



Updating Kick-Off Limit Values for substances with limited human health-hazard information

Geert Wieling

Theo Scheffers

DOHSBASE v.o.f.



Why update the kick-off values of 2005?

Kick-off values were introduced in 2005 in the Netherlands, so why update?

- Introduction CLP: different classifications, R-phrases
→ H-sentences
- Adjustments of CB-schemes since 2005
- More substances with harmonized (CLP-)classification
- Tendency to lower OELVs
- Our database with Classification data & OELVs: much larger than in 2005

Situation (1)

- Worldwide: > 64 million substances (CAS-register)
- EINECS: approx. 140 thousand substances
- REACH: 12.276 unique substances disseminated (> 100 t/a or >10 t/a if CMR);
- about 2.600 substances: no workplace exposure
- # of 2018 registered substances (the REACH deadline for 1 – 10/100 t/a) with CSR/DNEL: probably zero
- **Conclusion: workplace exposure in EU: at least 9700 substances**
- DOHSBase Compare database: approx. 3800 substances with OEL
- REACH-CSR substances with DNEL/DMELs and no OELV: 1600 (400 with both)



Situation (2)

Conclusion:

- Number of substances in EU with workplace exposure and no OELV or DNEL: at least 4300 (approx. 50%!!)

Challenge:

- Is it possible to derive limits (kick-off's) for these substances, using the established relation between existing OELs and Hazard Grouping?

Philosophy behind kick-off values (1)

- Definition of kick-off value: 10% lower tolerance limit per hazard class of CB-scheme
- If this value is feasible in practice, no extensive toxicological research is needed to establish a health-based company limit

Philosophy behind kick-off values (2)

Target group:

- Substances with no OELV or DNEL, but with (limited) health-hazard information (H3###-statements)

Research group:

- Substances with OELV and at least one H3###-statement

Legal status kick-off value

Substances with kick-off value have no formal OEL and no DNEL/DMEL → exposure assessment is not possible.

Is this acceptable?

Paradigm shift in NL: for all substances a company limit is a legal obligation

Kick-off value is a starting point if no OEL/DNEL is available

In the Netherlands: kick-off values are accepted by Labour Inspectorate/law enforcement for substances with no formal OEL or DNEL

Classification in Control Banding Schemes is not always consistent

Hazard category	DGUV IFA Spaltenmodell (TRGS600)	COSHH Essentials	BAUA EMKG (Einfaches Maßnahmenkonzept) (inhalation)
4/E	<u>H300, H310, H330</u> , EU032	H334, H341	H360F
3/D	H301, H311, H331 EUH070, EUH029, EUH031 H370, H317, H334, H318 H360 _{xy} , H351, H341	<u>H300, H310, H330</u> H351, H360 _{xy} , H361, H362,	<u>H300, H330</u> , H360D, EUH032
2/C	H302, H312, H332, H371, EUH071 H361 _{f/d} , H362 non-toxic gases which may cause asphyxiation	H301, H311, H331 H317, H318, <u>H335</u> , H370,, EUH071	H301, H331, H314, H334, H341, H351, H361f/d, H370, H371, EUH031
1/B	H319 H304, EUH066, <u>H335</u> , H336	H302, H312, H332 H371	H302, H332, H318
0/A	substances which experience shows to be harmless (e.g. water, sugar, paraffin etc.)	H303, H304, H305, H313, H316, H319, H320, H333, H336, EUH066 and all H-numbers not otherwise listed	H319, <u>H335</u> , H336, H304 No health hazard H-statements

The most comprehensive database of OEL's and measurement methods

Method to derive Kick-off values

1. Transposition R-phrases to H-statements
2. Exposure as gas/vapor or dust/aerosol?
3. Removal of some OELVs
4. Grouping of substances in hazard classes CB-schemes
5. Statistical analysis: OELV distribution and 10%-tile estimation

Step 1: Conversion R → H

- More hazard classes in CLP
- Different ranges in classification:
 - 1 R-phrase → 2 H-statements
 - 2 R-phrases → 1 H-statement

Nature, time and exposure	Dose (LD50)	Units	R-phrase/	CLP hazard class & - category	H-Statement
Acute toxicity: LD50 - oral	5	mg/kg	28	Acute Tox 1	300
Acute toxicity: LD50 - oral	5-25	mg/kg	28	Acute Tox 2	300
Acute toxicity: LD50 - oral	25-50	mg/kg	25	Acute Tox 2	300
Acute toxicity: LD50 - oral	50-200	mg/kg	25	Acute Tox 3	301
Acute toxicity: LD50 - oral	200-300	mg/kg	22	Acute Tox 3	301
Acute toxicity: LD50 - oral	300-2000	mg/kg	22	Acute Tox 4	302

