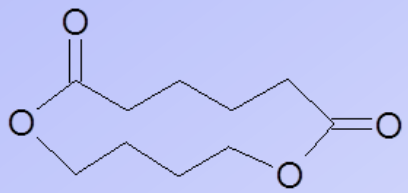
Release of Pollutants from Materials and Products for Indoor Use – A Summary of Recent Developments



T. Salthammer

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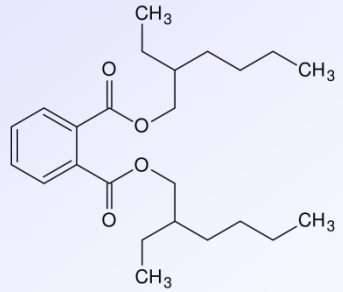
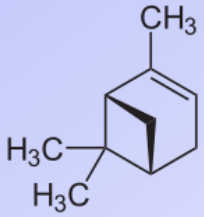
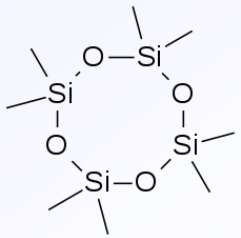
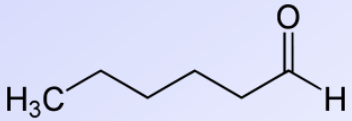
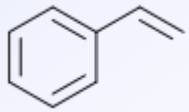
38108 Braunschweig, Germany







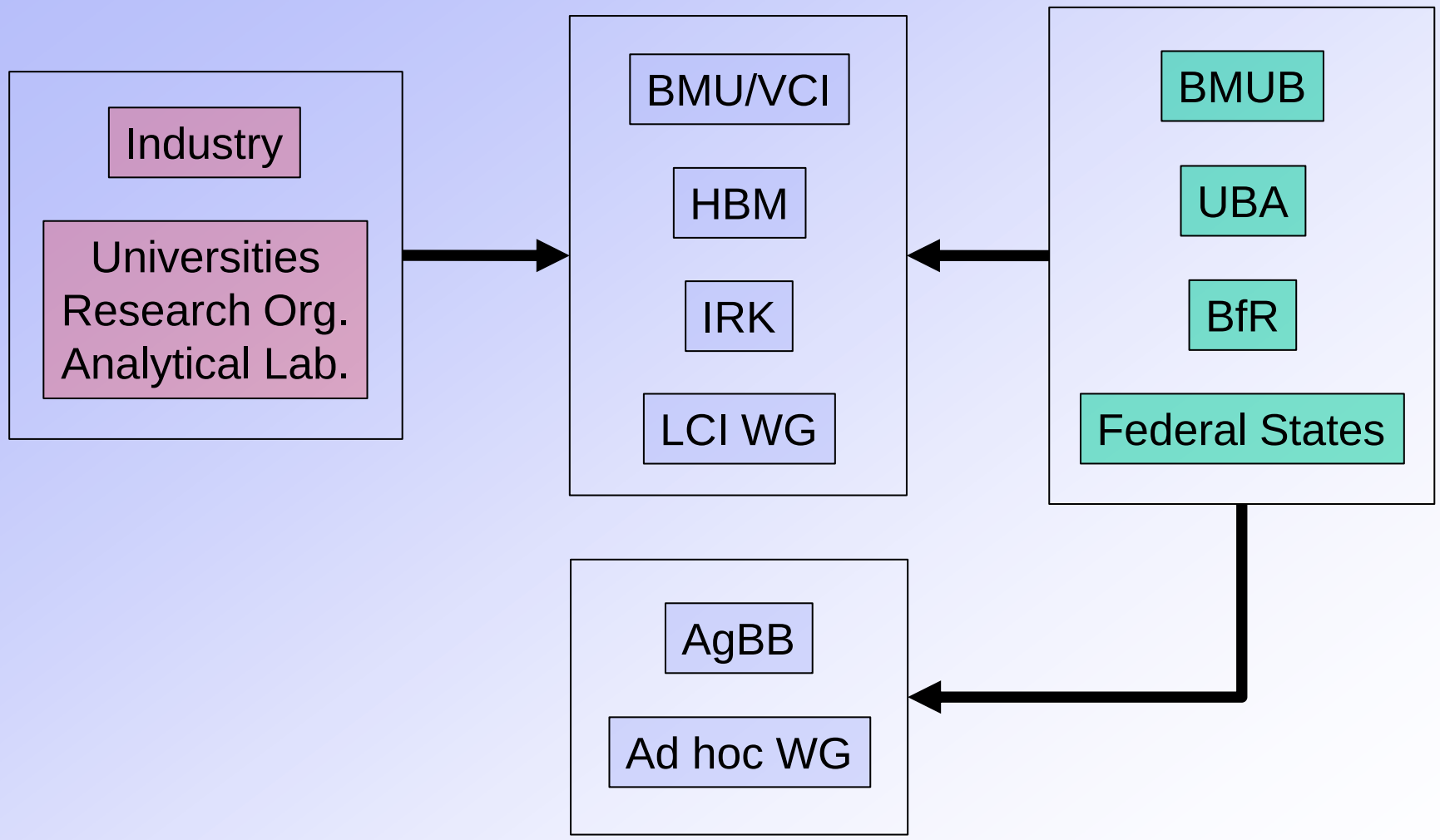




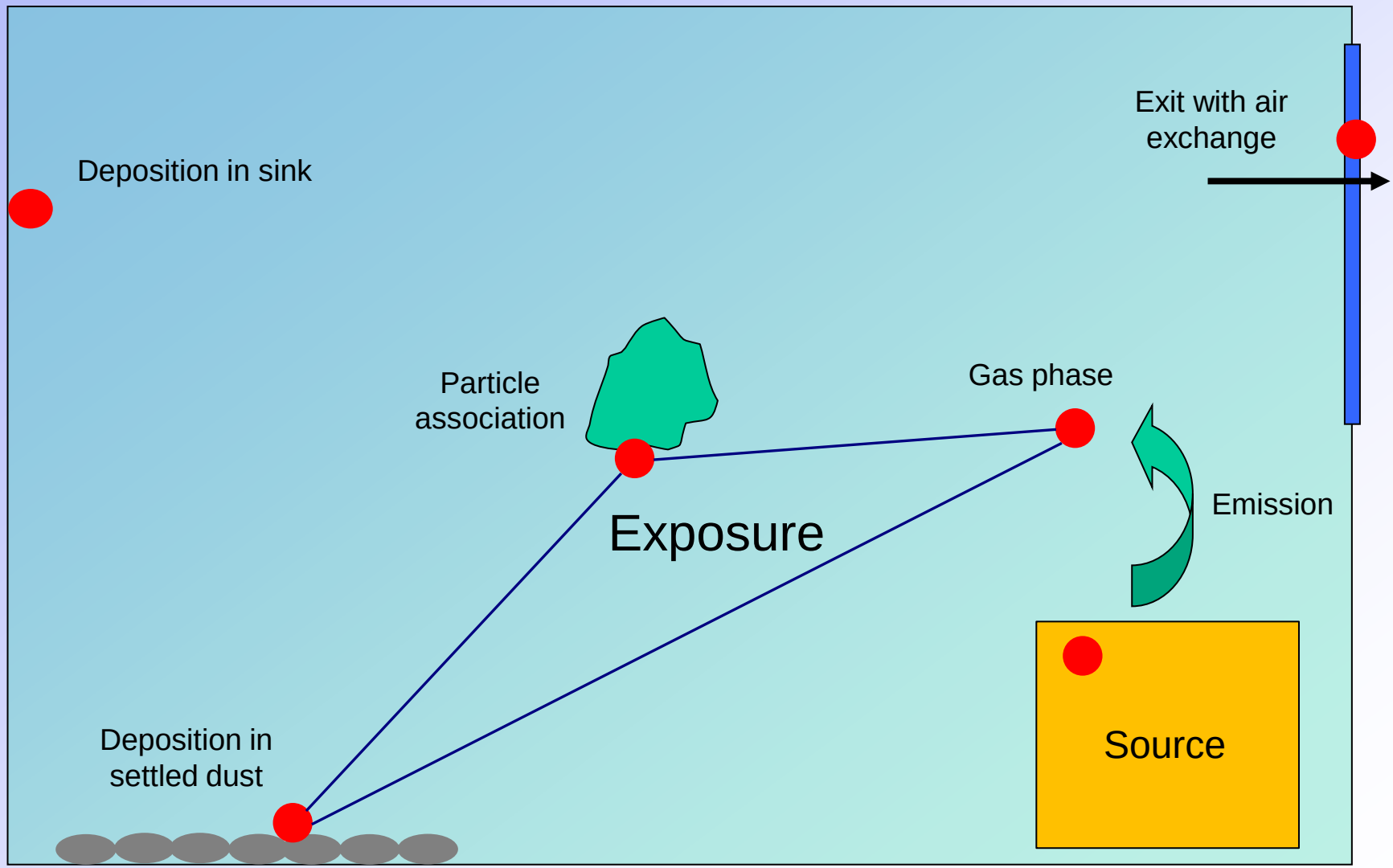
Content

- Indoor fundamentals
- Analytical tools (chambers and equipment)
- Recent trends in emission testing
- Indoor guidelines and recommendations
- Distribution of chemicals in the indoor environment
- Exposure to indoor pollutants
- Formaldehyde: a never ending story?
- Future developments and challenges

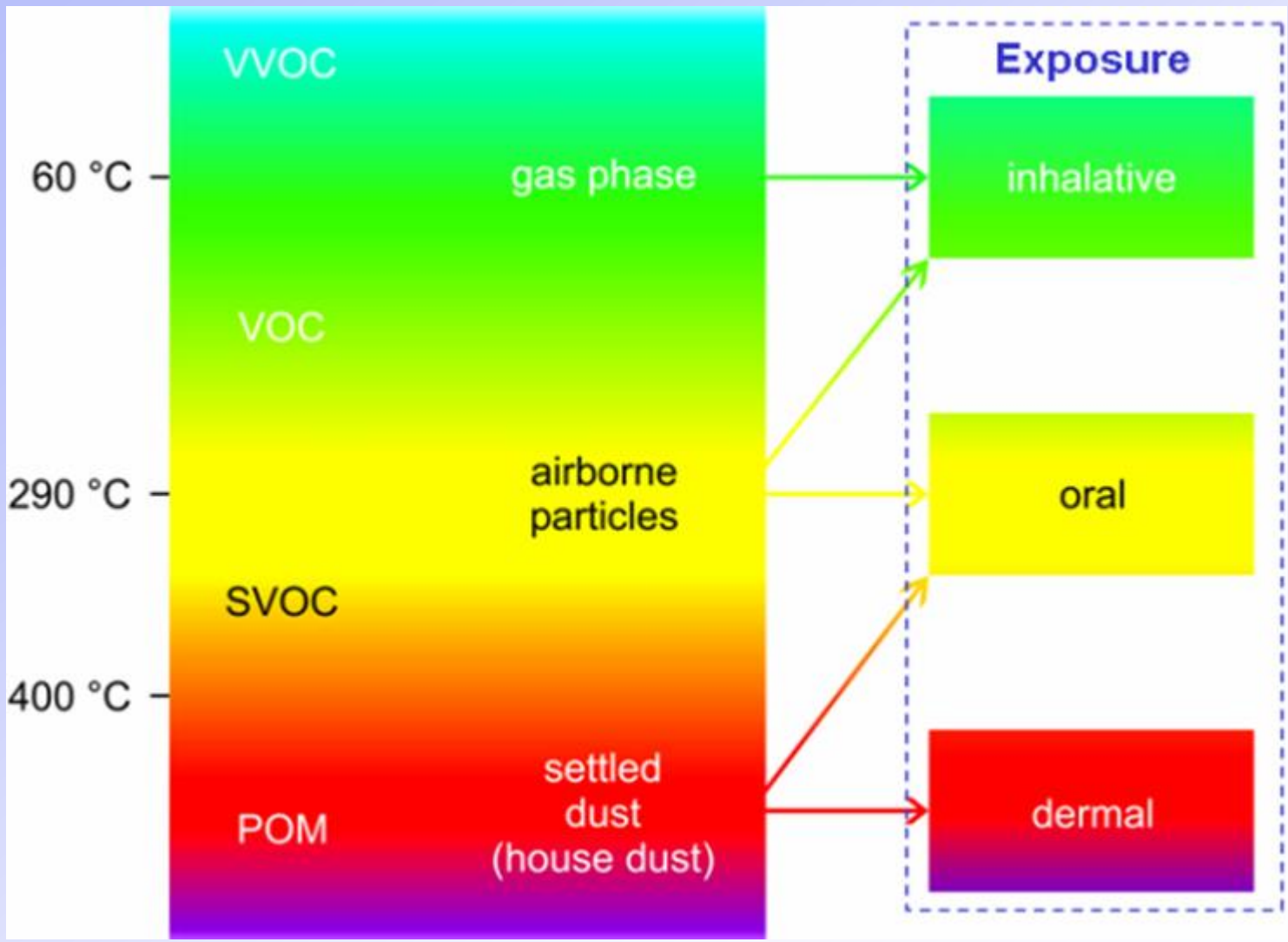
Indoor related governmental organizations in Germany



