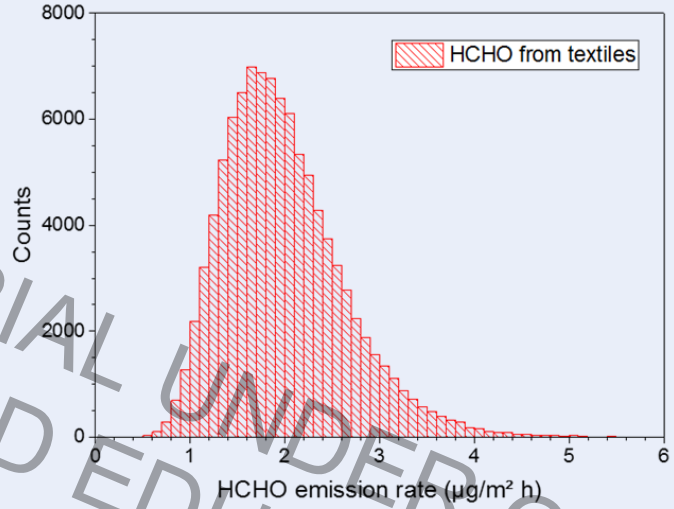


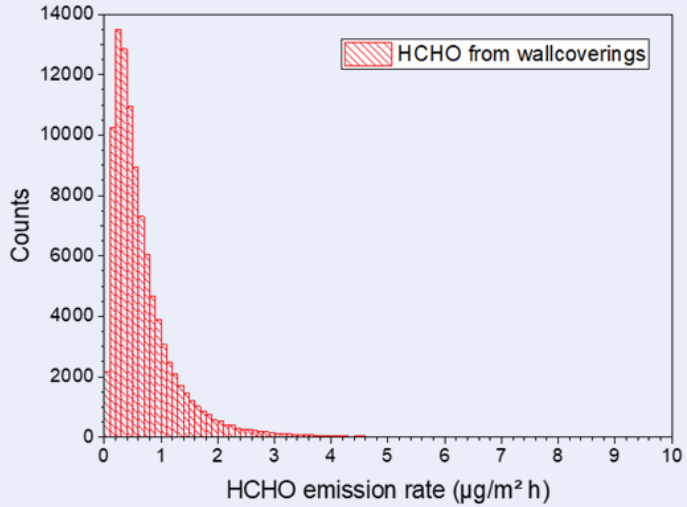
Mendez et al. (2015) Atmospheric Environment

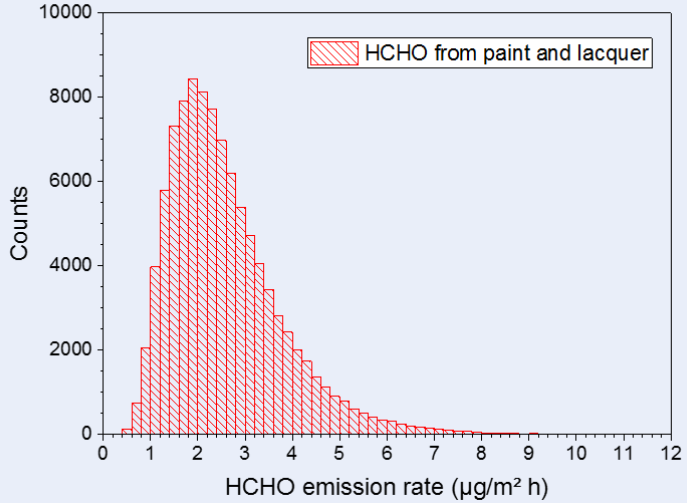
Fraunhofer WKI

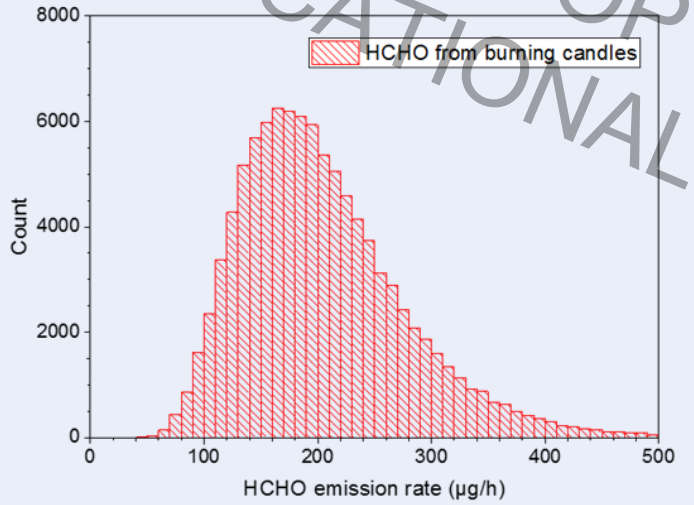
Probability distributions: emission rates of building and consumer products