Step 2: Physical appearance/exposure

For each substance:

- appearance as vapor/gas or as dust/mist

If:

- $OEL \ll C_{max}$: vapor/gas
- $OEL \gg C_{max}$: aerosol/dust

Step 3: removal of double OELVs

- Group OELVs reduced to 1 entry
-
- “Metal + compounds” => 1 entry
- Dutch Health Council advice on Xylene (o, m, p, mix) => 1 entry

Step 4: grouping in CB-schemes

All substances with OELV or DNEL, H3##-sentences and known physical appearance are grouped in the hazard classes of the CB-schemes:

- COSHH Essentials (HSE)
 - Einfache Maßnahmenkonzept Gefahrstoffe (EMKG)
 - GHS Spaltenmodell (DGUV IFA)
-
- → Statistical analysis

Step 5: Statistical Analysis

- Distribution of OELVs per hazard group
- Log Normal? Regression-analysis
- Analysis of variance (differences between groups): ANOVA

Number of substances used in our analysis

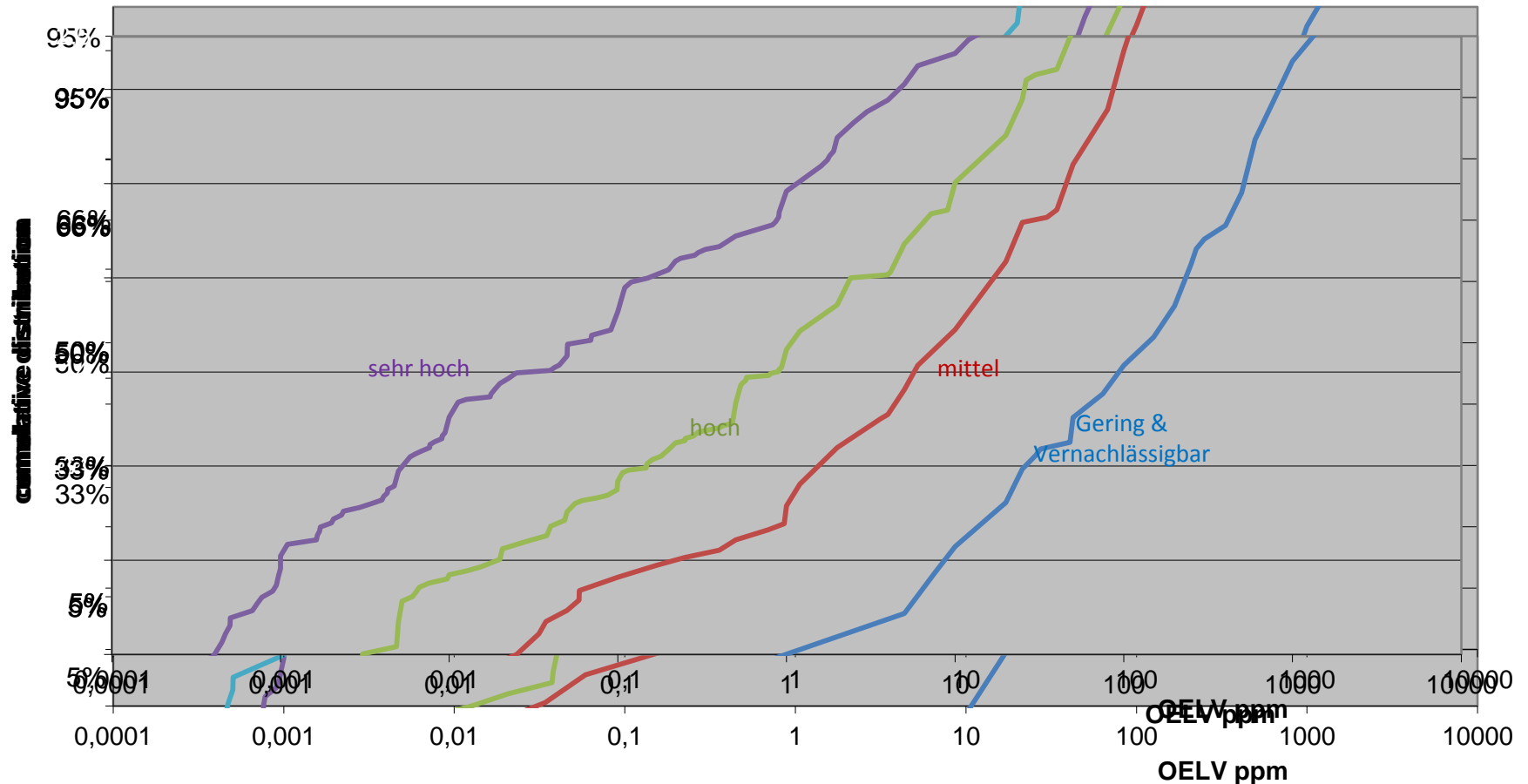
Substances with:

- OELV
- H3## statement
- Known exposure type

CB-Scheme	Vapor/Gas	Dust/Aerosol
IFA Spaltenmodell	631	338
EMKG-inhalation	629	338
COSHH-Essentials	631	334

Cumulative distribution – gases/vapours

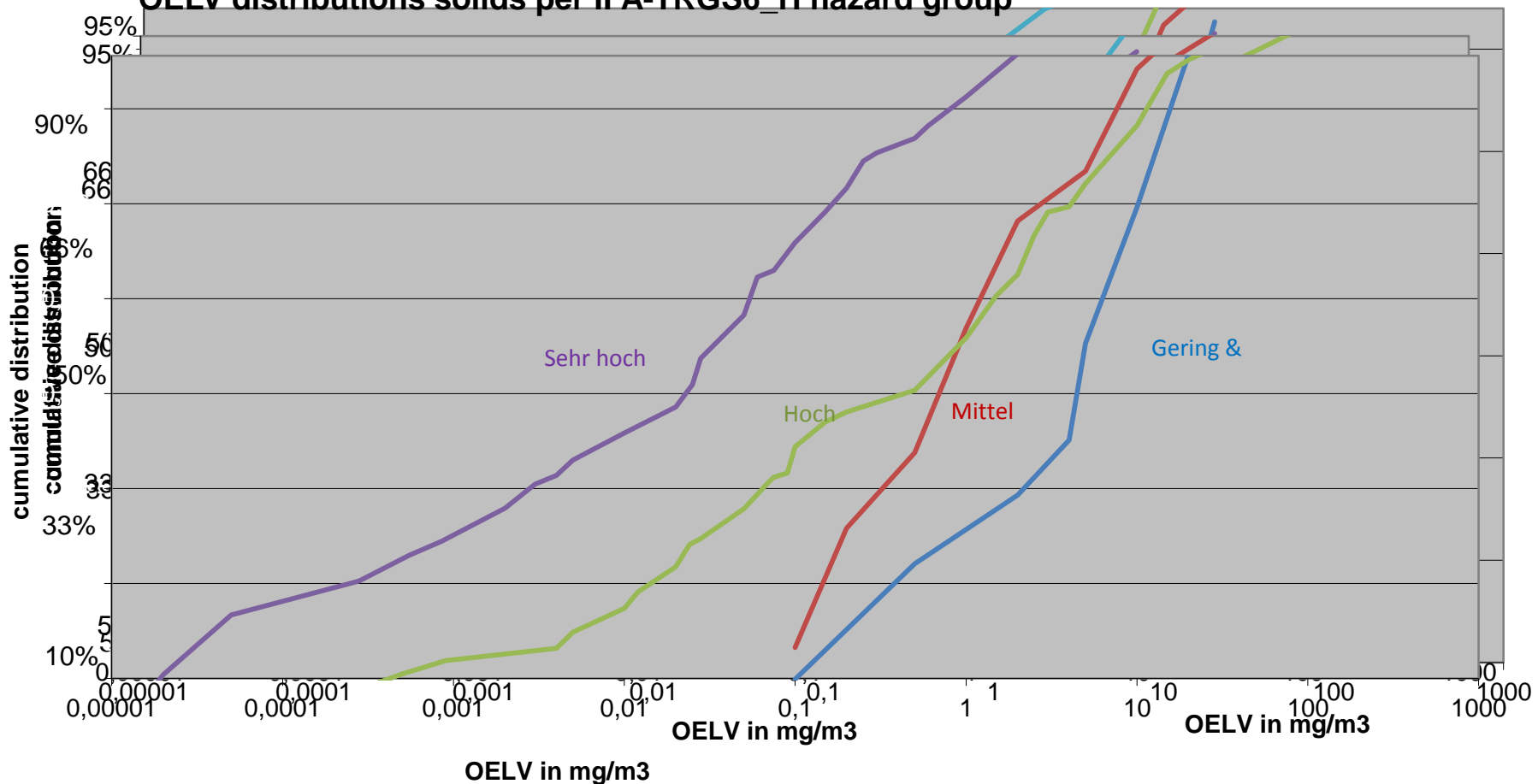
OELV distributions vapours per COSHH H hazard group
 OELV distributions vapours per EN 12061-2 hazard group classification