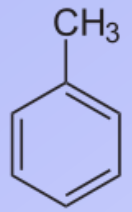
Fate of a single molecule indoors

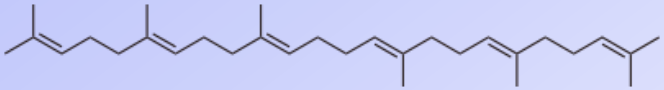


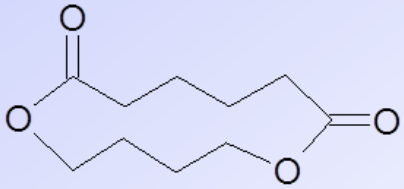
Indoor related classification of organic compounds

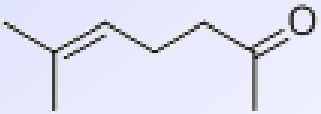


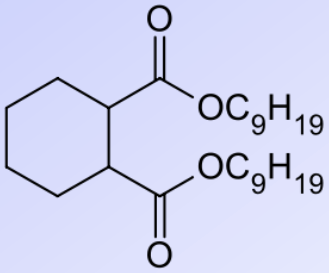
Indoor related chemicals

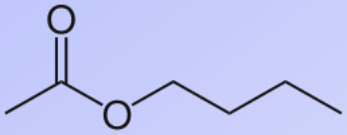


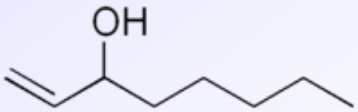












Classics

Avantgarde

Stealth *

* by courtesy of C. Weschler

Analytical tools (selection)

GC/MS

HPLC

Photoacoustics

PTR-MS

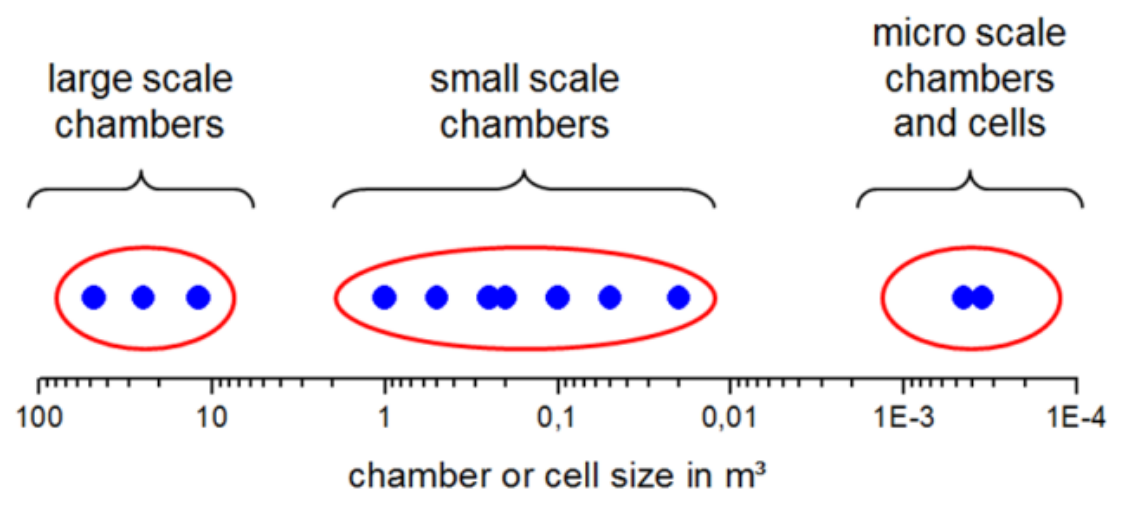
0.3 – 32 µm (size distribution)

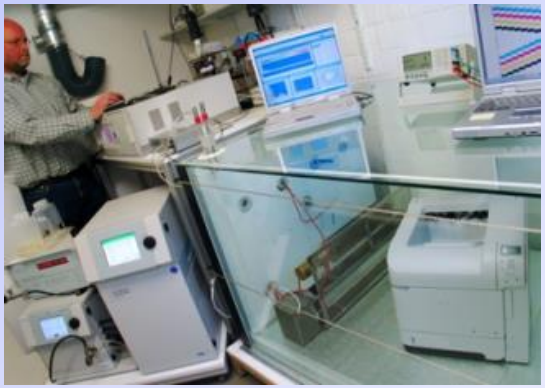
20 – 1000 nm (sum only)

5.6 – 560 nm (FMPS) (size distribution)

10 – 800 nm (SMPS) (size distribution)

Chambers for indoor related emission testing

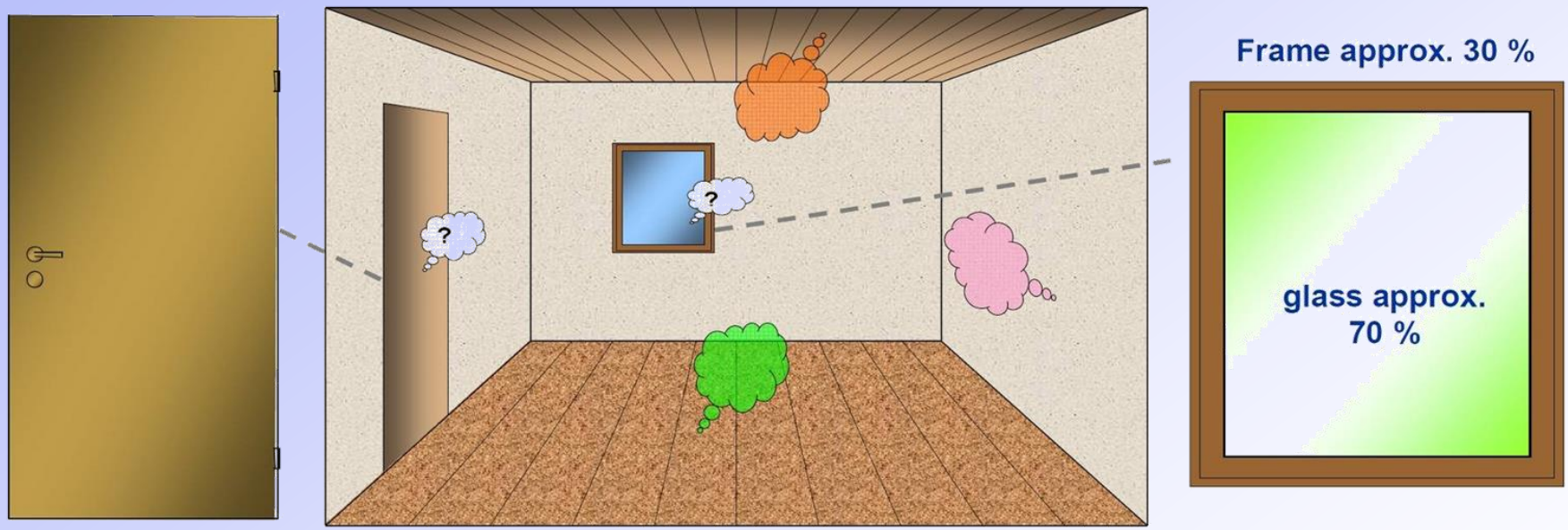




1 m³ glass chamber

24 m³ stainless steel chamber

CEN TC 351 (Draft) – Reference Room



CEN TC 351

Volume reference room: 30 m³

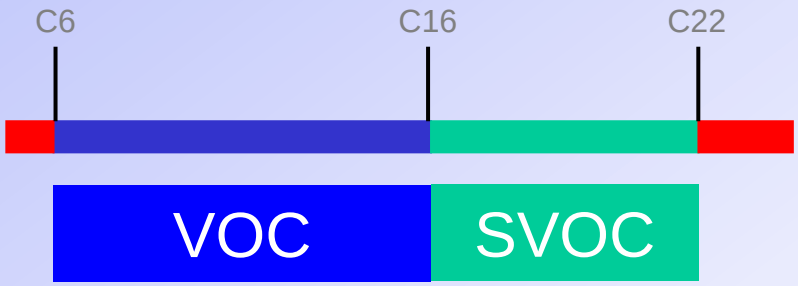
Wall: 31,4 m² Base / Ceiling: 12,0 m² Internal door: 1,6 m² Window: 2,0 m²