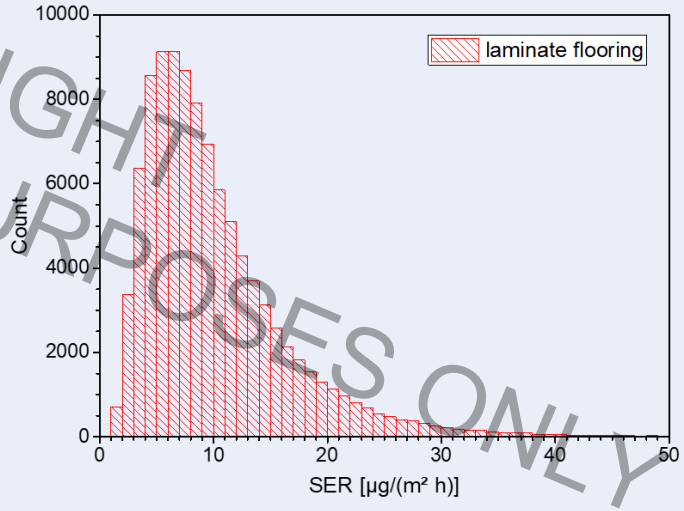




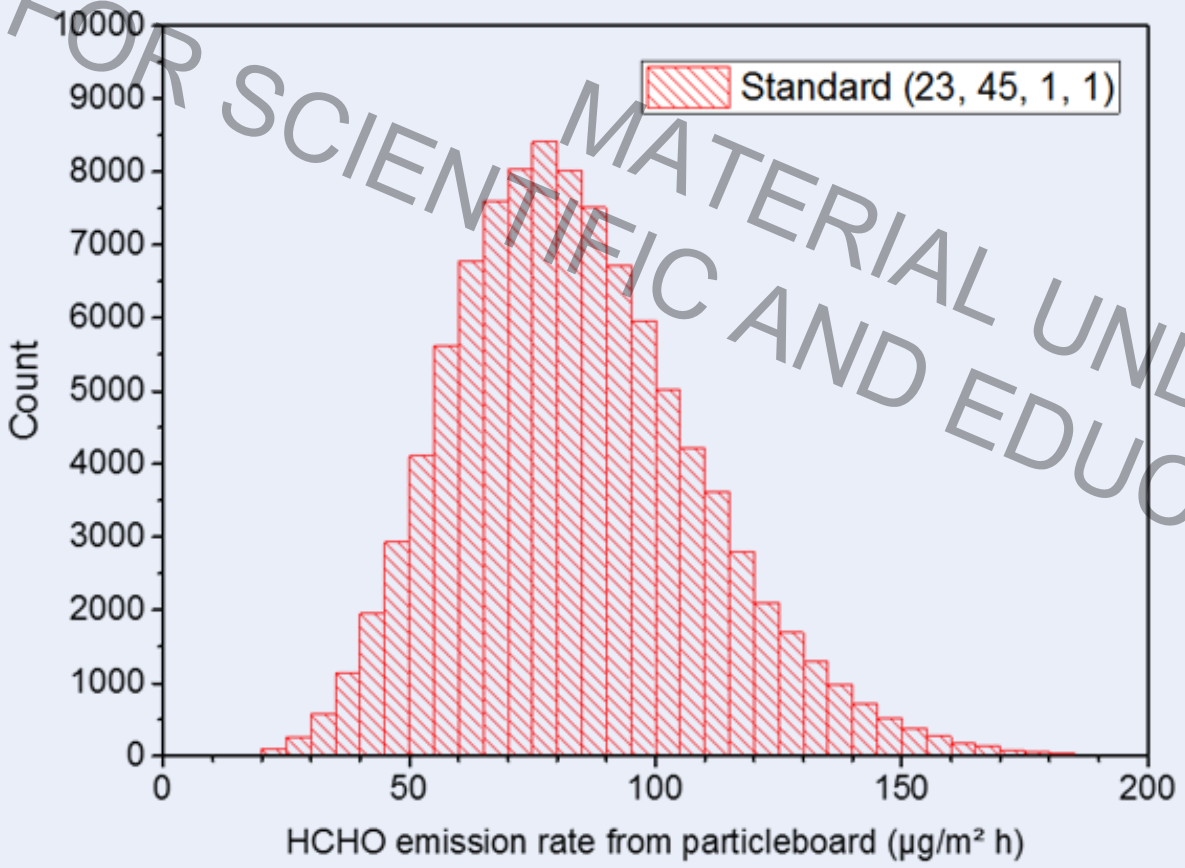


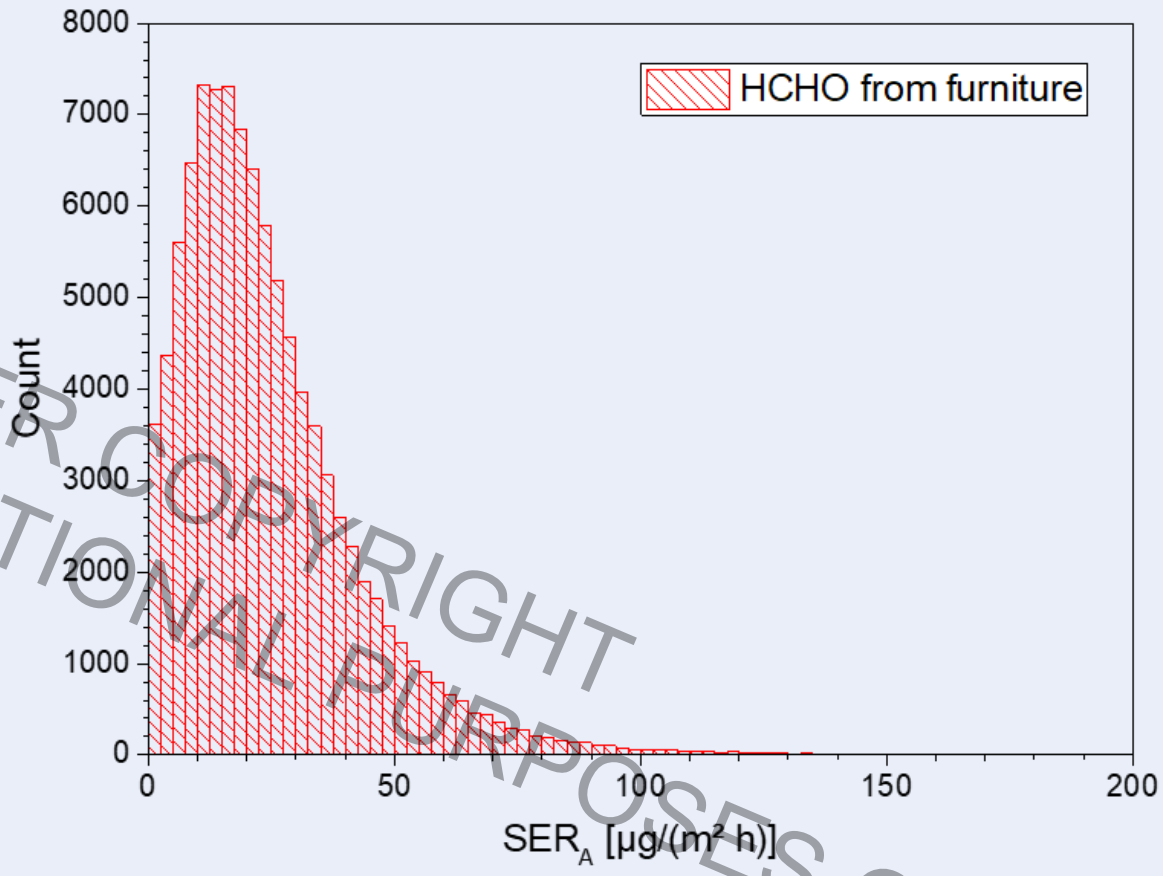




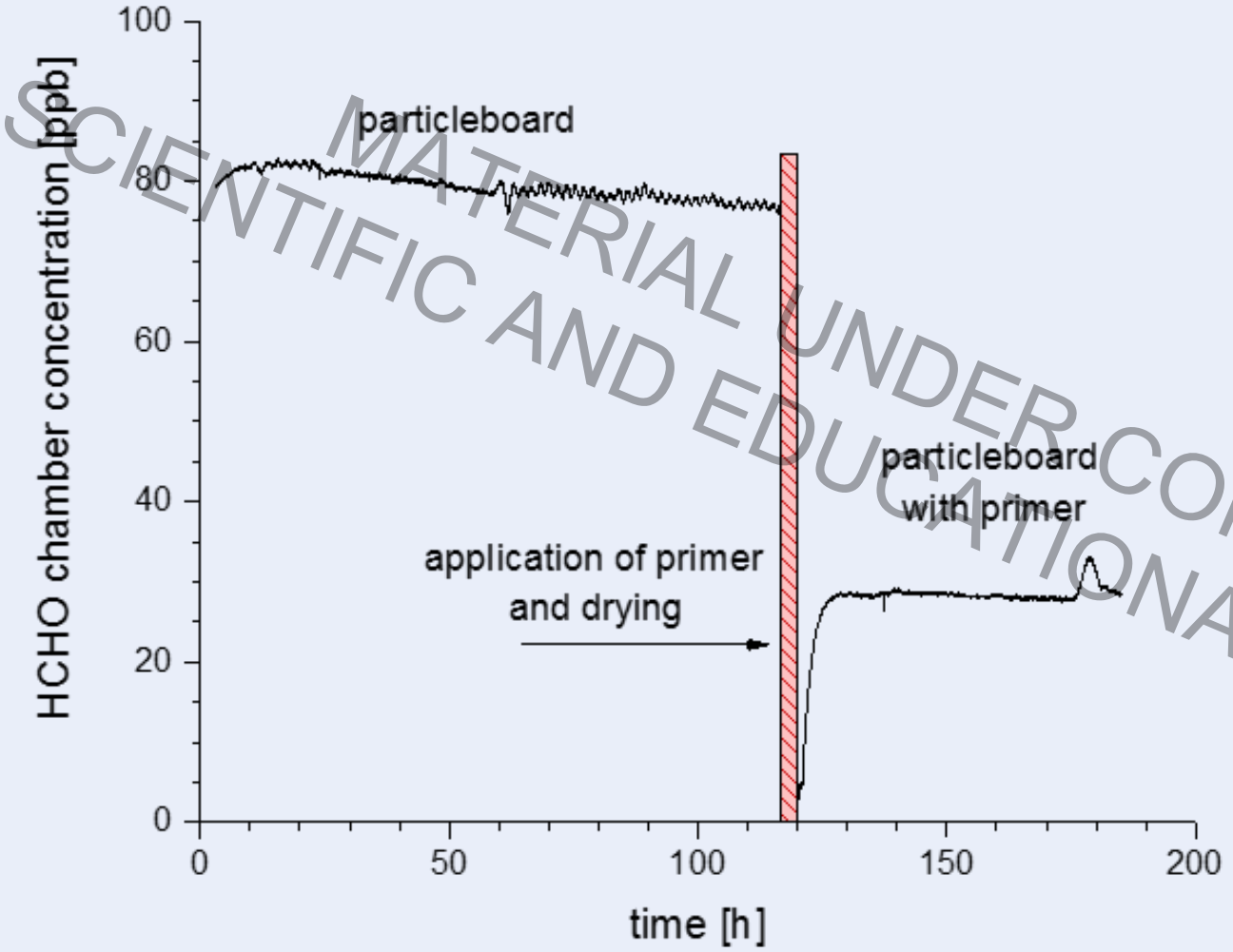


Probability distributions: particleboard and furniture





Emission testing does not necessarily picture real-life situations

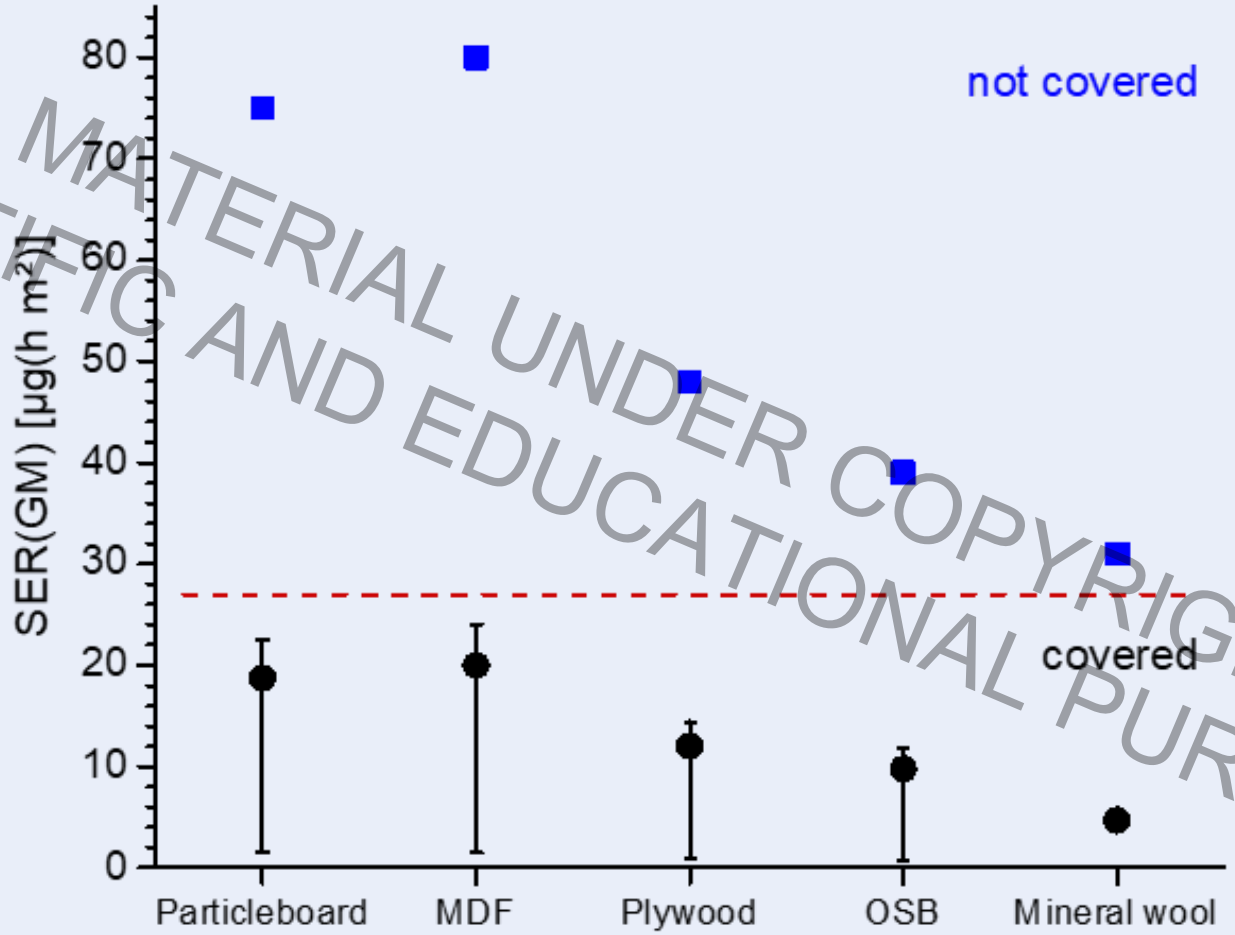


(Picture taken from a different study)