The most comprehensive database of OEL's and measurement methods

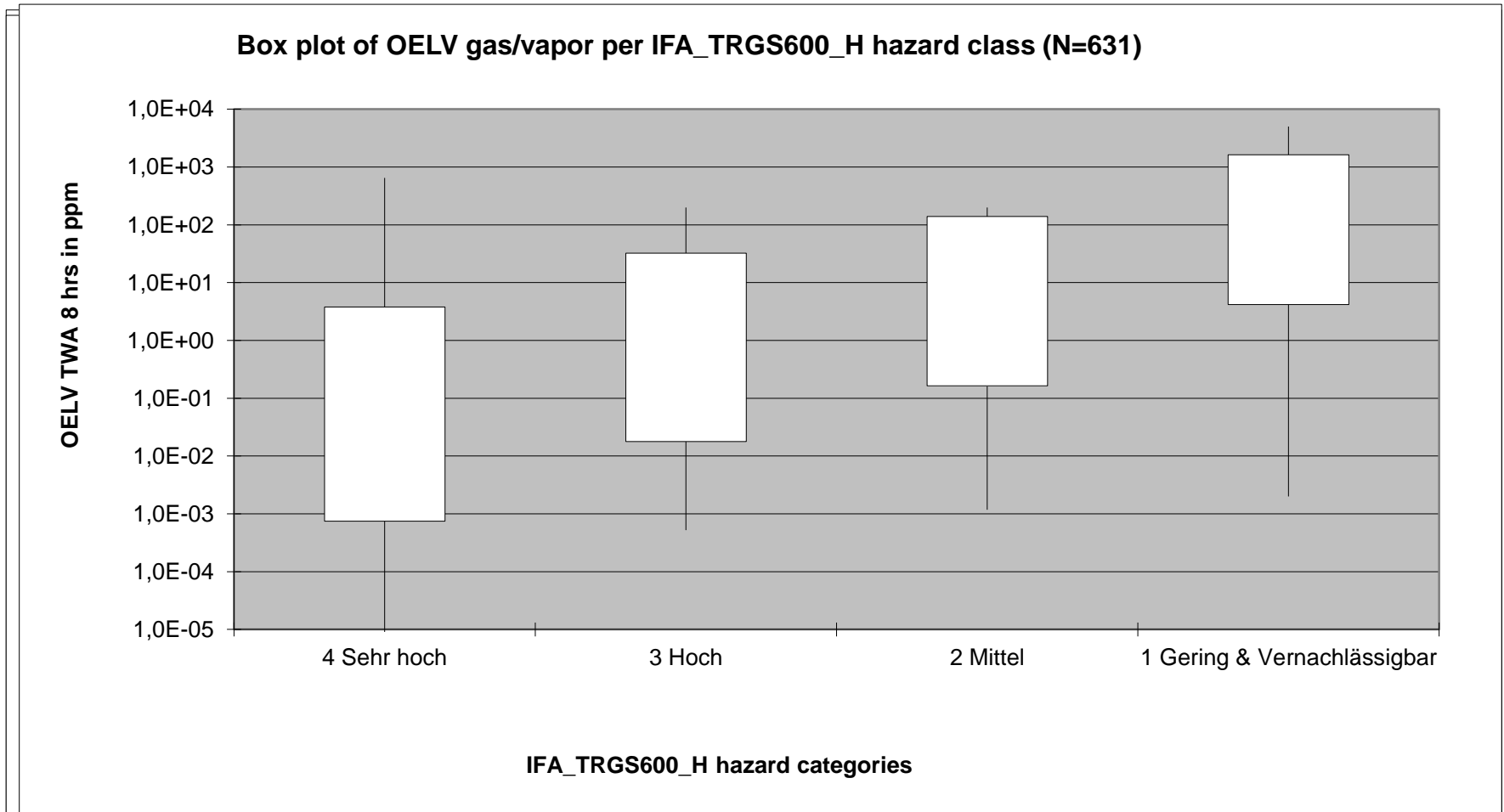
Cumulative distribution –dust/aerosol

OELV distributions solids per EIOB-H01 grouped hazard classification
OELV distributions solids per IFA-TRGS6_H hazard group