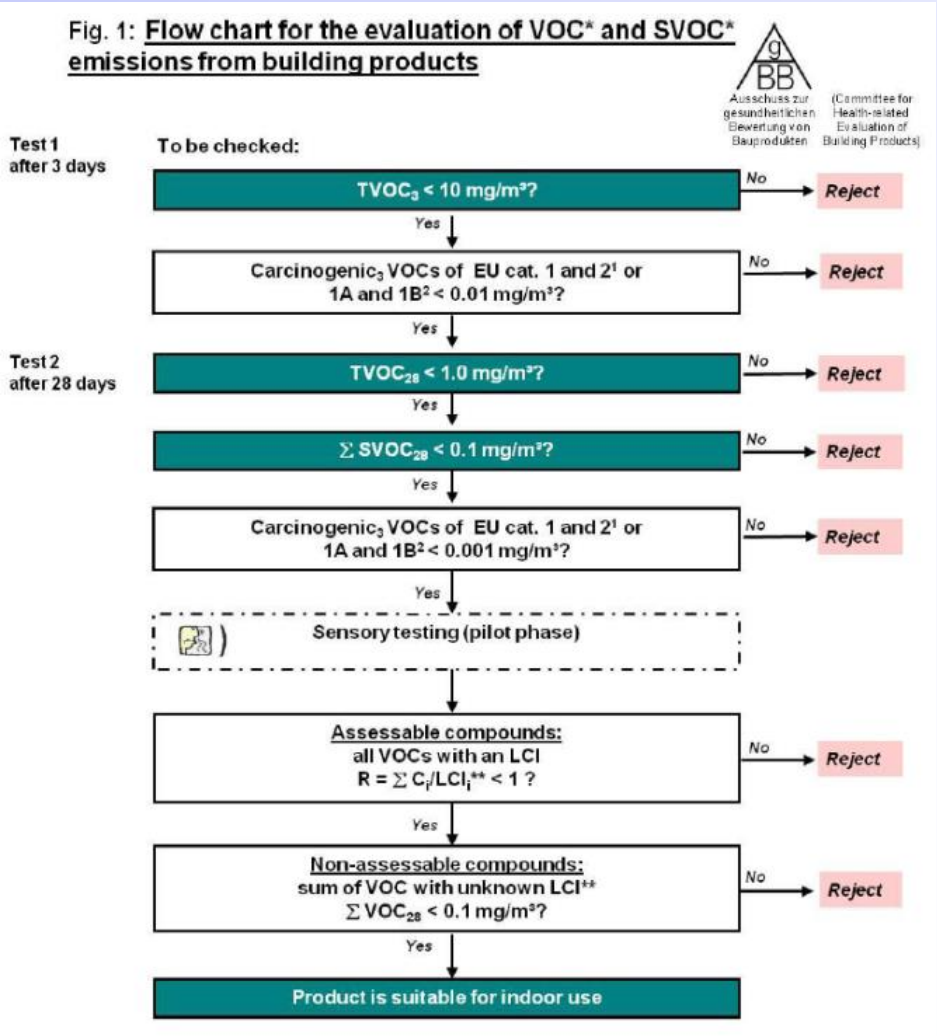
Principle of the AgBB-Scheme

www.umweltbundesamt.de

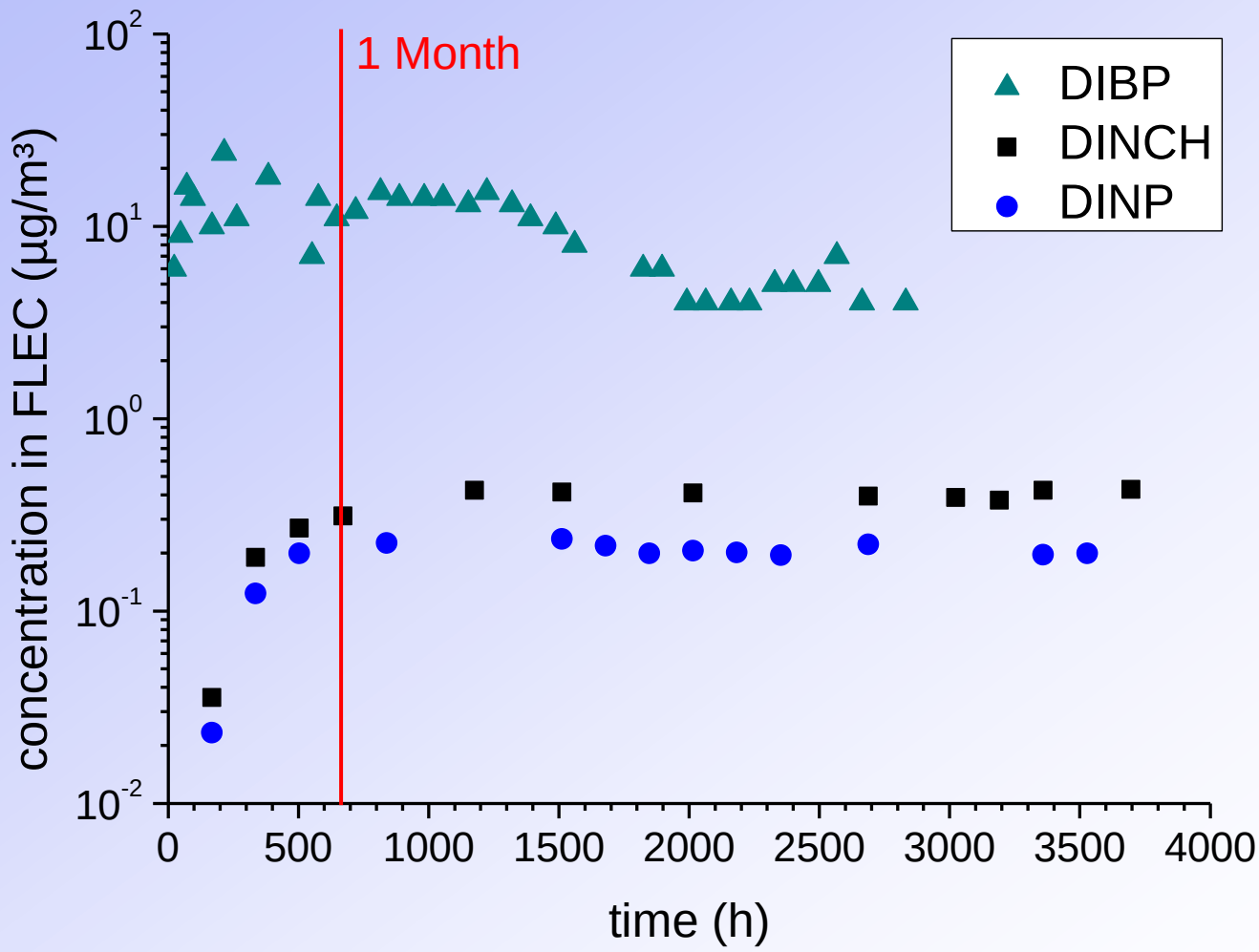
Key word: agbb

latest update: 2012





Long term emission of DIBP, DINCH and DINP from paint and PVC



Details of the AgBB-Scheme: Sensory Testing

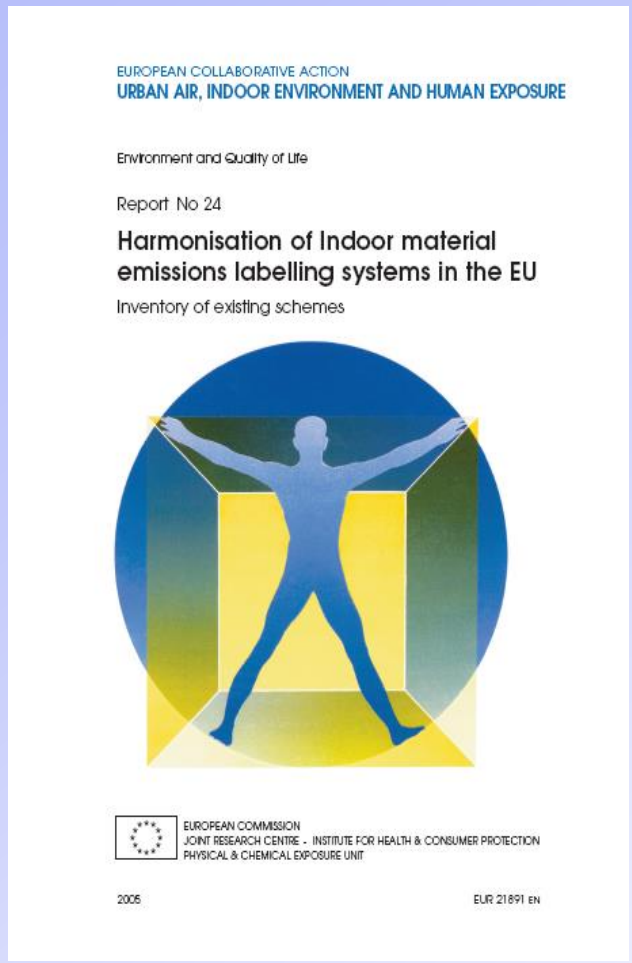
- **ISO 16000-28 (2012)**

  Determination of odour emissions from building products using test chambers
  - Acceptability
  - Intensity
  - Hedonics

- **ISO 16000-30 (Draft 2012)**

  Sensory testing of Indoor Air
  - Acceptability
  - Intensity
  - Hedonics

European Harmonization of Building Product Labeling I



EUROPEAN COLLABORATIVE ACTION
URBAN AIR, INDOOR ENVIRONMENT AND HUMAN EXPOSURE

Environment and Quality of Life

Report No 24

Harmonisation of Indoor material emissions labelling systems in the EU

Inventory of existing schemes

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE - INSTITUTE FOR HEALTH & CONSUMER PROTECTION
PHYSICAL & CHEMICAL EXPOSURE UNIT

2005 EUR 21891 EN

THE INDOOR CLIMATE LABEL

EMISSION CLASS FOR BUILDING MATERIAL M1

for better living natureplus®

AgBB

Teppichboden schadstoffgeprüft

CARPET contaminant-tested*

* by Deutsches Teppich-Forschungsinstitut e.V. in Cooperation with BITTG, Centexbel, DTI, ÖTI

Test No. 10 009

GUT (GEMEINSCHAFT UMWELTFREUNDLICHER TEPPICHBODEN e.V.)

Moquette testée sur présence de substances nocives

GEV-EMICODE EC 1 very low emission

Umweltzeichen weil emissionsarm Jury Umweltzeichen

European Harmonization of Building Product Labeling II

EUROPEAN COLLABORATIVE ACTION

URBAN AIR, INDOOR ENVIRONMENT AND HUMAN EXPOSURE

Environment and Quality of Life

Report No 29

Harmonisation framework for health based evaluation of indoor emissions from construction products in the European Union using the EU-LCI concept

JOINT RESEARCH CENTRE
Institute for Health and Consumer Protection
Chemical Assessment and Testing Unit

2013 EUR 26168 EN

EUROPEAN COLLABORATIVE ACTION

URBAN AIR, INDOOR ENVIRONMENT AND HUMAN EXPOSURE

Environment and Quality of Life

Report No 27

Harmonisation framework for indoor products labelling schemes in the EU

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE - INSTITUTE FOR HEALTH & CONSUMER PROTECTION
CHEMICAL ASSESSMENT AND TESTING UNIT

2012 EUR 25276 EN

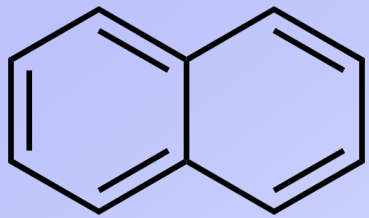
Priority EU-LCI values

Table 8. *Prioritised compounds for deriving EU-LCIs*

Compound	CAS No.
1,2,4-Trimethylbenzene	95-63-6
2-Butoxyethanol	111-76-2
Toluene	108-88-3
Xylene	1330-20-7
1,4-Dichlorobenzene	106-46-7
Ethylbenzene	100-41-4
Styrene	100-42-5
Acetaldehyde	75-07-0
Tetrachloroethylene	127-18-4
Formaldehyde	50-00-0
ε-Caprolactam	105-60-2
α-Pinene	80-56-8
n-Butanal	123-72-8

Source: ECA Report No. 29

Development of indoor air guideline values. Example: Naphthalene



LOAEL 5 mg/m³ (rats)
Exposure time adjustment (subchronic, chronic)

↓ Interspecies factor (12)

Threshold for effects in humans

↓ Intraspecies factor (10)

Threshold for susceptible individuals

↓ Children factor (2)

Threshold for susceptible individuals and children

↓

RW II = 20 µg/m³ ← RW II / 10 — RW I = 2 µg/m³

Guidelines and recommendations for indoor air pollutants (Germany)

(Formaldehyde	*1977)*
Toluene	1996
Pentachlorophenol	1997
Carbon Monoxide	1997
Dichloromethane	1997
Nitrogen Dioxide	1998
Styrene	1998
Mercury	1999
Diisocyanates	2000
Tris(2-chloroethyl)phosphate	2002
Terpenes (bicyclic)	2003
Naphthalene	2004
Alkanes (C9-C14)	2005
TVOC	*2007*
Carbon Dioxide	*2008*
Aldehydes (C4-C11)	2009
Terpenes (monocyclic)	2010
Benzyl Alcohol	2010
Benzaldehyde	2010
Siloxanes (D3-D6)	2011
2-Furaldehyde	2011
Phenol	2011
Cresols	2012
Alkylbenzenes (C9-C15)	2012
Ethylbenzene	2012
2-Ethyl-hexanol	2013
Glycols	2013
MIBK	2013
Acetaldehyde	2013

Odour guide values for indoor air (Germany)

$vGLW\ I = 6\ ODT_{50}$

$vGLW\ II = 48\ ODT_{50}$

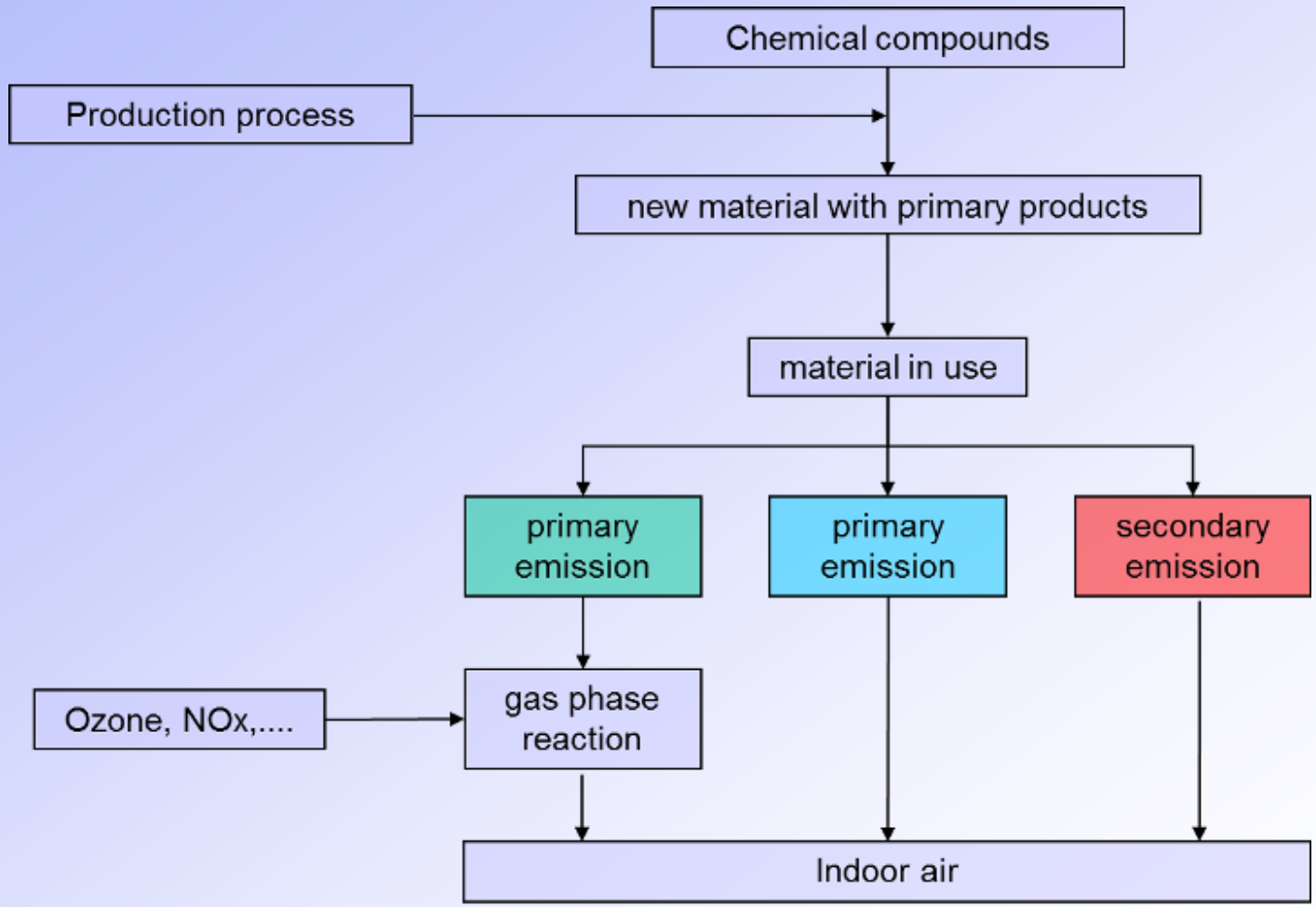
2 YEAR PILOT PHASE RECOMMENDED !!!