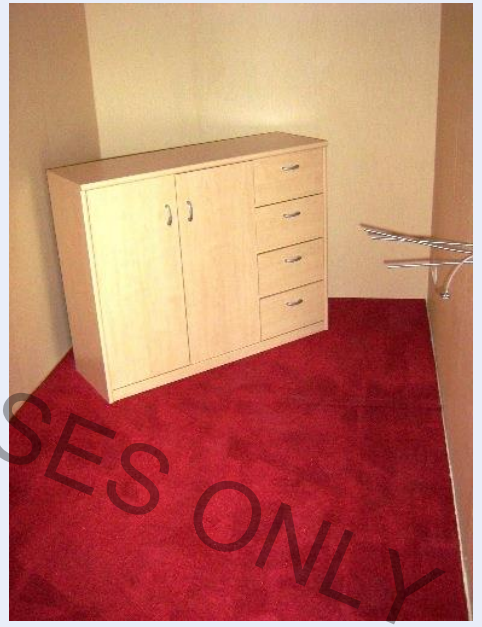
„Covering“ effect on formaldehyde emission from particleboard

Test	Covering	rel. SER_A [%]	reduction of rel. SER_A [%]
1	no covering	100	0
2	with primer	30	70
3	with primer and dispersion paint	24	76
4	with primer and plaster	22	78
5	with primer and wallpaper (fleece)	6	94
6	with primer and latex paint	2	98

Wood based products: reduction of emission rates through covering



WKI/EURIMA test house study



Salthammer et al. (2010) Chemical Reviews
Salthammer and Mentese (2008) Chemosphere

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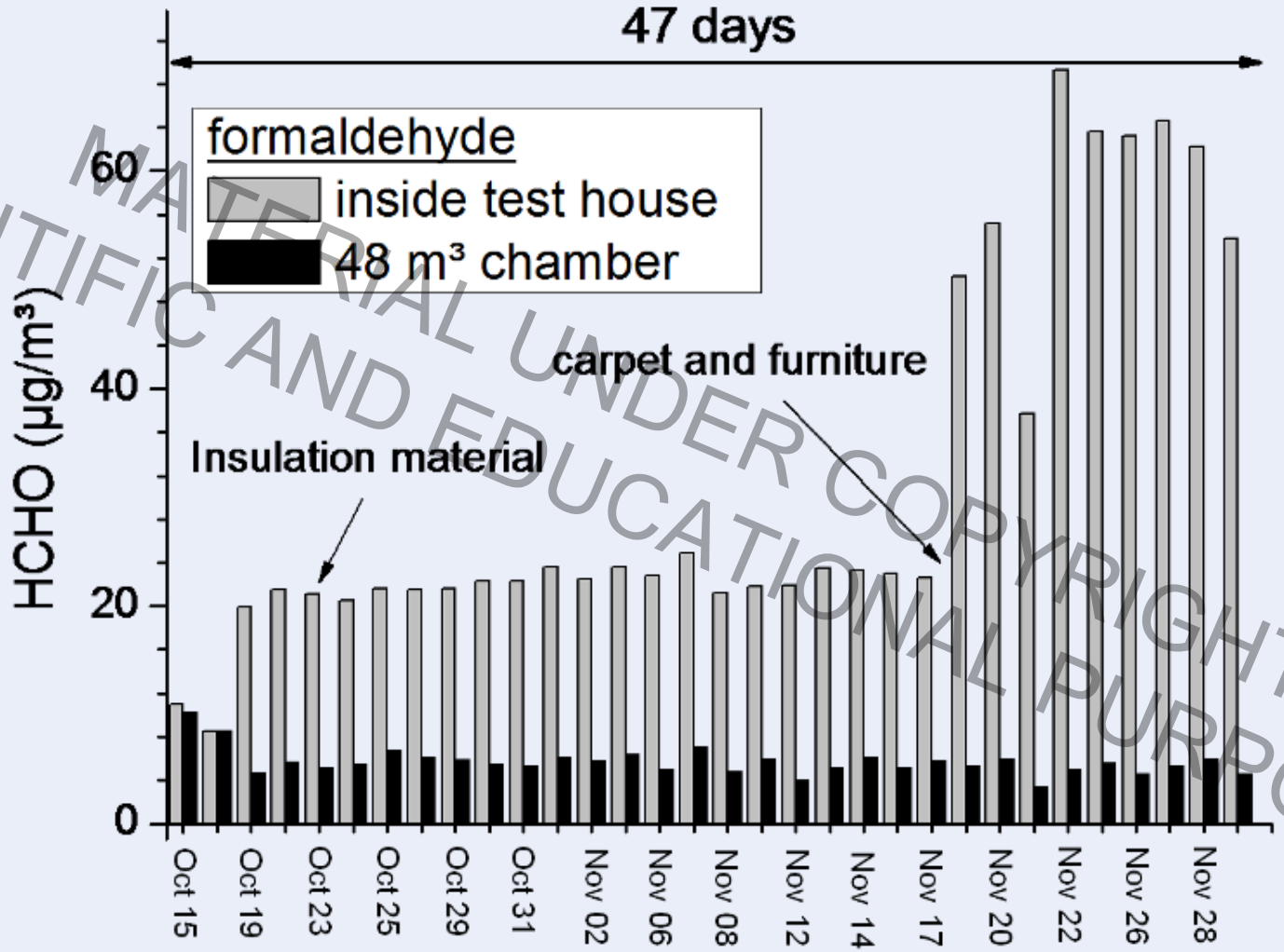
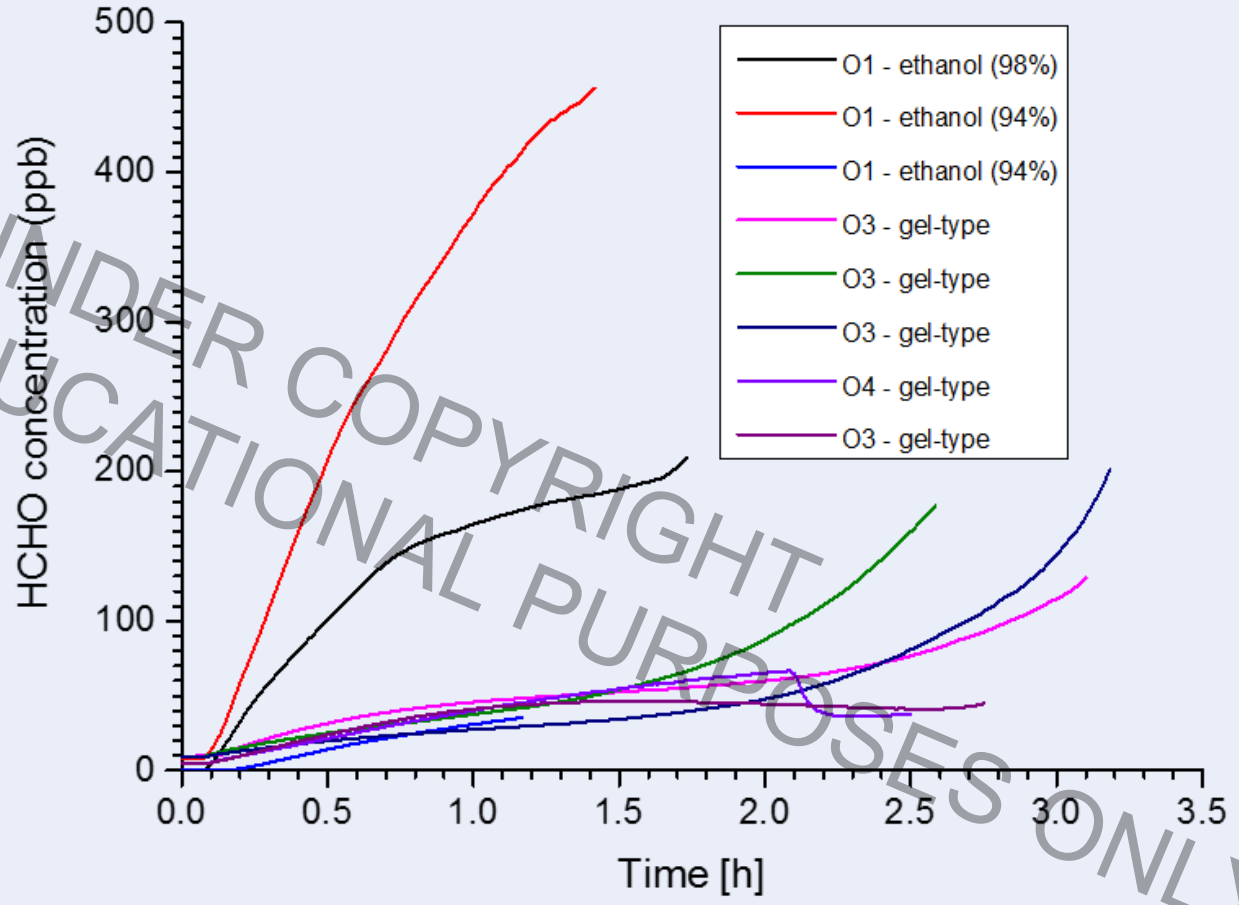
Results of formaldehyde measurement (n = 0.3 h^{-1} inside the house)



Salthammer et al. (2010) Chemical Reviews
Salthammer and Mentese (2008) Chemosphere