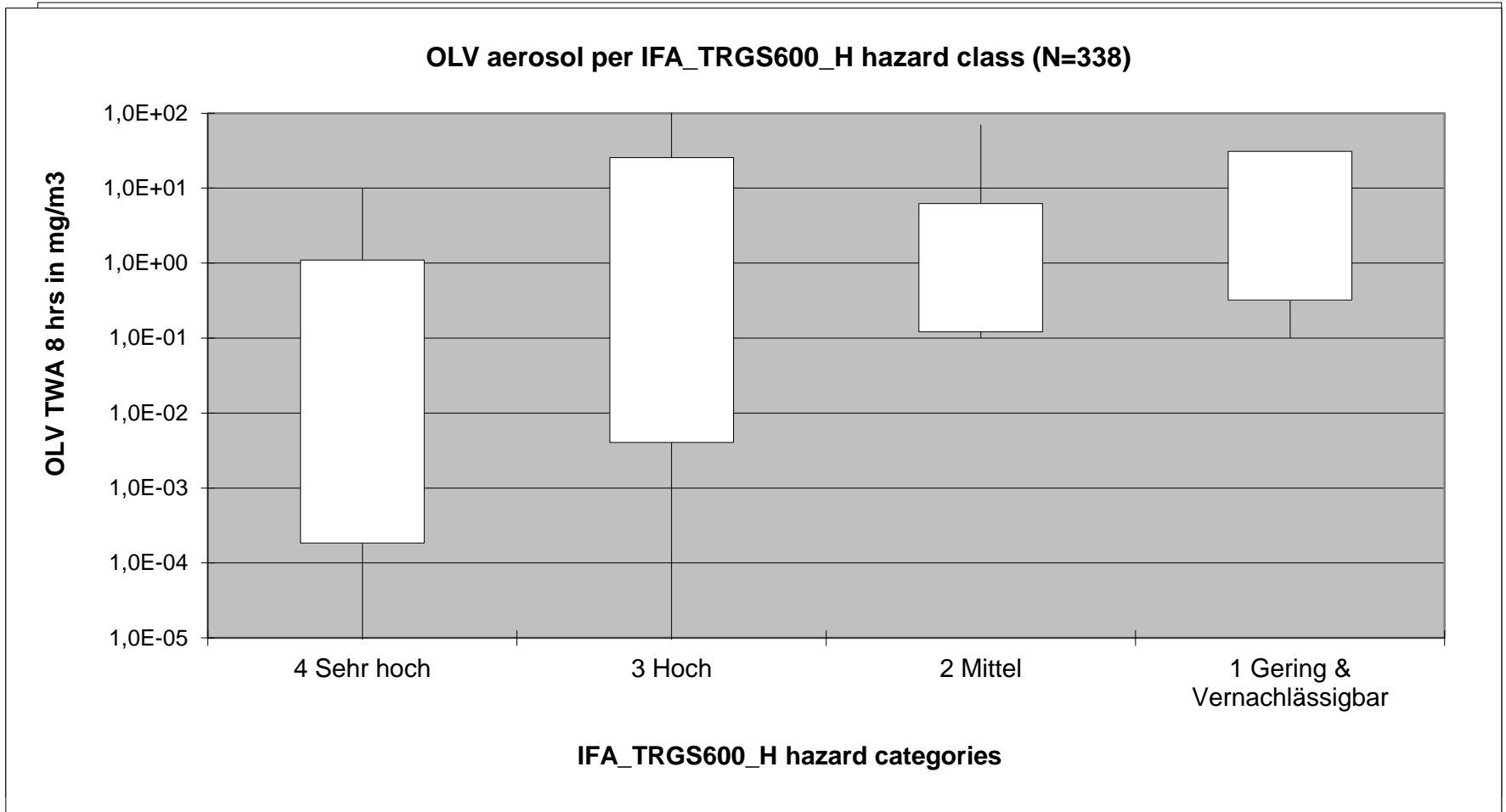
The most comprehensive database of OEL's and measurement methods