Tab. 2 Geruchswahrnehmungsschwellen ODT_{50} und vorläufige Geruchsleitwerte I und II

Geruchsstoff	CAS-Nr.	ODT_{50} (µg/m³)	Zitat	vGLW I (mg/m³)	vGLW II (mg/m³)
Ethanal	75-07-0	2,8	15	0,02	0,1
Butanal	123-72-8	1,4	14	0,008	0,07
Pentanal	110-62-3	1,5	15	0,009	0,07
Hexanal	66-25-1	1,4	14	0,008	0,07
Heptanal	111-71-7	0,9	15	0,005	0,04
Octanal	127-13-0	0,9	14	0,005	0,04
Nonanal	124-19-6	3,2	14	0,02	0,15
Decanal	112-31-2	2,6	15	0,02	0,1
Pentandial	111-30-8	1	9	0,006	0,05
1-Butanol	71-36-3	16	12	0,1	0,8
1-Hexanol	111-27-3	29	12	0,2	1,4
1-Octanol	111-87-5	23	12	0,1	1
Ethylacetat	141-78-6	897	11	5	43
n-Butylacetat	123-86-4	10	11	0,06	0,5
Phenol	108-95-2	22	15	0,1	1
o-Kresol	95-48-7	1,3	15	0,008	0,06
m-Kresol	108-39-4	0,45	15	0,003	0,02
p-Kresol	106-44-5	0,24	15	0,001	0,01
TXIB	6846-50-0	14	8	0,08	0,7
Toluol	108-88-3	300	13	2	14
Ethylbenzol	100-41-4	27	13	0,2	1
1,4-Diethylbenzol	105-05-5	2	15	0,01	0,1
n-Butylbenzol	104-51-8	14	13	0,1	0,7
α-Pinen	80-56-8	100	15	0,6	5
β-Pinen	127-91-3	190	15	1	9
Limonen	138-86-3	90	10	0,5	4
Ethansäure	64-19-7	13	28	0,08	0,6
Propansäure	79-09-4	20	15	0,1	1
Butansäure	107-92-6	1	28	0,006	0,05
Hexansäure	142-61-1	5	28	0,03	0,2
Octansäure	124-07-2	5	28	0,03	0,2
Benzothiazol	95-16-9	0,7	29	0,004	0,03

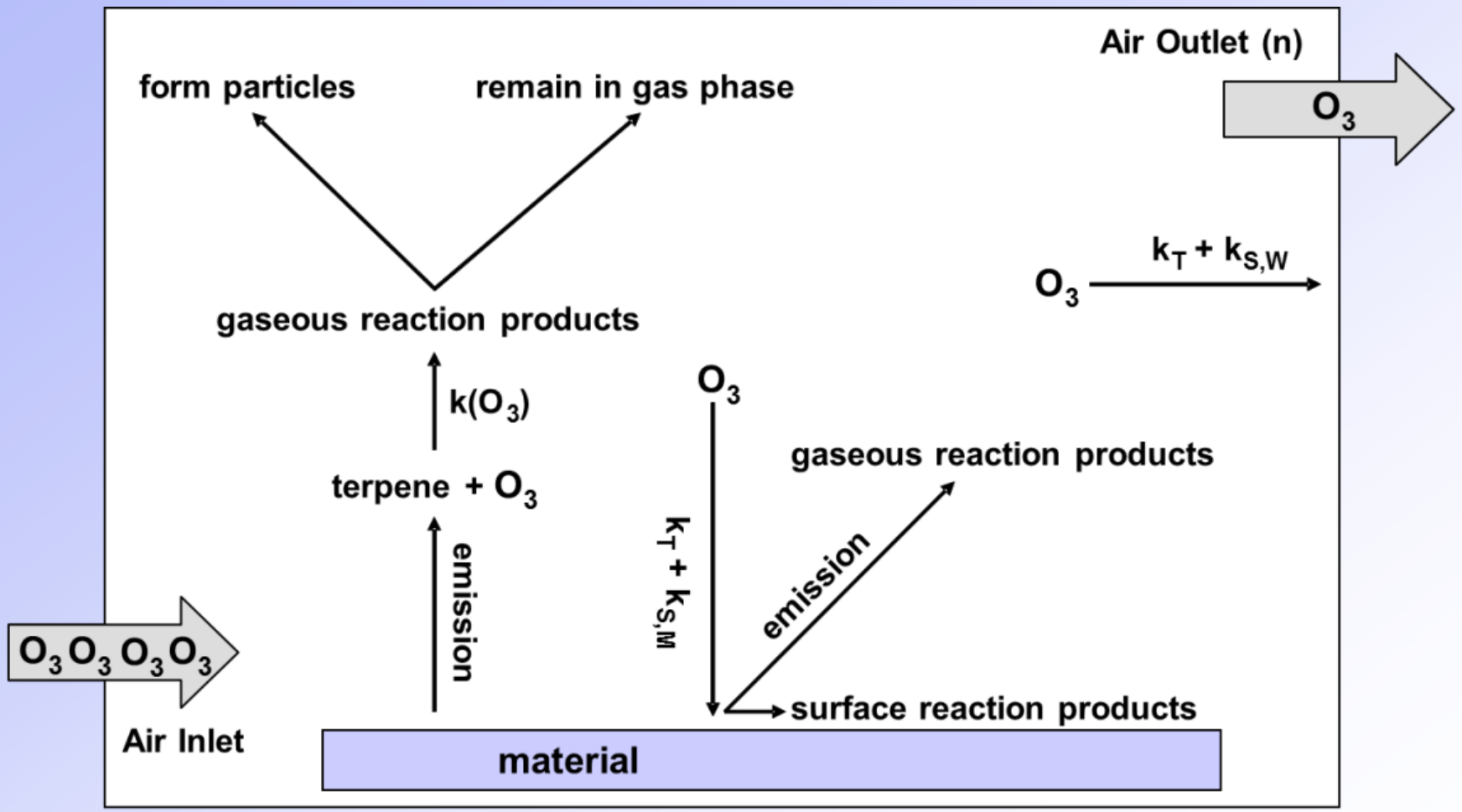
Ad hoc Working Group (2014) Bundesgesundheitsblatt 57, 148-153

Primary and secondary emissions from building products

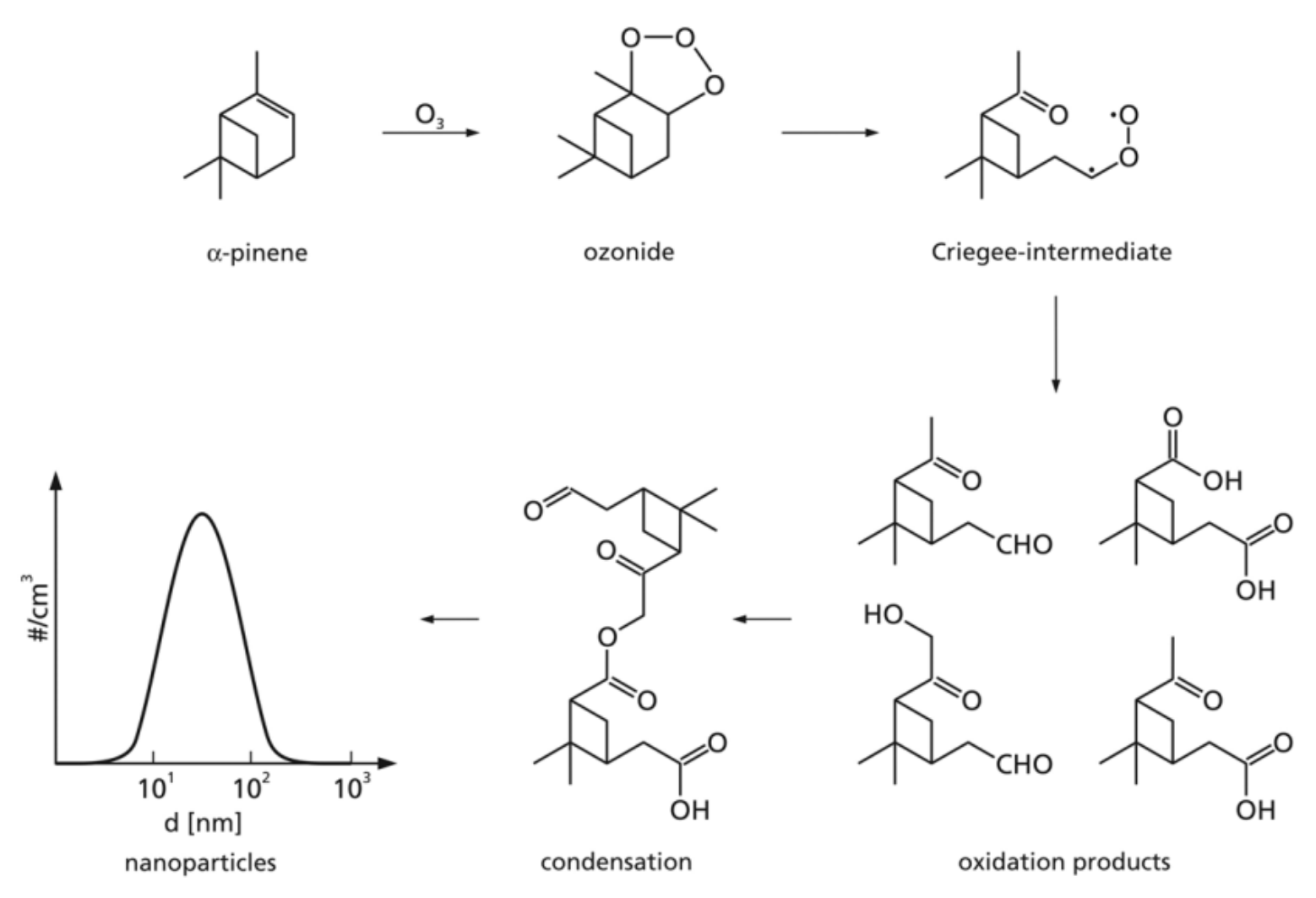


Uhde and Salthammer (2007) Atmospheric Environment 41, 3111-3128

Terpene/ozone reaction: gas phase and surface chemistry

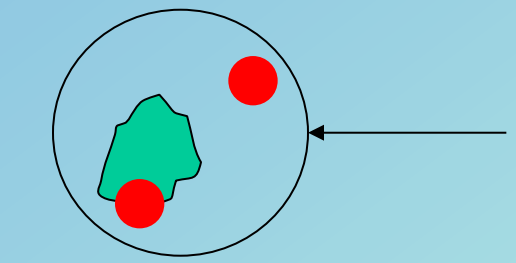


Particle formation from terpene/ozone reaction



Gas/particle distribution of SVOCs

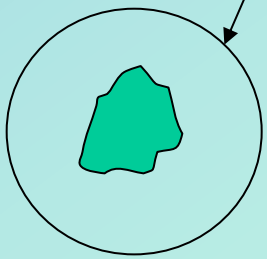
Gas/particle distribution coefficient $\longrightarrow K_p = \frac{[F]}{[A_g] \cdot [TSP]}$



$[A_g + F]$

C_{Dust}

[TSP]