Ethanol combustion is by far the strongest formaldehyde source indoors

Experiments in a 48 m³ stainless steel chamber



Schripp et al. (2014) ES&T

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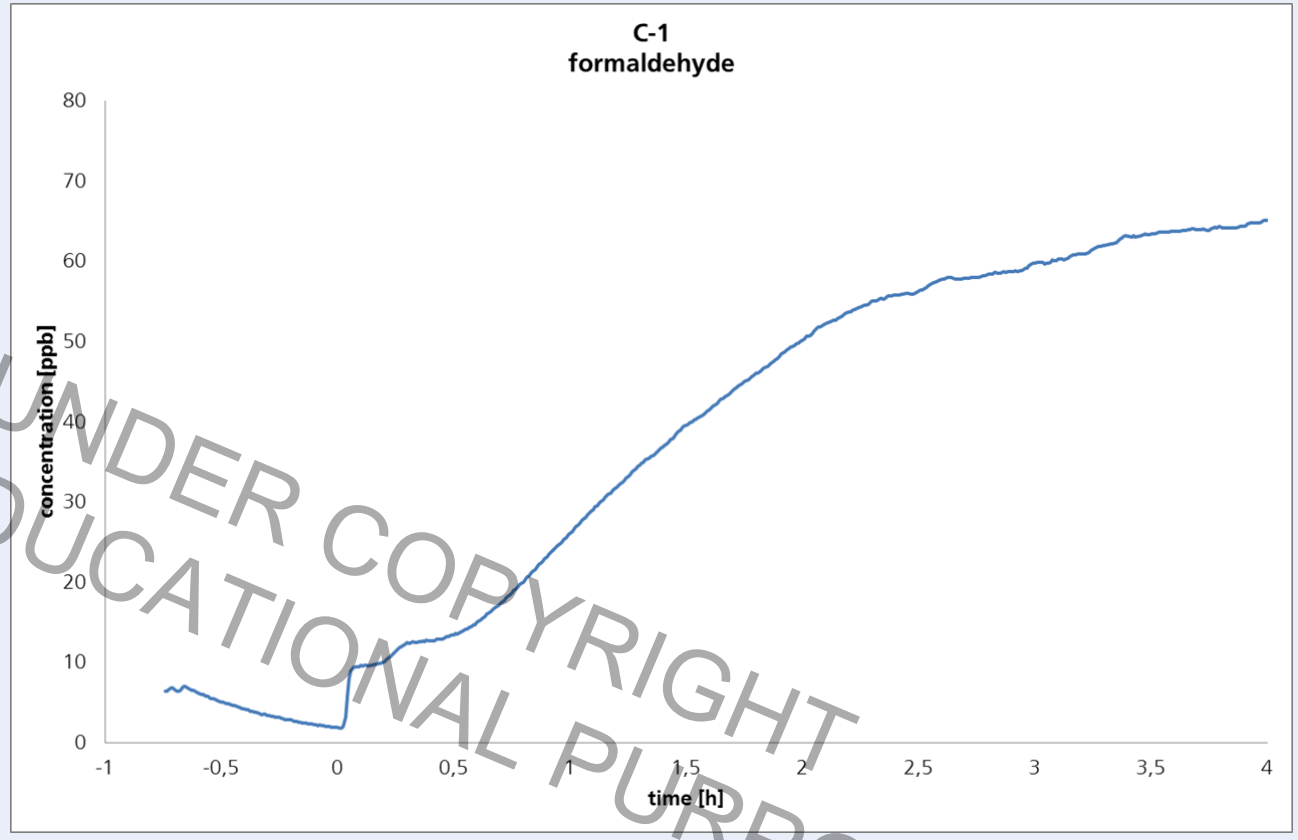
Release of formaldehyde from burning candles



Experiment in a 1 m³ chamber with 2 burning candles.

Mesured emission rates are between 60 – 80 µg formaldehyde per hour and candle

Wensing et al. (2019) to be published

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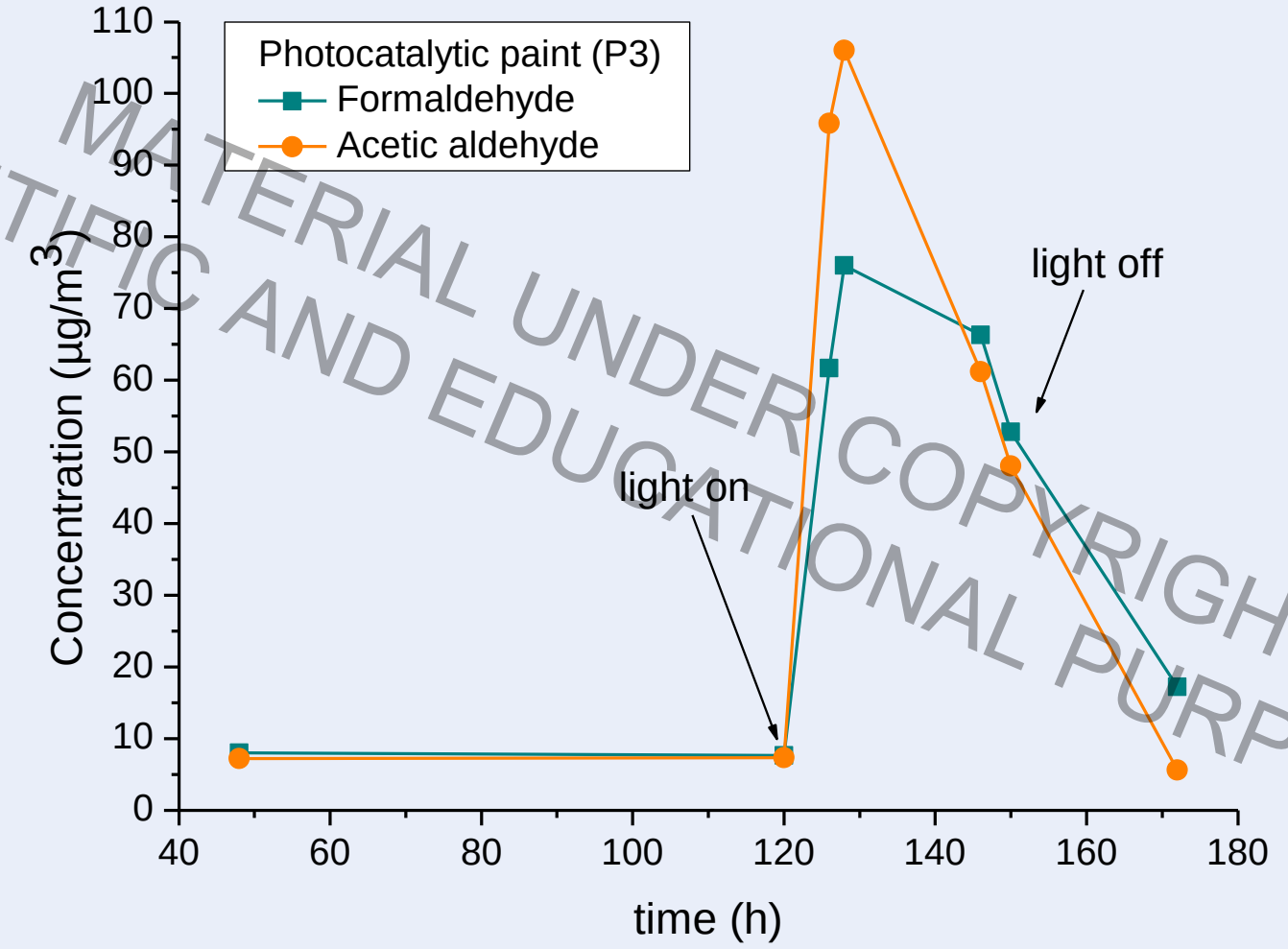
Unexpected formaldehyde emission: photocatalytic wall paint



Salthammer and Fuhrmann (2007) ES&T

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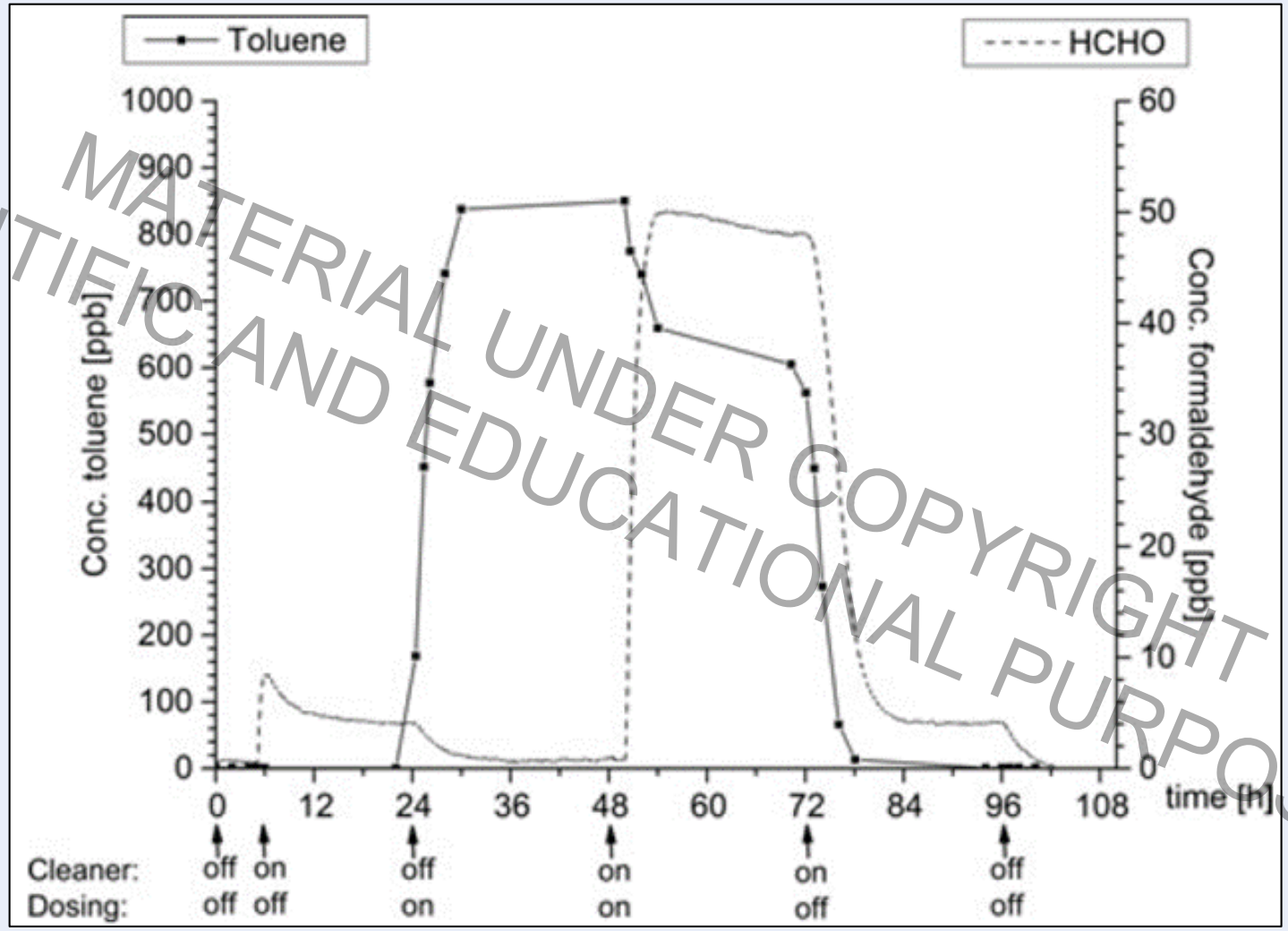
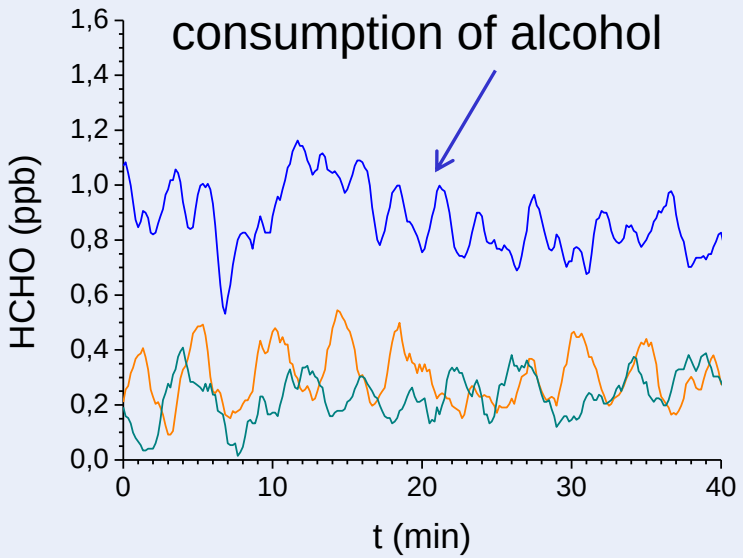
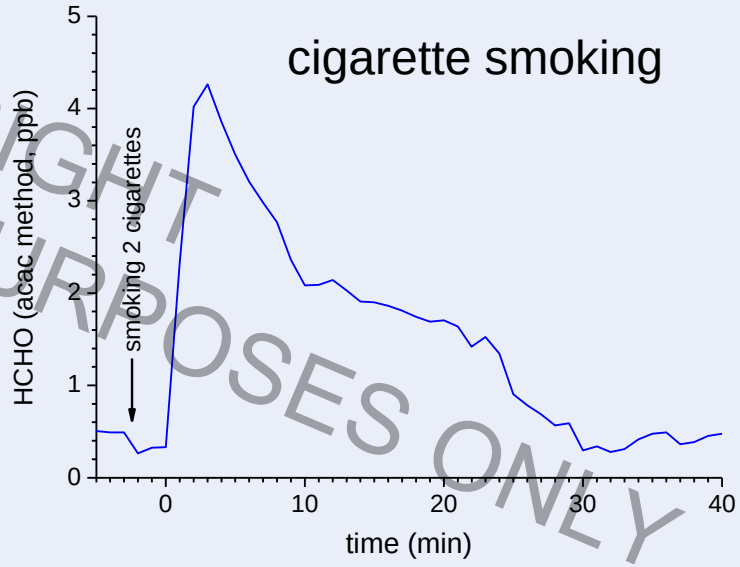
Release of formaldehyde during operation of air cleaning devices