Boxplots – gas/vapor



Box-plots – dust/aersol

The most comprehensive database of OEL's and measurement methods

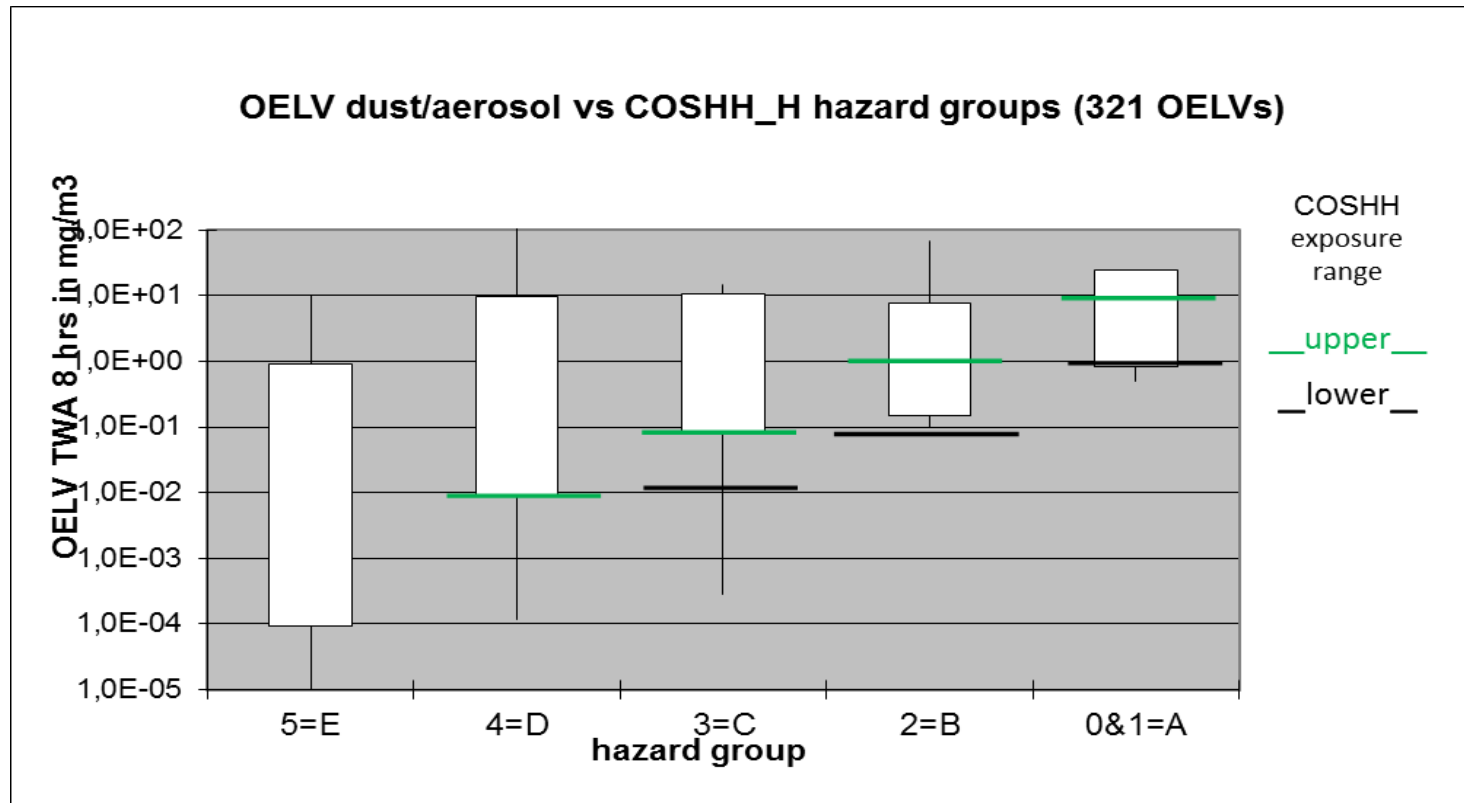


Results (1)

- The OELV distributions per hazard group can, within the 10 to 90%-tile, in some cases be described by Lognormal distribution
- Not all CB-schemes are equally good in differentiating the OEL-distribution per hazard classes
- It is possible to derive kick-off values