Distribution of DEHP between gas phase and particle phase

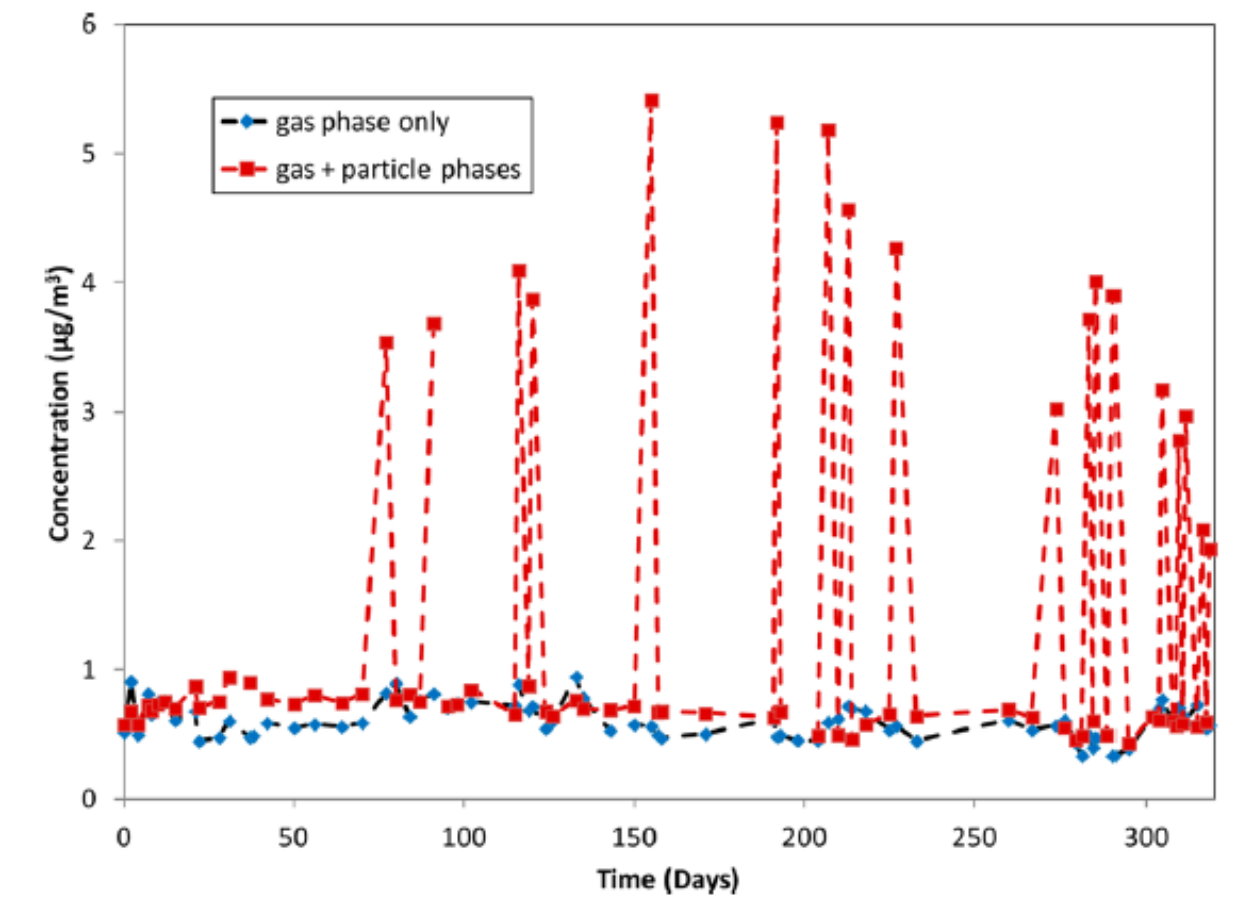
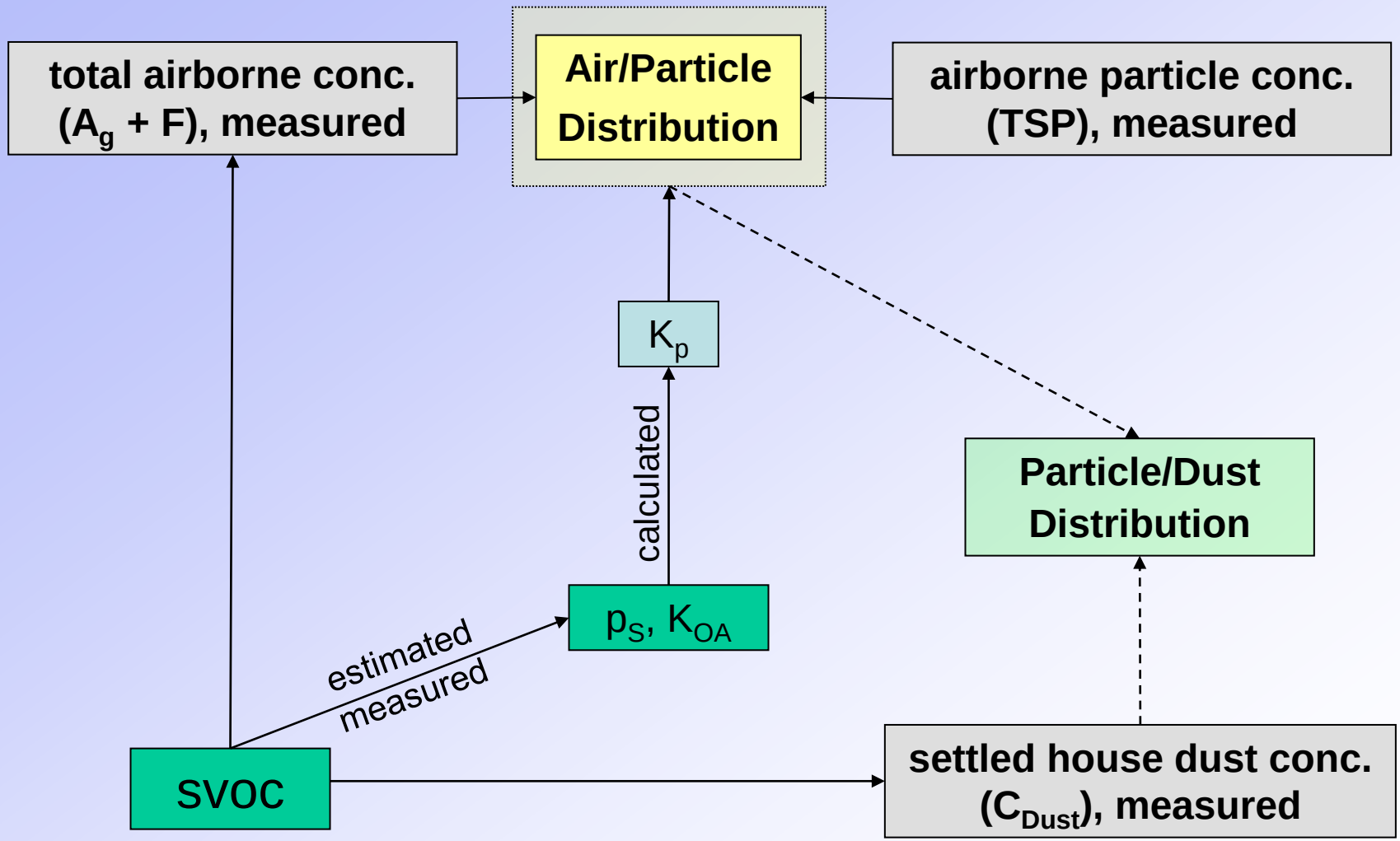


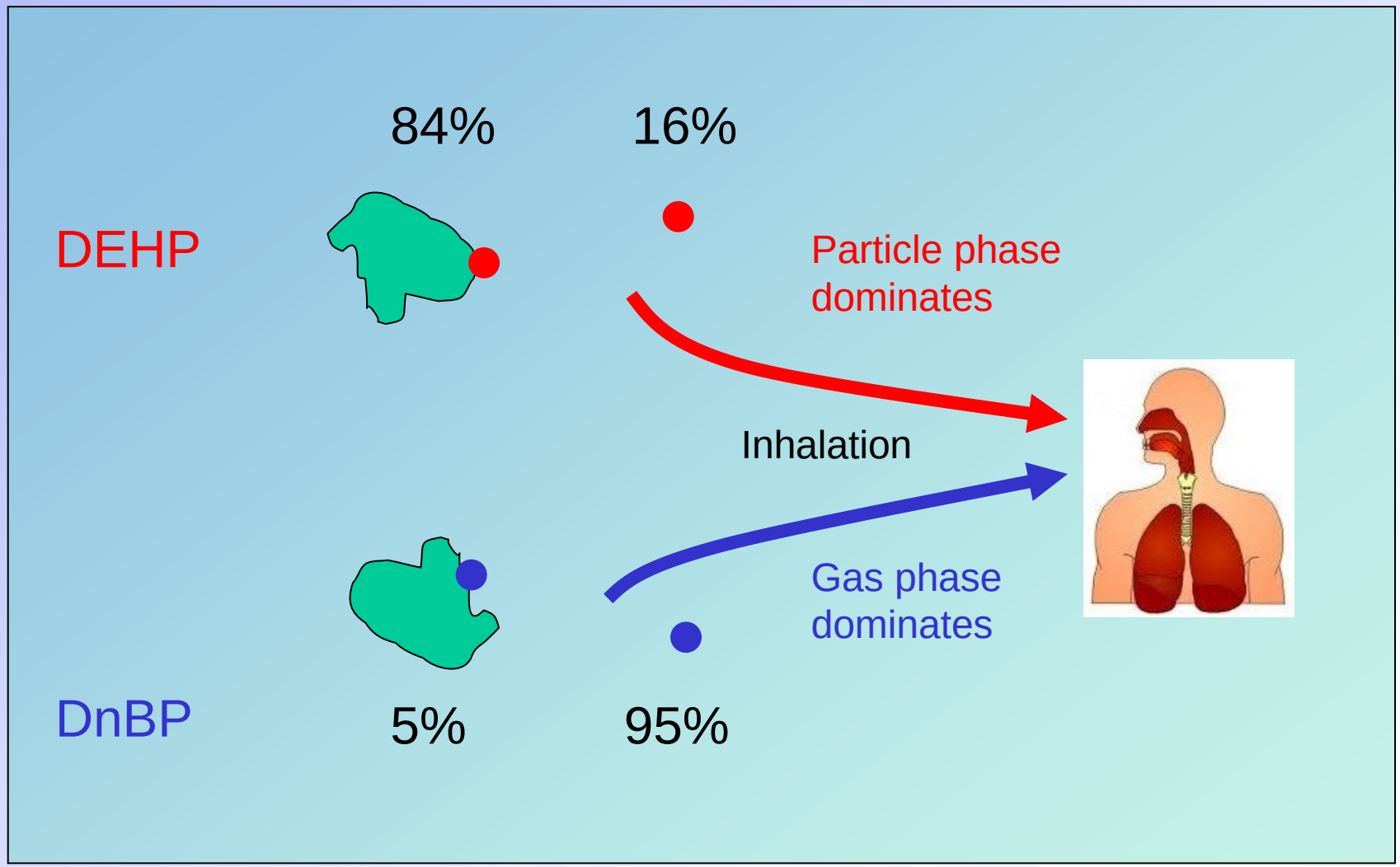
Figure 3. Measured DEHP concentrations in the chamber exhaust in the gas-phase only and in the gas- plus particle-phases combined.

Benning et al. (2013) ES&T 47, 2696-2703

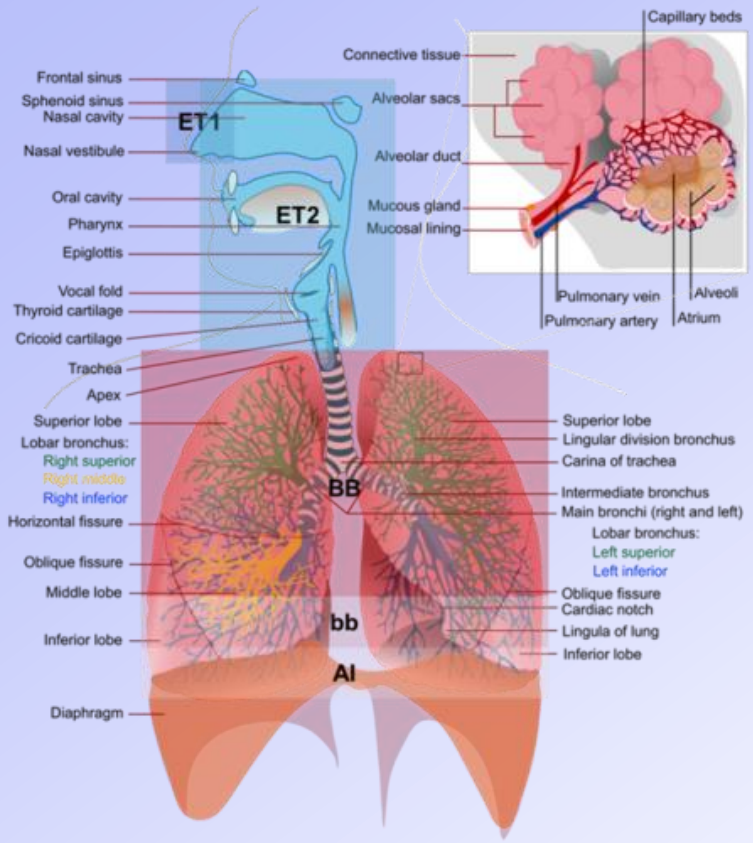
Determination of SVOC air/particle and particle/dust distribution

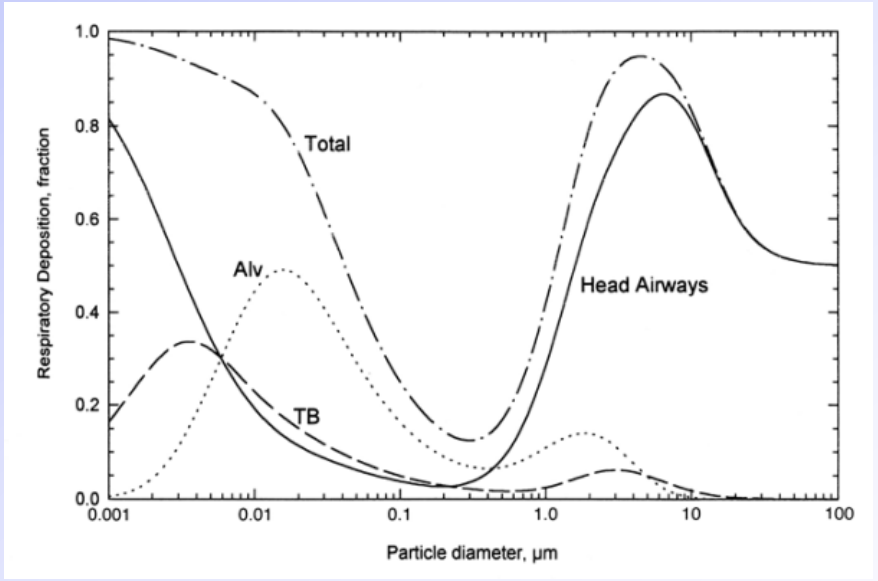


Gas phase and particle phase related inhalation of SVOCs



ICRP Model – schematic illustration of several regions of the human respiratory tract