Gunschera et al. (2016) Environ. Sci. Pollut. Res.

Formaldehyde emission from exhaled breath gas





Riess et al. (2010) Analytica Chimica Acta

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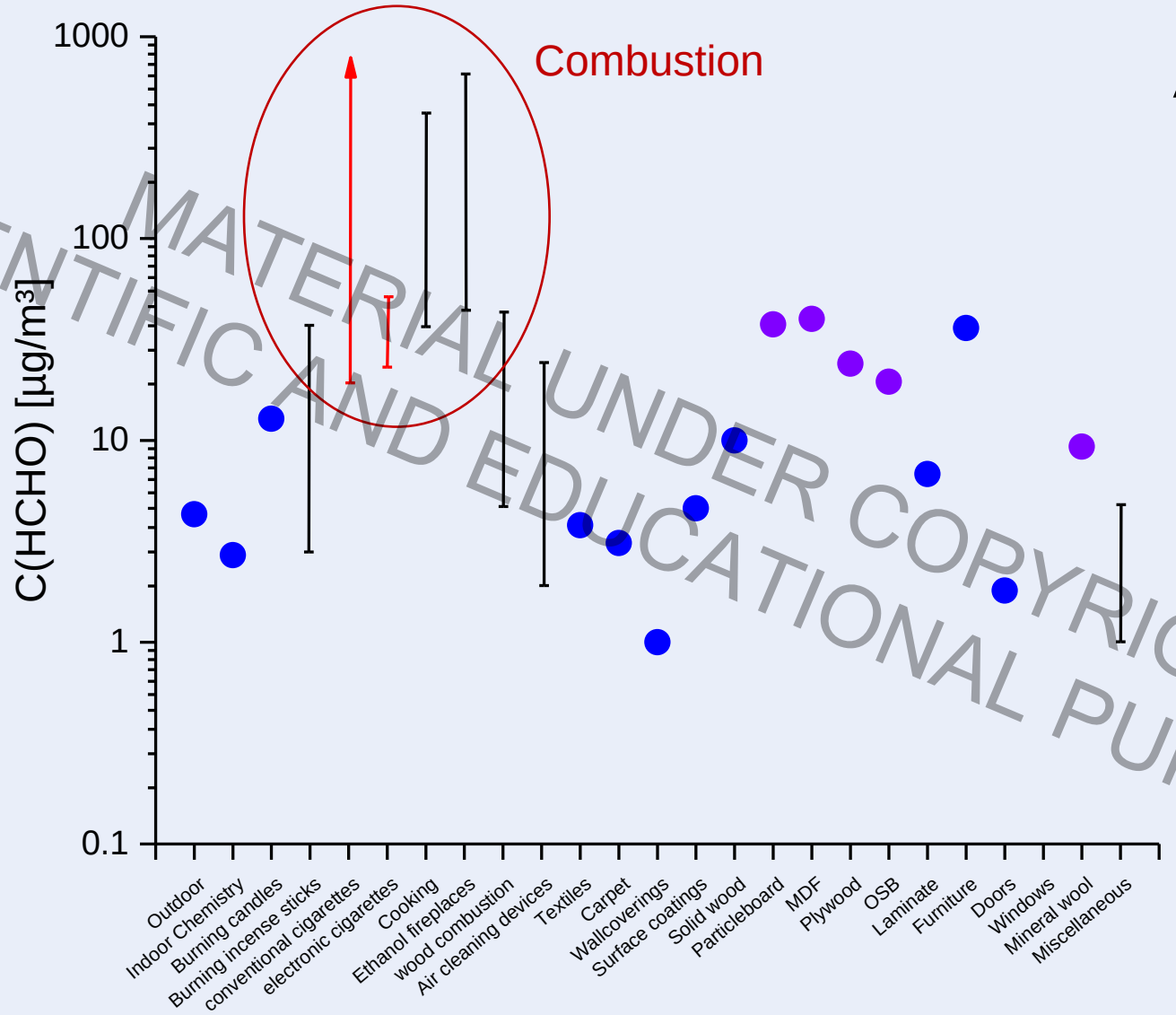
Comparison of formaldehyde sources by Reference Room concentrations