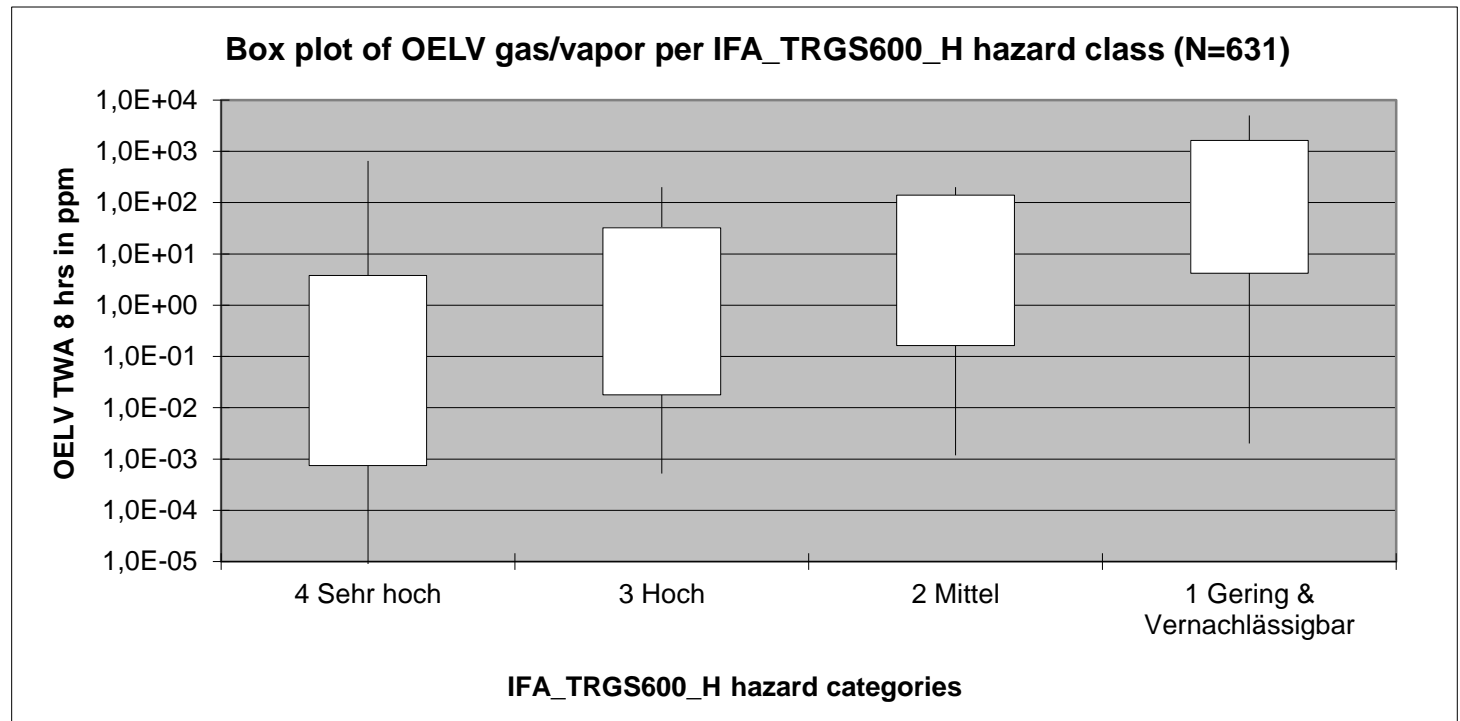
Results (2)

COSHH differentiates best the OELV distributions per hazard groups for dust/aerosol



Results (3)

IFA Spaltenmodell differentiates best the OELV distributions per hazard groups for vapor/gas



Proposed H3## based kick-off values for dust/aerosols

Basis: COSHH Essentials

Hazard Group	1	2	3 *	4
H-statements	H334, H340, H341, H350, H350i	H300, H310, H330, H351, H360F/D/FD/Fd /Df, H361f/d/fd, H362, H372	H301, H302, H311, H312, H314, H317, H318, H331, H332, H335, H370, H371, H373, EUH071	H303, H304, H305, H313, H315, H316, H319, H320, H333, H336, EUH066, all other H3##-statements
Dusts (mg/m ³)	0,00001	0,01	0,1	1

‘*’ Hazard Groups B+C combined

Proposed H3## based kick-off values for gases/vapors

Basis: DGUV IFA Spaltenmodell (TRGS600)