ET: Extrathoracic Region

ET1: Anterior Nose Region

ET2: Posterior Nasal Region / larynx / pharynx / mouth

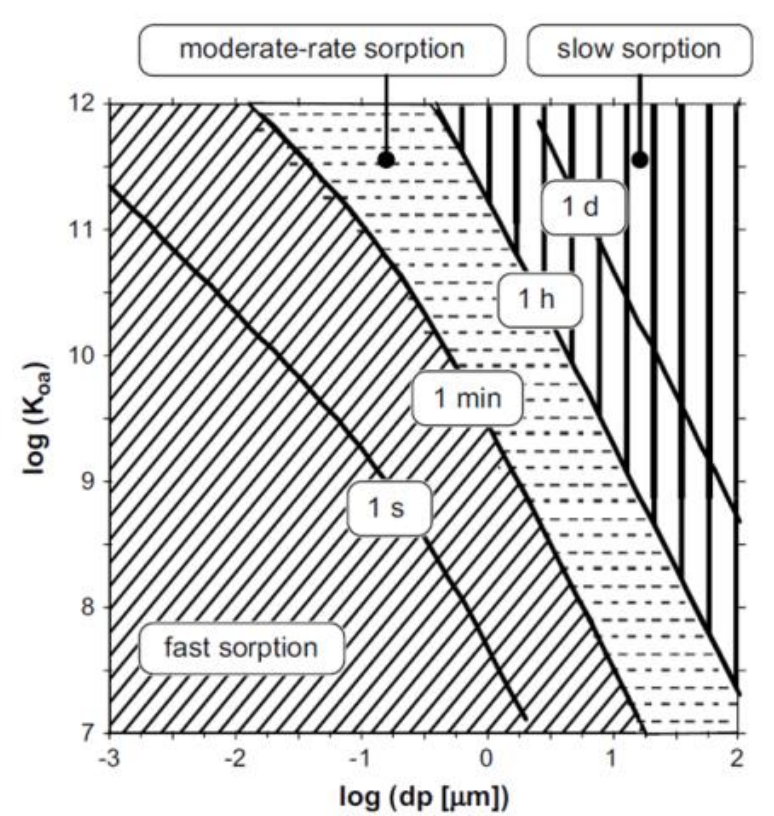
BB: Bronchial Region

bb: Bronchiolar Region

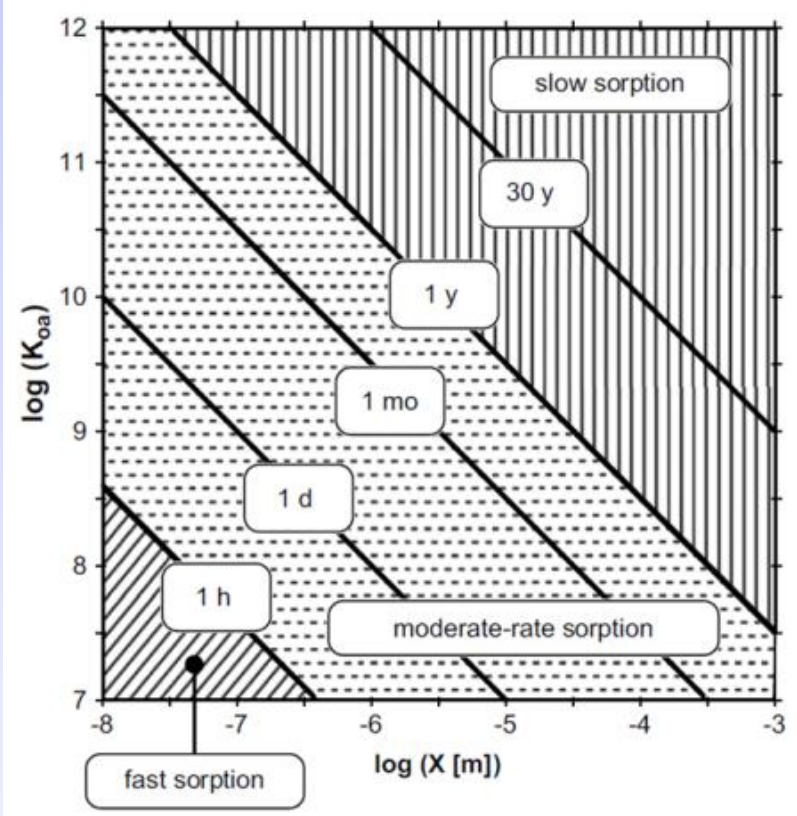
AI: Alveolar-Interstital Region

Hinds (1999) Aerosol Technology, WILEY

Sorption of SVOCs into particles and settled house dust



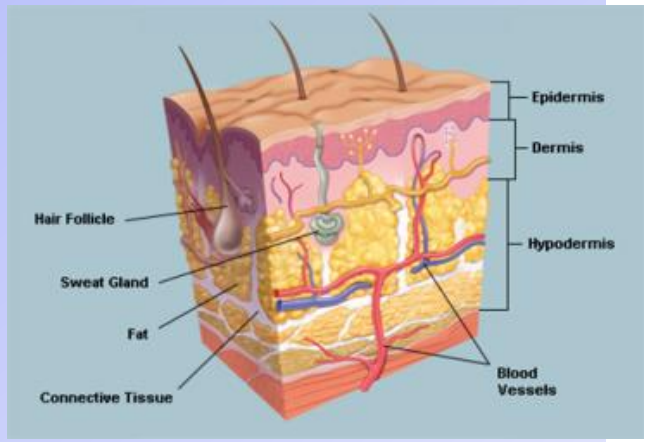
Time for an SVOC with K_{OA} to achieve equilibrium partitioning between air and an organic sorbing airborne particle of diameter d_p.

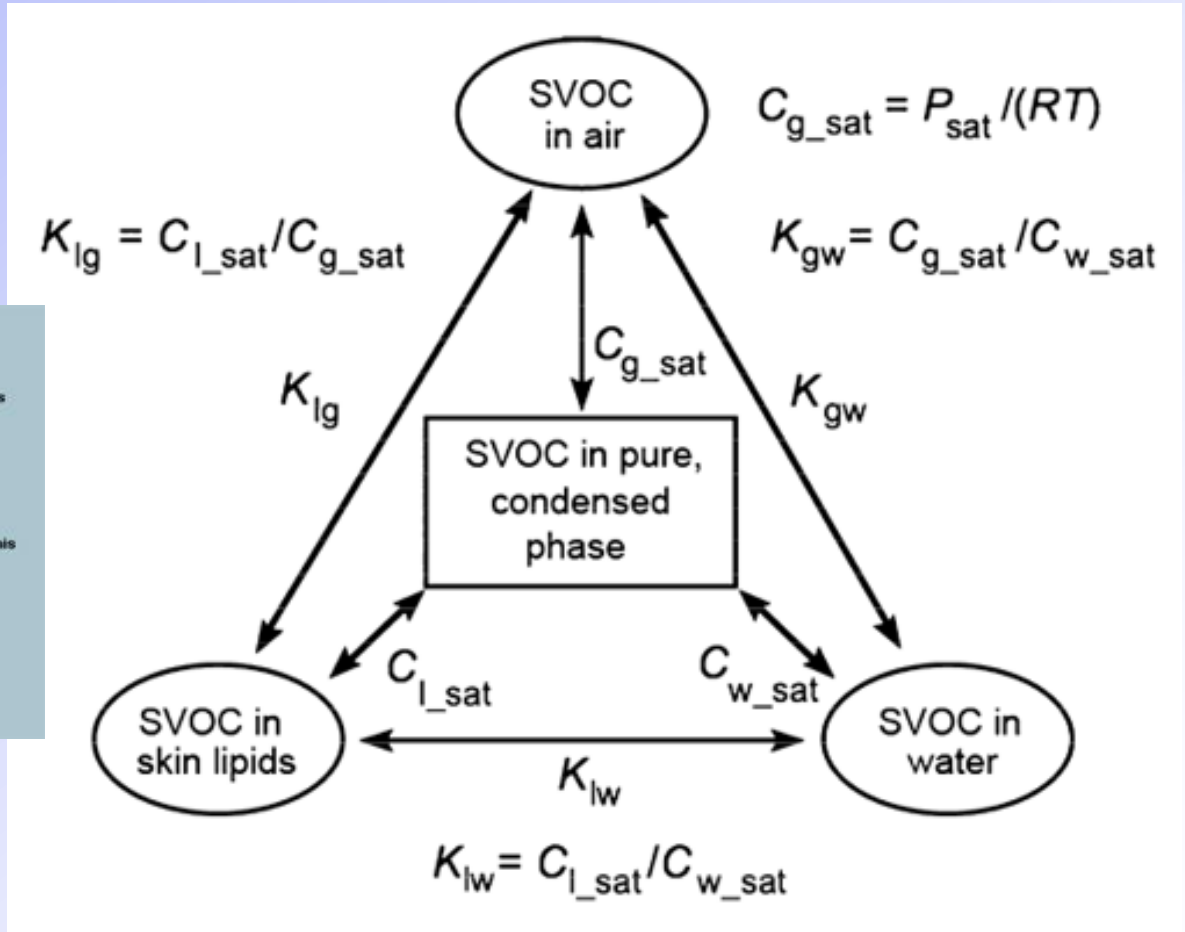


Time for an SVOC with K_{OA} to achieve equilibrium partitioning between air and an organic sorbing substrate possessing a thickness X.

Weschler and Nazaroff (2008) Atmospheric Environment 42, 1449-1460

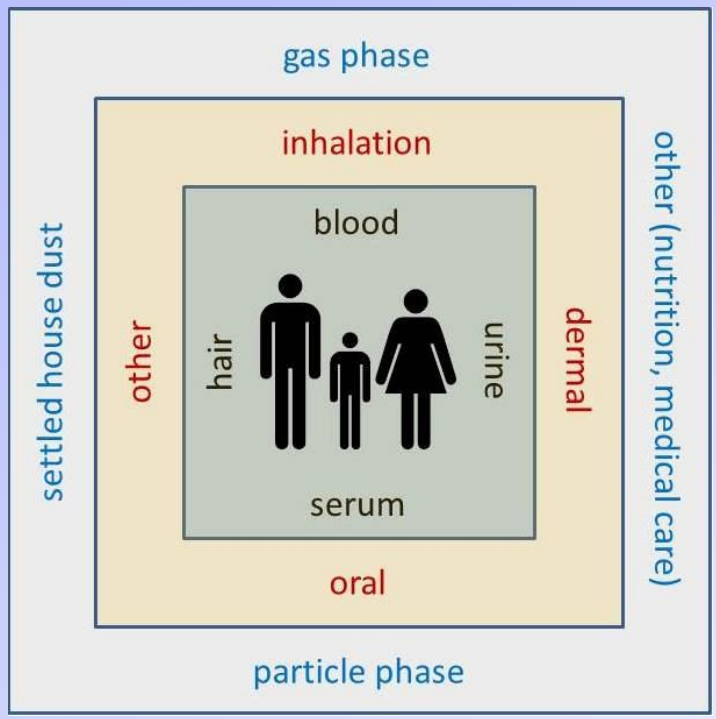
New Challenges: SVOC Exposure Via Dermal Pathways





Weschler and Nazaroff (2012) Indoor Air 22, 356-377

New Challenges: SVOC Exposure Via Dermal Pathways



Dermal exposure experiments at DTU in Lyngby, February 2014

Weschler et al. (2014) to be published

Priority chemicals of the BMUB/VCI HBM group

Pilotphase erfolgreich beendet

Bundesumweltministerium und Chemieverband arbeiten bei Human-Biomonitoring weiter zusammen

03.06.2013 | Pressemitteilung

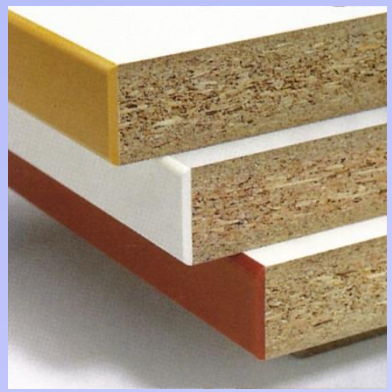
Bundesministerium
für Umwelt, Naturschutz,
Bau und Reaktorsicherheit

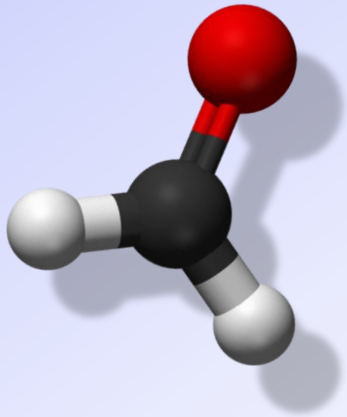
VCI
Verband der
Chemischen
Industrie e.V.