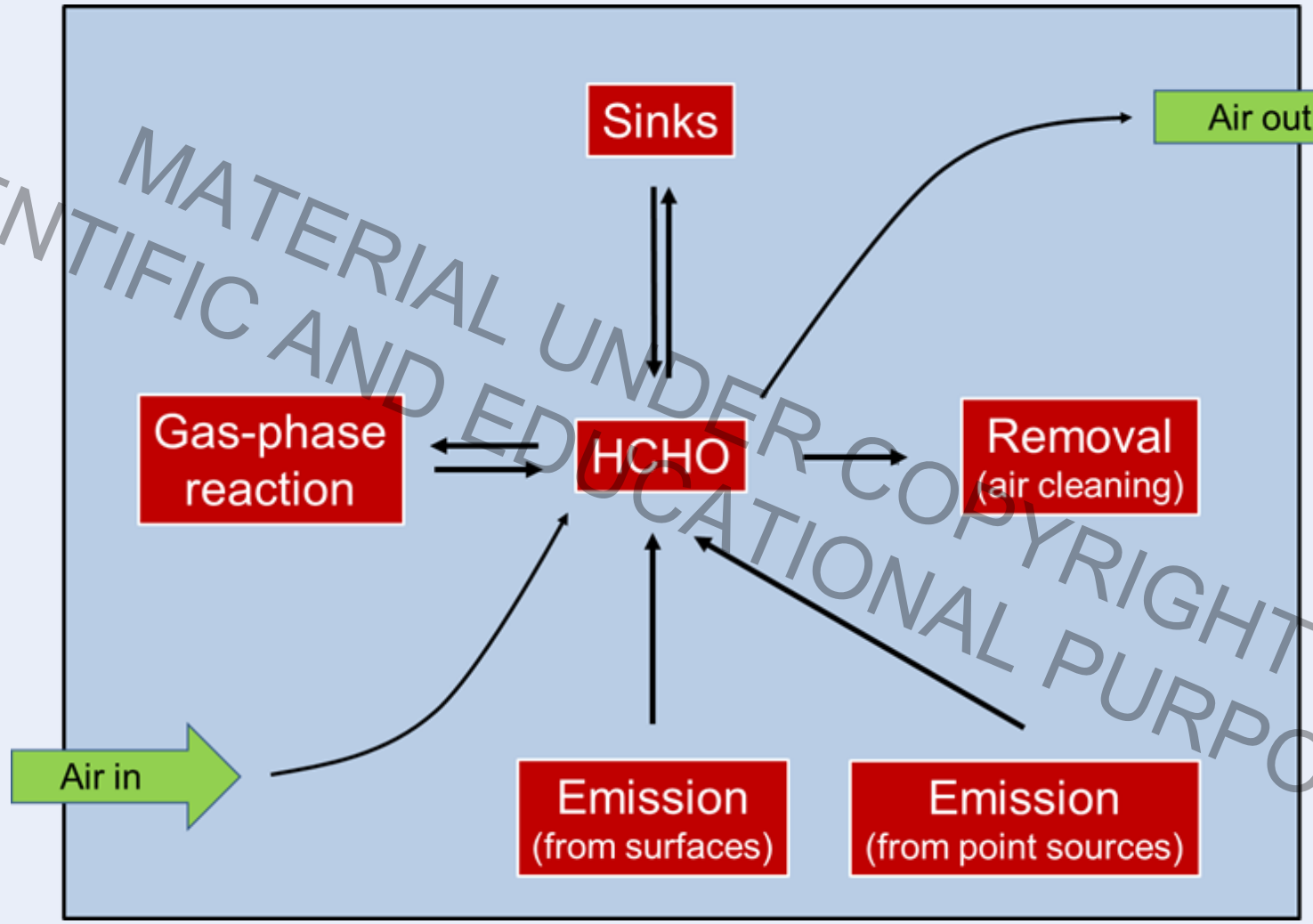


ACH = 0.5 h^{-1}

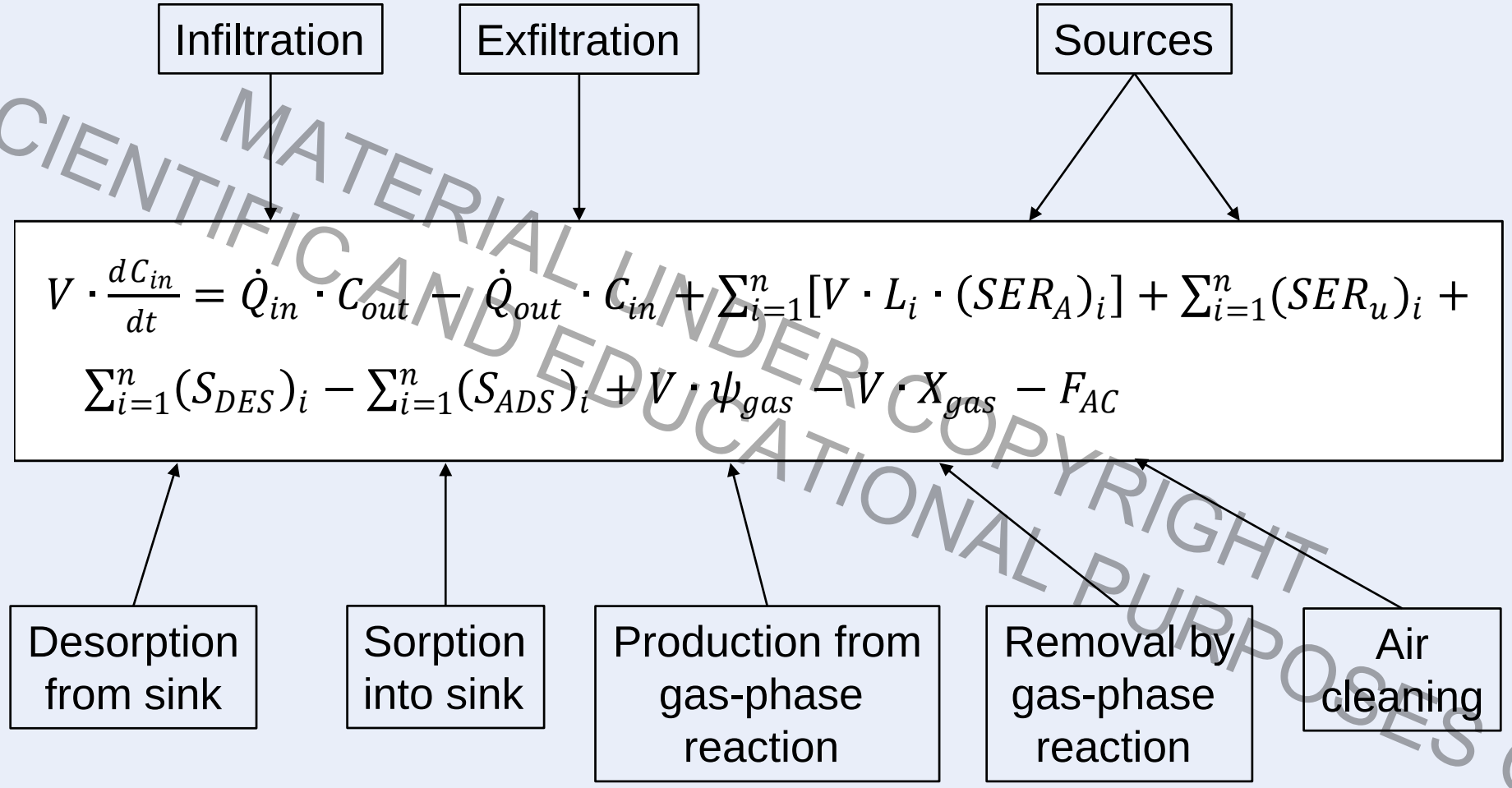
L = 1 m^2/m^3

L = 1 item per 30 m^3

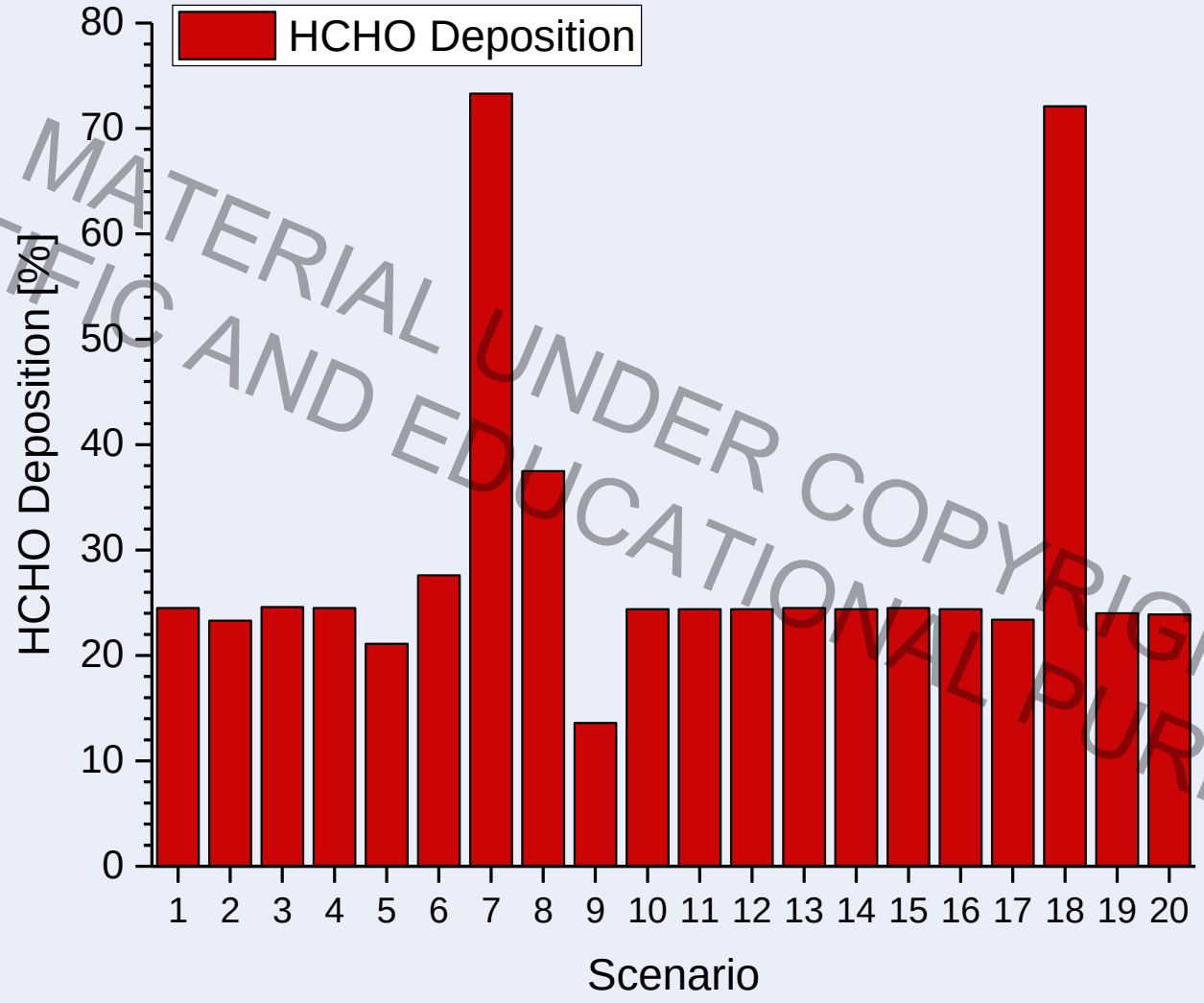
Formaldehyde sources and sinks in the indoor environment



The fundamental mass balance equation



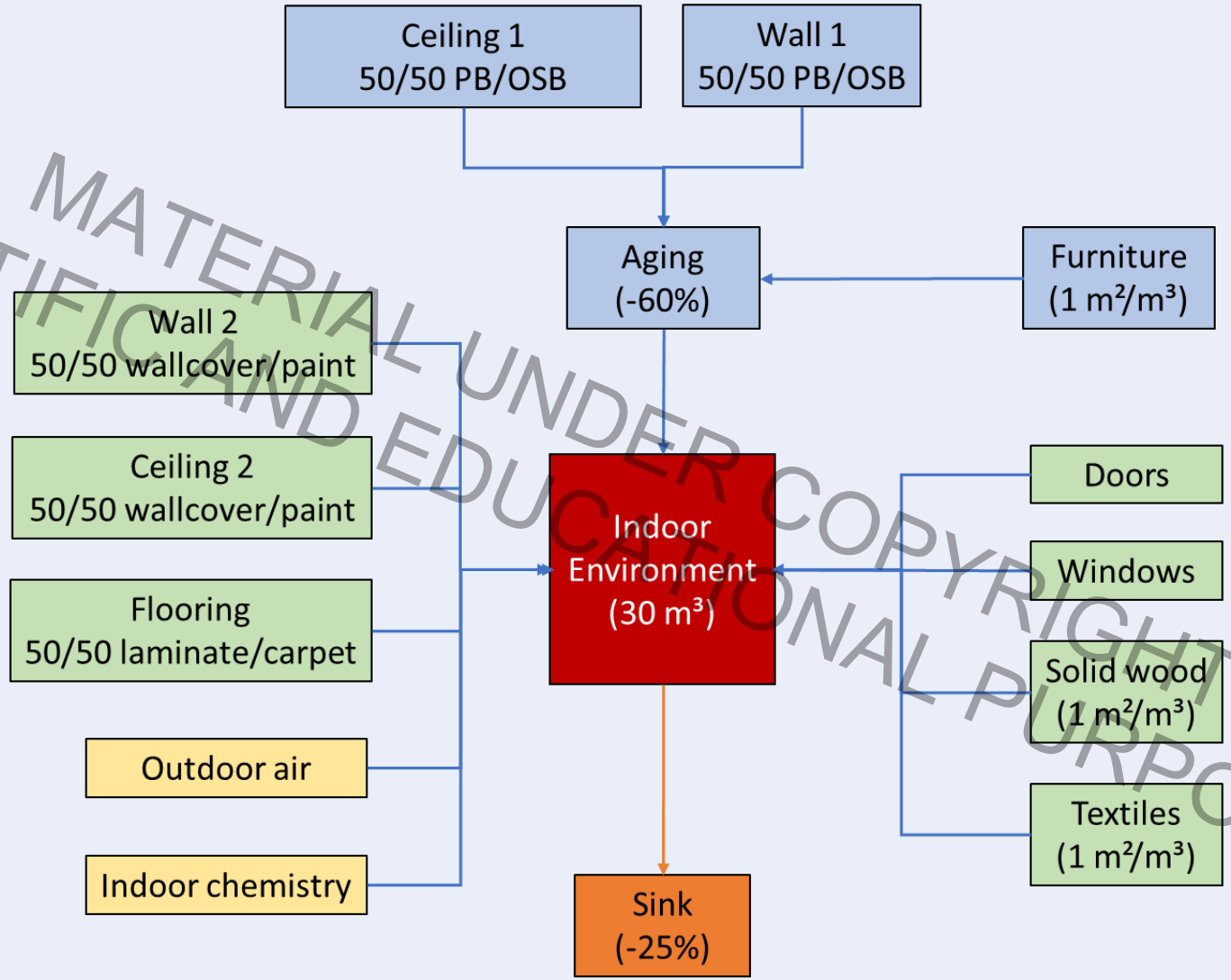
Removal of formaldehyde from indoor air into sinks