Hazard Group	1	2	3	4
H-statements	H300, H310, H330, H340, H350, H350i, EUH032	H301, H311, H317, H318, H331, H334, H341, H351, H360F/D/FD/Fd/Df, H370, H372, EUH029, EUH031, EUH070	H302, H312, H314, H332, H361f/d/fd, H362, H371, H373, EUH071	H304, H315, H319, H335, H336, EUH066, all other H3##-statements
Gases/vapors (ppm)	0,001	0,01	0,1	5



Differences between kick-offs 2005 and 2014

Hazard Group	1	2	3	4
H-statements/R-phrases in 2014 or 2005 only	<p>In 2014: H334 (R42), H341 (R68)</p> <p>In 2005: R26 (H330), R27 (H310), R28 (H300), R32 (EUH032), R48/23,24,25 (H372)</p>	<p>In 2014: H300 (R28), H310 (R27), H330 (R26), H360D (R61), H360Fd (R60), H360Df (R61), H362 (R64), H372 (R48/23,24,25)</p> <p>In 2005: R23 (H330/H331), R24 (H311), R25 (H301), R29 (EUH029), R31 (EUH031), R33 (H373), R35 (H314), R43 (H334), R48/20,21,22 (H373)</p>	<p>In 2014: H301 (R25), H311 (R24), H317 (R43), H331 (R23), H335 (R37), H370 (R39/23..28), H373 (R48/23,24,25, R33), EUH071 (-)</p> <p>In 2005: R20 (H332), R21 (H312), R22 (H302), R62 (H361f), R63 (H361d), R64 (H362)</p>	<p>In 2014: H302 (R22), H303 (-), H305 (-), H312 (R21), H313 (-), H316 (-), H320 (-), H332 (R20), H333 (-), H371 (R68/20..22),</p> <p>In 2005: R37 (H335)</p>
Dusts (mg/m ³)	<p>2014:0,0001</p> <p>2005: 0,01</p>	<p>2014: 0,01</p> <p>2005: 0,02</p>	<p>2014: 0,1</p> <p>2005: 0,06</p>	<p>2014: 1</p> <p>2005: 0,24</p>

The most comprehensive database of OEL's and measurement methods

Differences between kick-offs

2005 and 2014

More in detail

Hazard Group	1	2	3	4
H-statements/R-phrases in 2014 or 2005 only	<u>2005:</u> R48/23,24,25 (H372)	<u>In 2014:</u> H318 (R41), H370 (R39/23..28), , H360Fd (R60), H360Df (R61), H372 (R48/23,24,25), EUH070 (R39-41) <u>2005:</u> R33 (H373), R35 (H314), R23 (H330), R48/20,21,22 (H373)	<u>In 2014:</u> H314 (R34 & R35), H371 (R68/20..22), H373 (R48/23,24,25, R33), EUH071 <u>In 2005:</u> R41 (H318), R63 (H360Fd), R62 (360Df)	No differences in H-/R- in 2005 and 2014
Gases/vapors (ppm)	2014: 0,001 2005: 0,001	2014: 0,01 2005: 0,01	2014: 0,1 2005: 0,2	2014: 5 2005: 4

Conclusions

- We have succeeded in basing kick-off values based on H3##-statements, using the Hazard Groups in Control Banding Systems
- They can be applied on substances without an OELV but with harmonised **and** notified CLP H-statements (>> 4300)
- Kick-off values are an indispensable addition if no OELVs or DNELs are available



Conclusions (2)

- Differences in Hazard groups 2005 and 2014: updating the kick-off values was relevant
- Underpinning of kick-offs greatly improved from 2005 to 2014 (larger databases)
- Kick-offs group 4 (lowest health hazard) are now higher ('less severe')
- Kick-offs in group 1 (highest health hazard) are now lower ('more severe')



Commentary Round

Invitation to comment on the kick-off values:

- Concept/idea
- Use of CB-schemes
- Statistics
- Values

Mail to: consultancy@dohsbase.nl



Follow up

- Evaluation of the received comments
- Establish definitive kick-off values
- (Scientific) publication
- Incorporation in our software DOHSBase Compare, update 2015-01 (expected December 2014): for substances with **harmonised** classification
- Published on our website: www.dohsbase.nl to derive kick-off values for substances with **notified** classification



Thanks!!

Geert.Wieling@dohsbase.nl