	Chemikalien	CAS-Nummer	Verwendungsbeispiel
1	**DINCH** (Di-iso-nonylcyclohexan-1,2-dicarboxylat)	166412-78-8 Isomerengemisch	Weichmacher, Phthalat- Substitut
2	**DPHP** (Di(2-propylheptyl)phthalat)	53306-54-0	Weichmacher, Phthalat- Substitut hauptsächlich für PVC
3	**ASE/ASEP („Mesamoll")** (Alkylsulfonsäureester)	91082-17-6	Phthalat- Substitut, häufig verwendet (u. a. in Kinderspielzeugen)
4	**TOTM** (Tri(2-ethylhexyl) trimellitat)	3319-31-1	Phthalat- Substitut vor allem in Medizinprodukten (Innenbeschichtung von Schläuchen), Kleber
5	**DEHTP (od. DEHT, DOTP)** (Diethylhexylterephthalat)	6422-86-2	Phthalat- Substitut verwendet für Lebensmittelverpackungen (Flaschen), Spielzeug
6	**HBCD** (Hexabromcyclododecan)	25637-99-4	Flammschutzmittel
7	**4-MBC** (3-(4-Methylbenzyliden)- campher)	36861-47-9	UV-Filter in Kosmetika, Sonnenschutz
8	**OMC** (Octylmethoxycinnamat)	5466-77-3	UV-Filter in Sonnenschutzmitteln oder Cremes
9	**4D** (Octamethylcyclotetrasiloxan)	556-67-2	Kosmetika; Silikonherstellung; Schmier- und Lösemittel
10	**D5** (Decamethylcyclopentasiloxan)	541-02-6	s. D4
11	**D6** (Dodecamethylcyclohexasiloxan)	540-97-6	s. D4
12	**Geraniol**	106-24-1	Duftstoff, Allergene Substanz
13	**MDI** (Methylendiphenyldiisocyanat)	101-68-8 und 26447-40-5	Allergene Substanz; Produktion von Polyurethan, Einkomponentenschaum, Spezialkunststoff, Klebstoffe
14	**CIT/MIT** mixture (5-Chloro-2-methyl-4-isothiazolin-3-on/ 2-Methylisothiazol-3(2H)-on)	26172-554 und 2682-20-4	Allergene Substanz, Biozid, Konservierungsmittel
15	**BHT** (Butylated Hydroxy-Toluene; 2,6 Di-tert-butyl-p-kresol)	28-37-0	Alterungsschutzstoff für Kunststoffe, Antioxidans in Lebens- Futter- und Arzneimitteln
16	**2-MBT** (Mercaptobenzothiazol)	149-30-4	Vulkanisator, Akzelerator bei der Gummiproduktion
17	**4-Nonylphenol**	104-40-5	Tensidherstellung
18	**4-tert-Octylphenol**	140-66-9	Antioxidans/ Stabilisator in technischen Ölen
19	**NMP** (N-methyl-2-pyrrolidon)	872-50-4	Lösungsvermittler für Farben und Kunststoffe, in Abbeizern, Felgenreiniger
20	**NEP** (N-ethyl-2pyrrolidon)	2687-91-4	Lösungsvermittler für Farben und Kunststoffe, in Abbeizern, Felgenreiniger

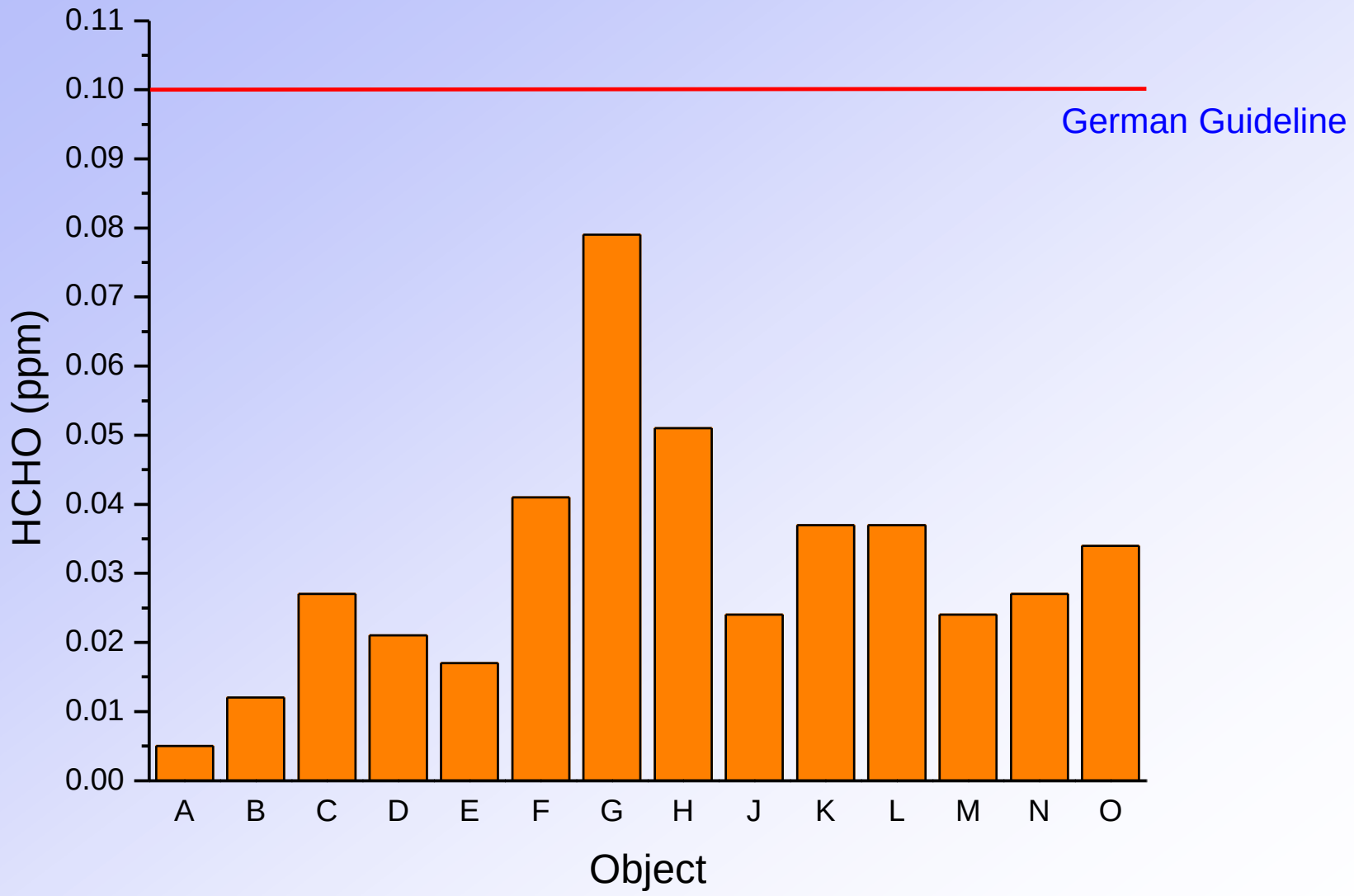
Quelle: Umweltbundesamt

Formaldehyde – a never ending story?

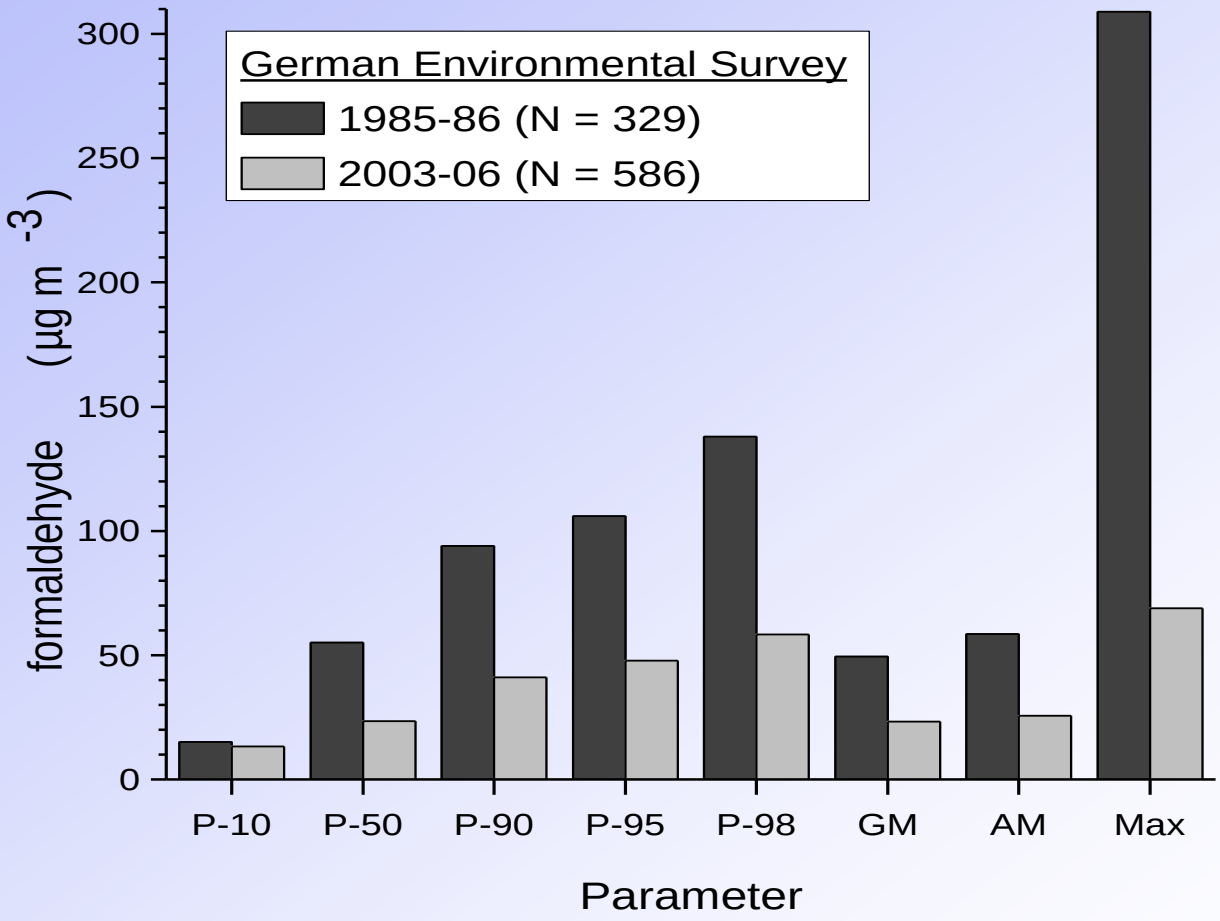




Formaldehyde in newly built pre-fabricated houses in Germany



Formaldehyde: results of German environmental surveys under normal living conditions

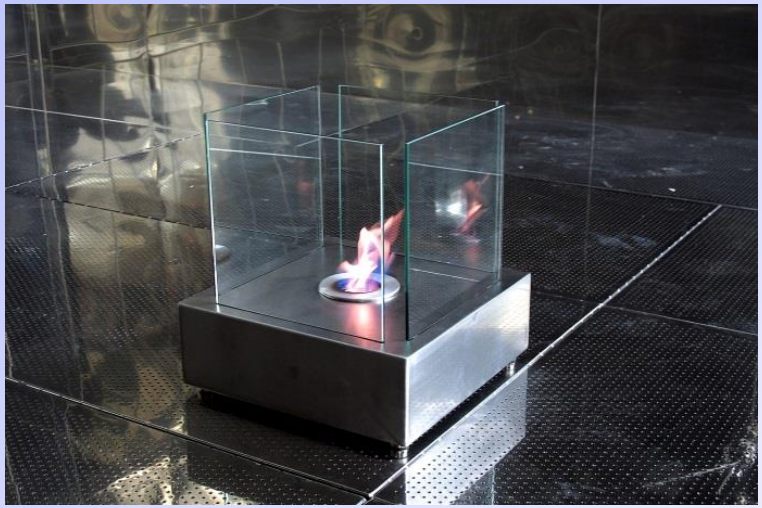


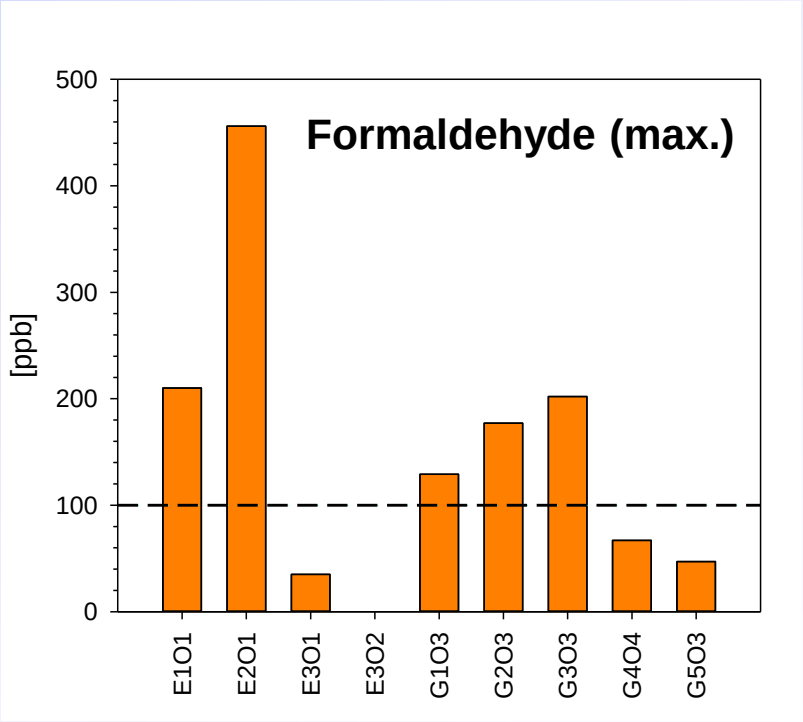
Salthammer et al. (2010) Chemical Reviews