Mendez et al. (2018) Atmospheric Environment

Fraunhofer WKI

Monte-Carlo simulation of a Reference Room (V = 30 m³) scenario

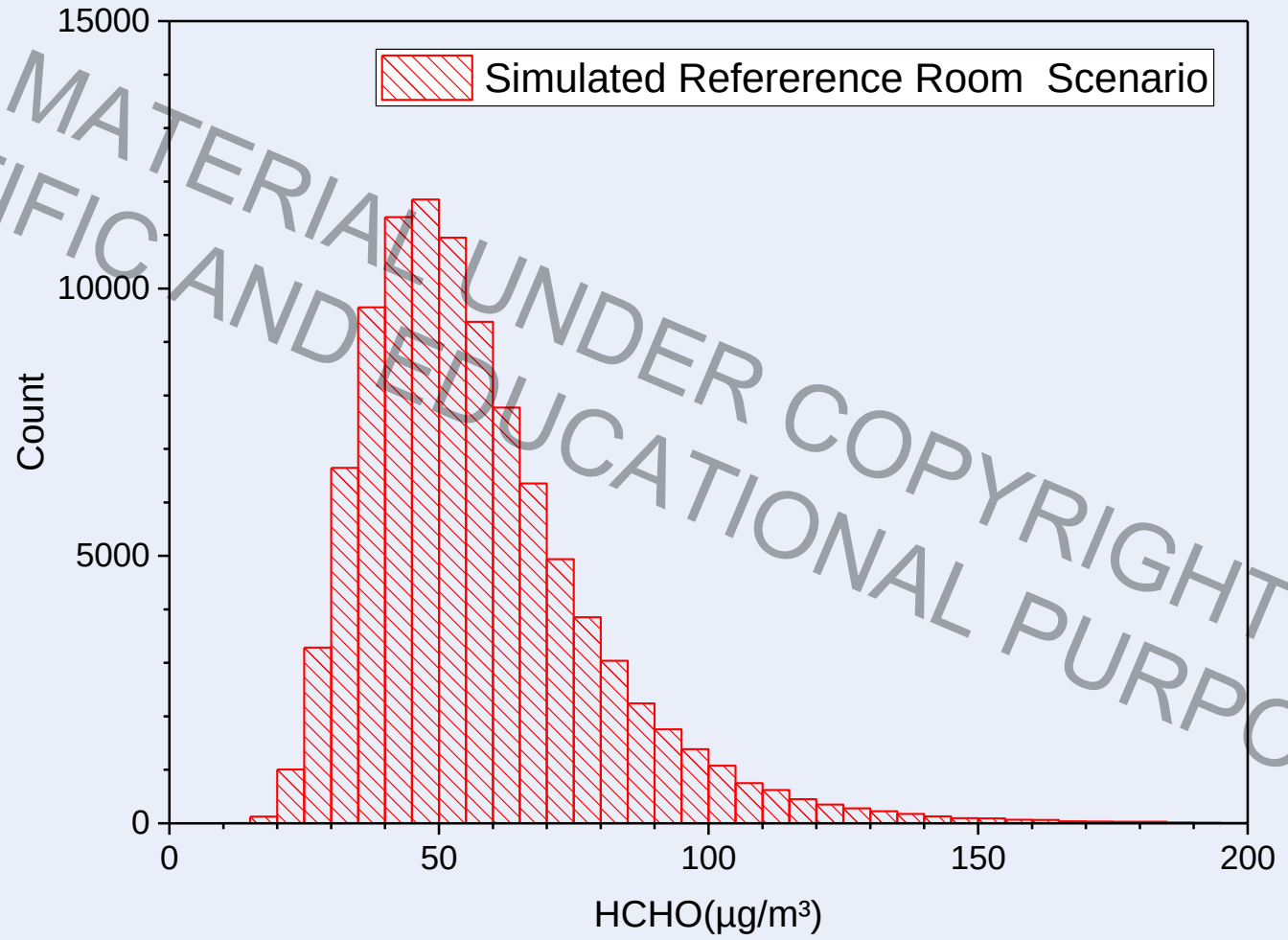


Monte-Carlo simulation of a Reference Room (V = 30 m³) scenario

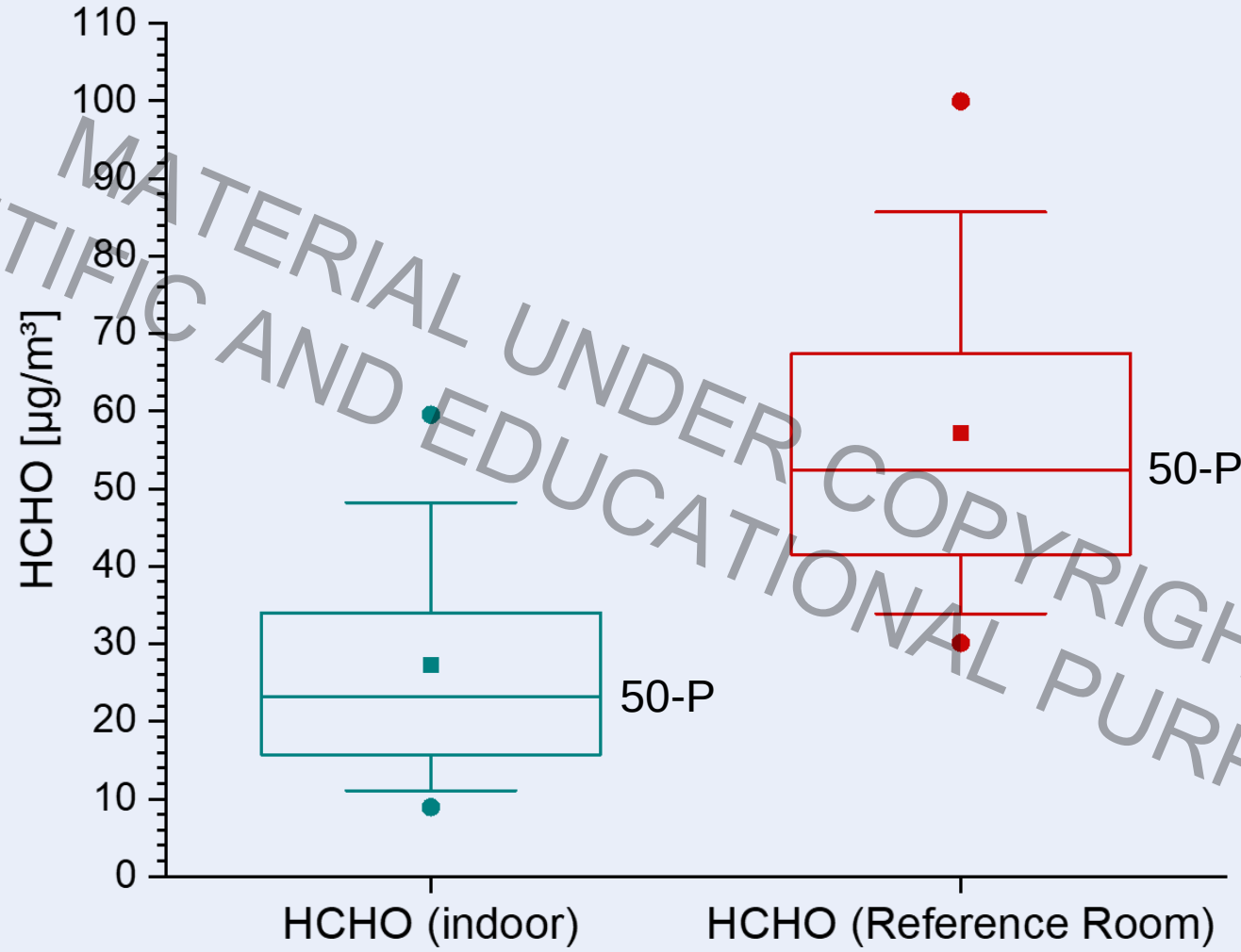
Scenario	Sink [%]	25-P [µg/m³]	50-P [µg/m³]	75-P [µg/m³]	90-P [µg/m³]	95-P [µg/m³]	Remark
Flooring	No	3.4	5.0	7.5	10.9	13.6	50% laminate, 50% carpet
+ Wall 1	No	27.2	36.2	48.1	62.5	73.0	50% PB, 50% OSB
+ Wall 2	No	29.7	39.3	52.1	67.3	78.6	50% wallcover, 50% paint
+ Ceiling 1	No	38.4	51.3	68.6	89.4	104.9	50% PB, 50% OSB
+ Ceiling 2	No	39.4	52.6	70.1	91.4	107.2	50% wallcover, 50% paint
+ Furniture	No	67.3	94.0	133.4	184.1	223.2	1 m²/m³
+ Solid wood	No	75.5	102.4	141.9	193.0	232.0	1 m²/m³
+ Doors	No	77.8	105.5	145.7	197.1	237.1	0.05 m²/m³
+ Windows	No	79.8	107.5	147.7	199.1	239.1	0.05 m²/m³
+ Textiles	No	83.0	111.4	152.5	204.9	245.6	1 m²/m³
+ Outdoor air	No	88.7	117.2	158.4	211.1	251.6	---
+ Indoor chem.	No	91.7	120.4	161.8	214.3	255.3	---
- Aging effect	*No*	*55.9*	*70.4*	*89.9*	*113.3*	*131.2*	*Factor = 0.4*
- Sink	*yes*	*41.9*	*52.8*	*67.4*	*84.9*	*98.4*	*25%*