Formaldehyde from ethanol open fireplaces

Experiments in 48 m³ stainless-steel emission test chamber

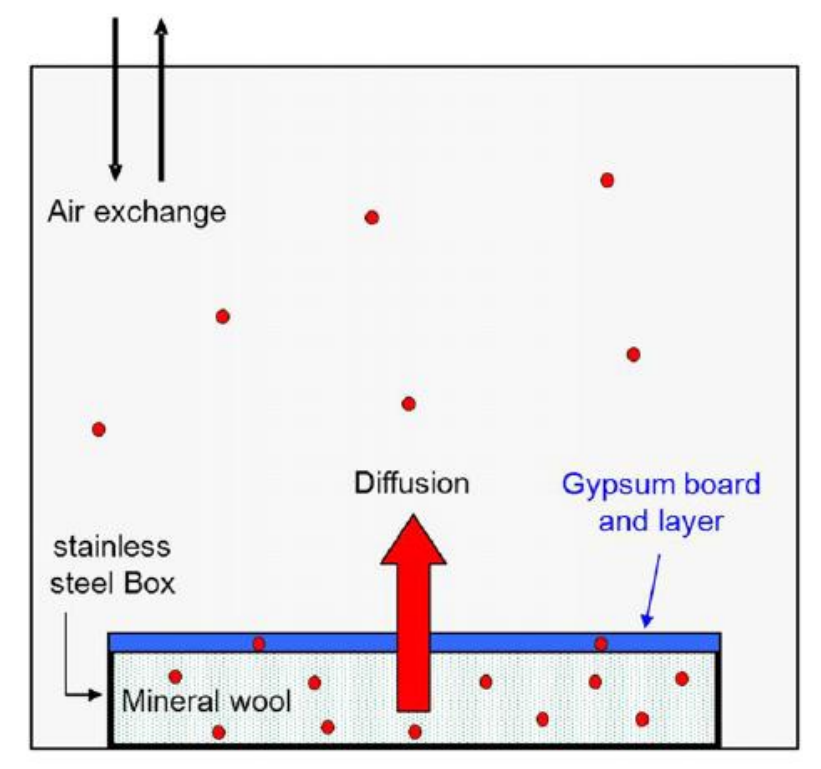
Ventilation according to manufacturer specifications (0.4 – 0.9 ACH)

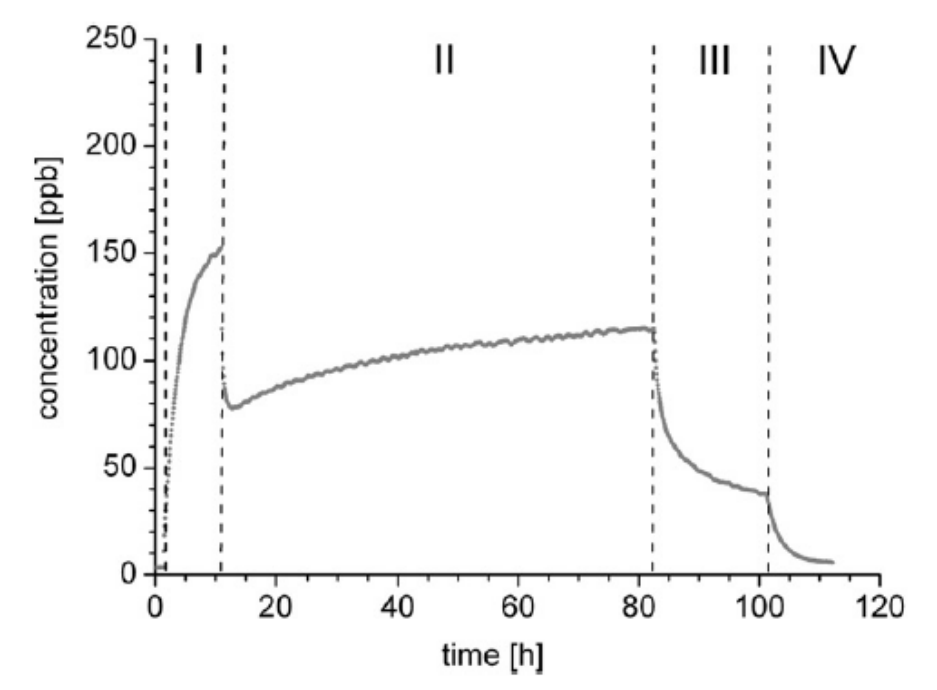




Schripp et al. (2014) ES&T, available online

Formaldehyde diffusion and adsorption/desorption experiments



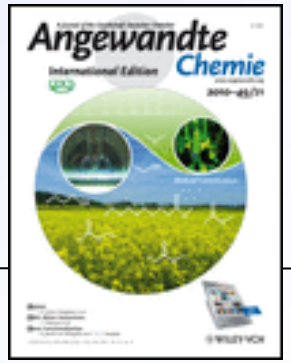


Diffusion

Adsorption/Desorption

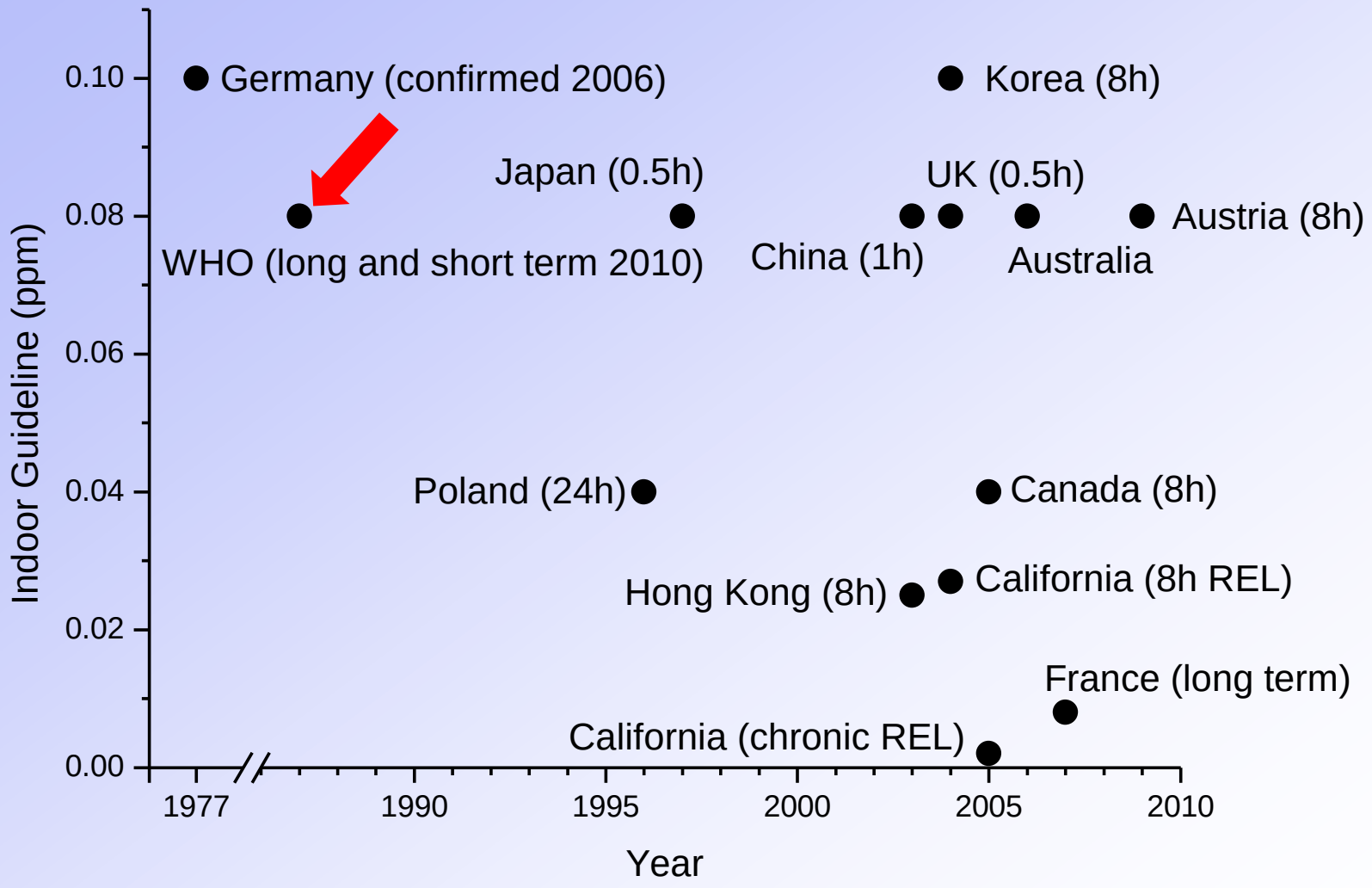
Biofuel combustion produces carbonyl compounds

The increased use of biofuel will also increase the formaldehyde concentration in ambient air.



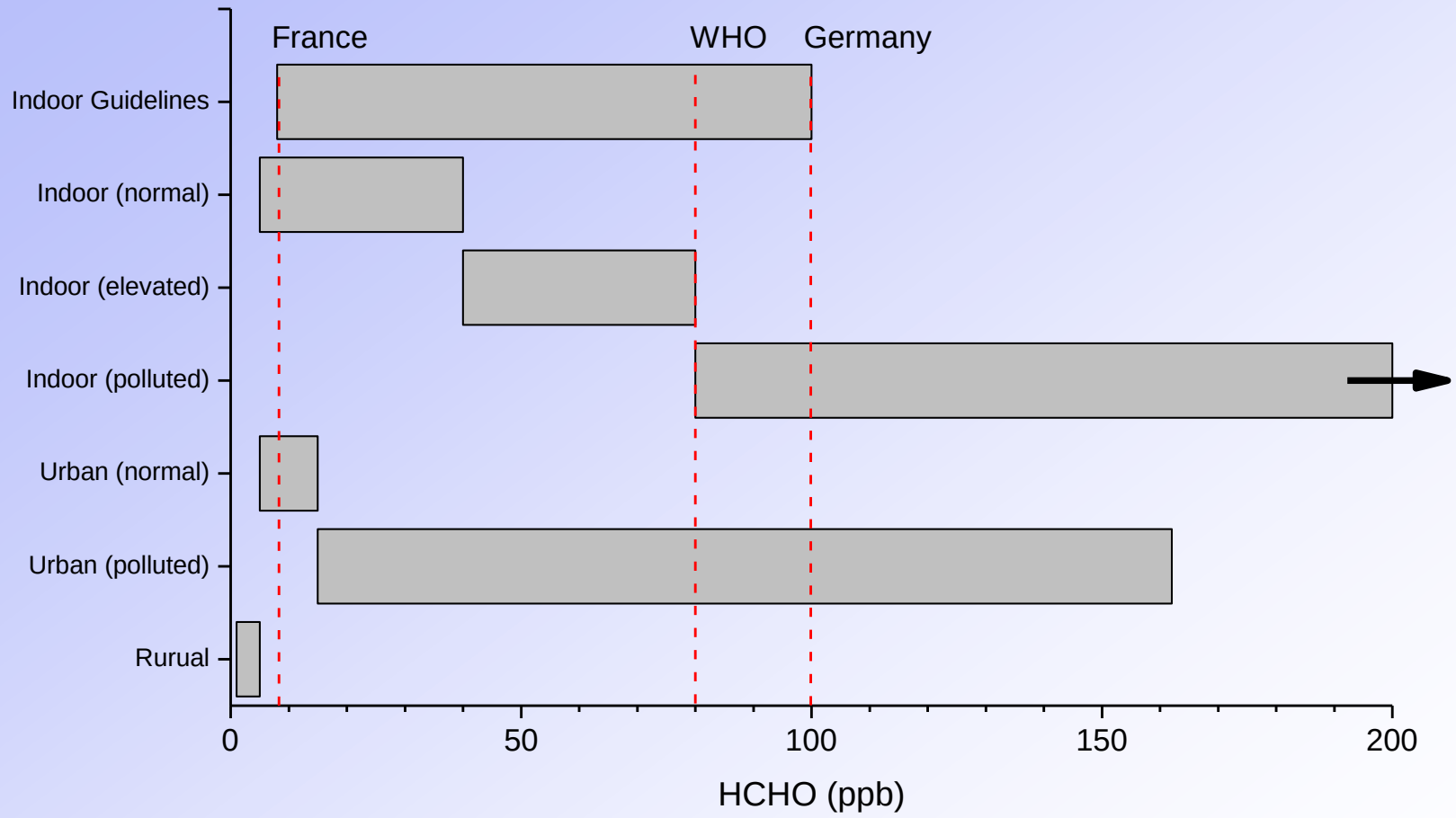
Kohse-Höinghaus et al. (2010) Angewandte Chemie Int. Ed.

International indoor air formaldehyde guidelines



Salthammer (2011) Chemosphere (modified)

Indoor and outdoor formaldehyde concentration ranges



Future developments and challenges