Monte-Carlo simulation of a Reference Room (V = 30 m³) scenario - results

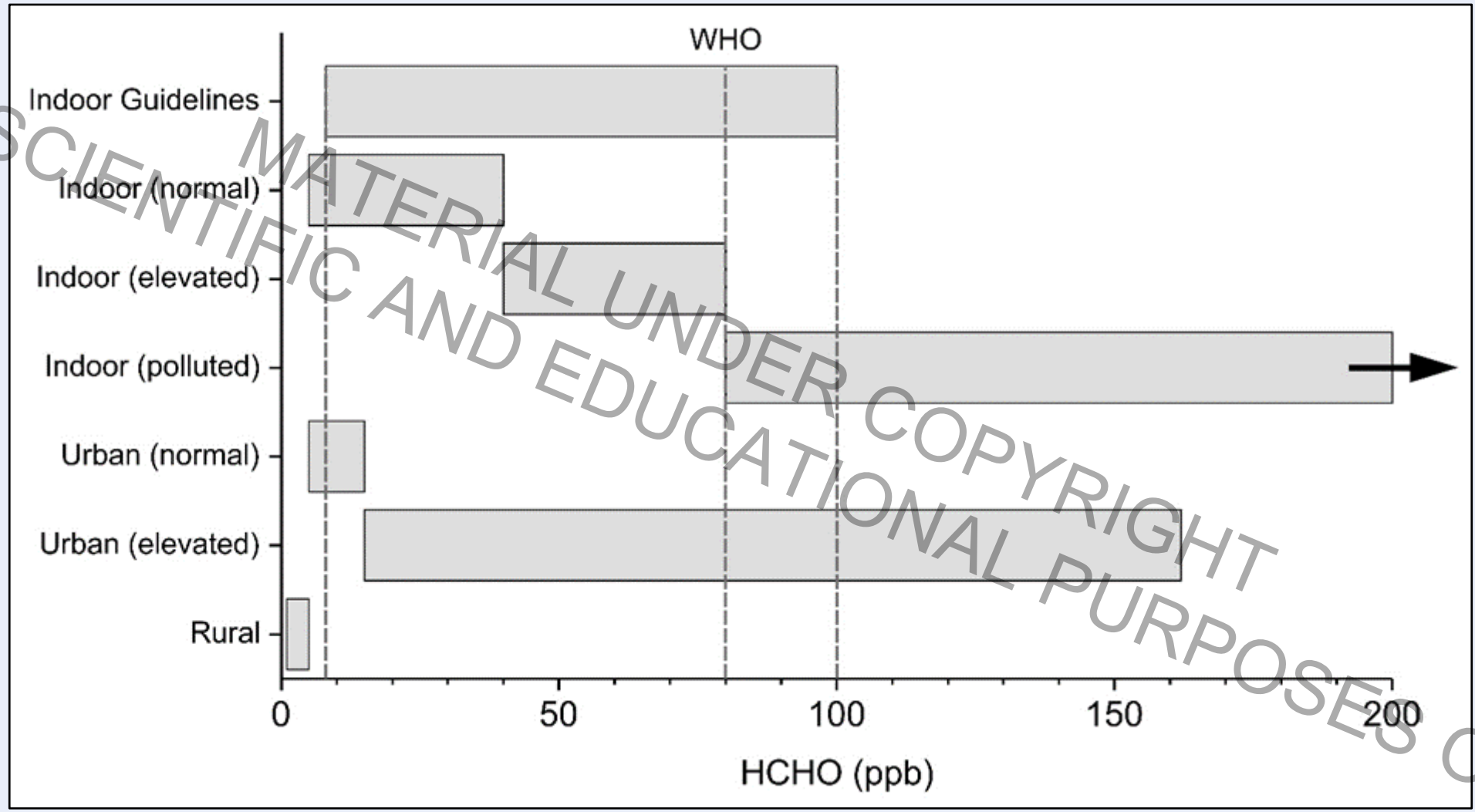
Only permanent emission sources are considered, air exchange rate = 0.5 h^{-1} (geometric mean)



Comparison of the Reference Room scenario with measured formaldehyde concentrations



Range of formaldehyde concentrations in indoor and outdoor air



Salthammer (2013) Angewandte Chemie Int. Ed.

Question 1:

Is the lower guideline always the better guideline ?

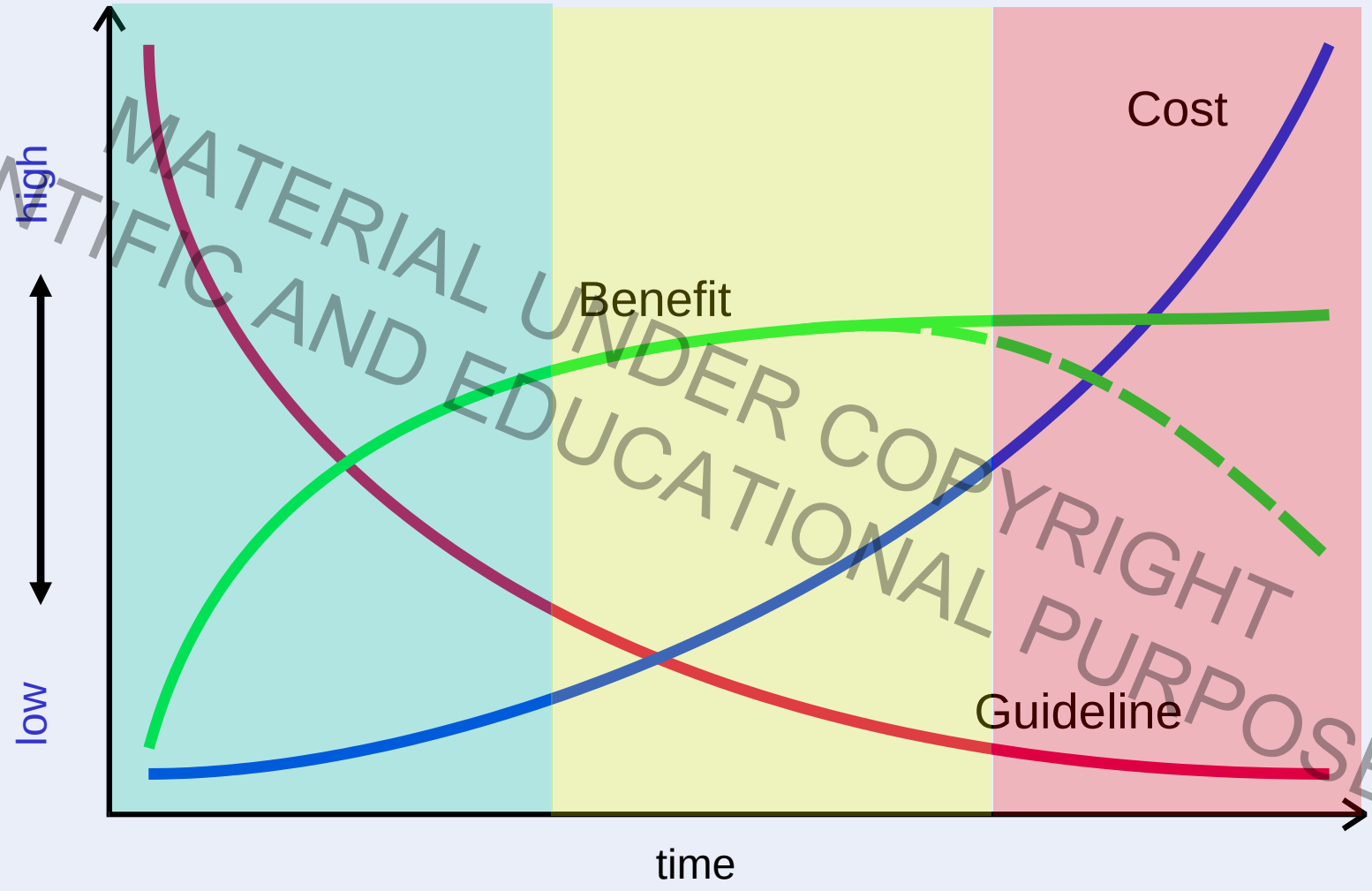
“The end justifies the means”

N. Machiavelli

Question 2:

Does the benefit always justify the effort ?

Is the lower indoor guideline always the better guideline ???



Salthammer (2011) Chemosphere

Fraunhofer WKI

Summary and Conclusions

- Under normal living conditions, formaldehyde concentrations in European homes are between 20 µg/m³ and 30 µg/m³ (50-P).
- It is a myth that average air exchange rates are in the range of 0.1 h^{-1} or lower.
- There are many potential formaldehyde sources. Some are permanant, some are intermitting.
- Some analytical methods like the MBTH method overestimate formaldehyde concentrations.
- Conversion of product specific emission rates into reference room concentrations does not explain real-life concentrations.
- In the indoor environment, formaldehyde peak concentrations are caused by combustion processses (especially ethanol combustion).
- The Reference Room is suitable for the comparison of emission rates, but the calculation of exposure scenarios remains questionable.

Some final remarks…..

"…it becomes clear that the political measures to limit formaldehyde (regardless of whether on the national or international level) currently face a dilemma.

On one hand great efforts are being made to politically impose ever-lower formaldehyde limits on building product emissions and indoor air concentration.

Some of these are hardly justifiable from a prevention point of view and definitely not justifiable from a toxicological point of view.

On the other hand one can observe a certain ambivalence, as secondary sources in indoor and outdoor spaces – and the influence of building and construction – generally remain unconsidered.

Indoor formaldehyde concentrations are tending to fall, but outdoor concentrations are tending to rise."