



Occurrence and levels of VOCs in containers arriving in Sweden, including aspects on personal exposure, ventilation and sampling position

Gunnar Johanson

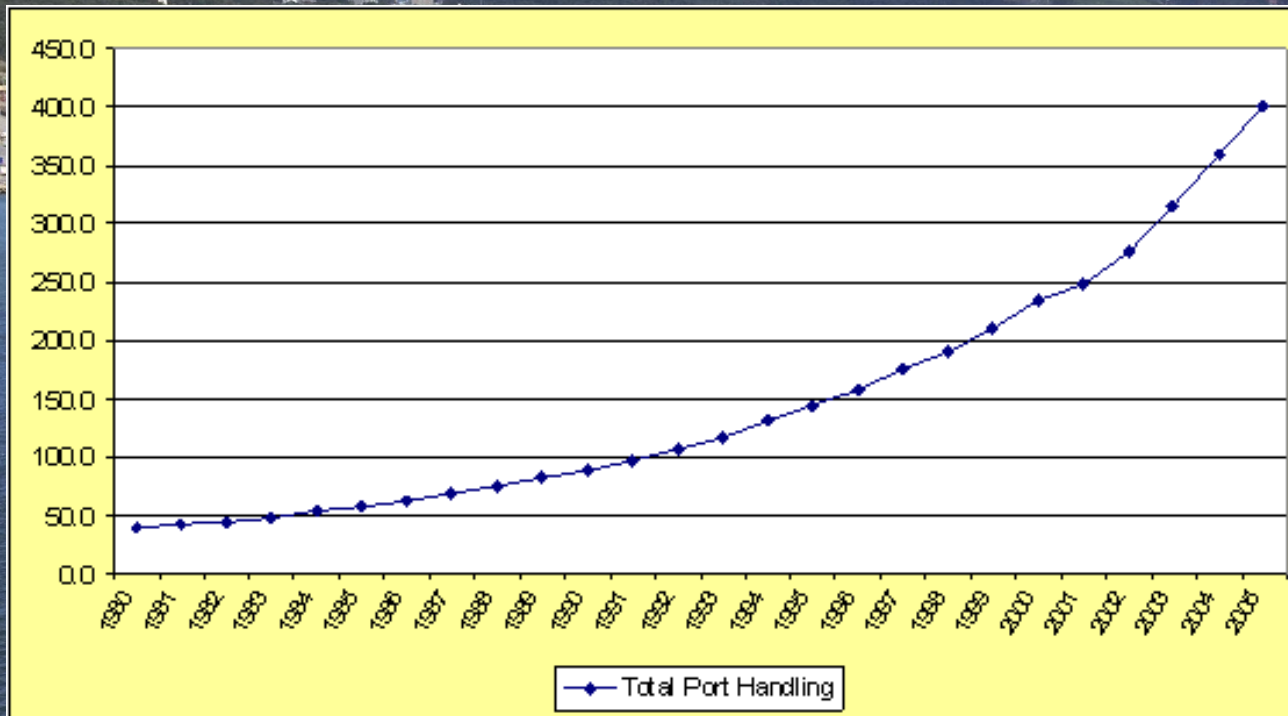
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Source: based on The Drewry Container Market Review 2005/06, p.19



The world's largest container vessel arrives to Gothenburg. More than 600 million TEUs are handled by ports annually in the world (photo: Port of Göteborg).

Background

- More than 600 million container units are stuffed, shipped and stripped annually
- International rules cover use of fumigants (but poor compliance)
- Emissions from products not given much recognition, few studies
- Workers are mostly uninformed of potential risks
- Occupations at risk: inspectors, coast guards, customs, warehouse workers, seafarers (yet to be determined?)

Three types of chemical exposure:

1. Residual levels of highly toxic fumigants
2. “Natural” emissions from products and package materials
3. Emissions from broken goods

Two types of chemical risk:

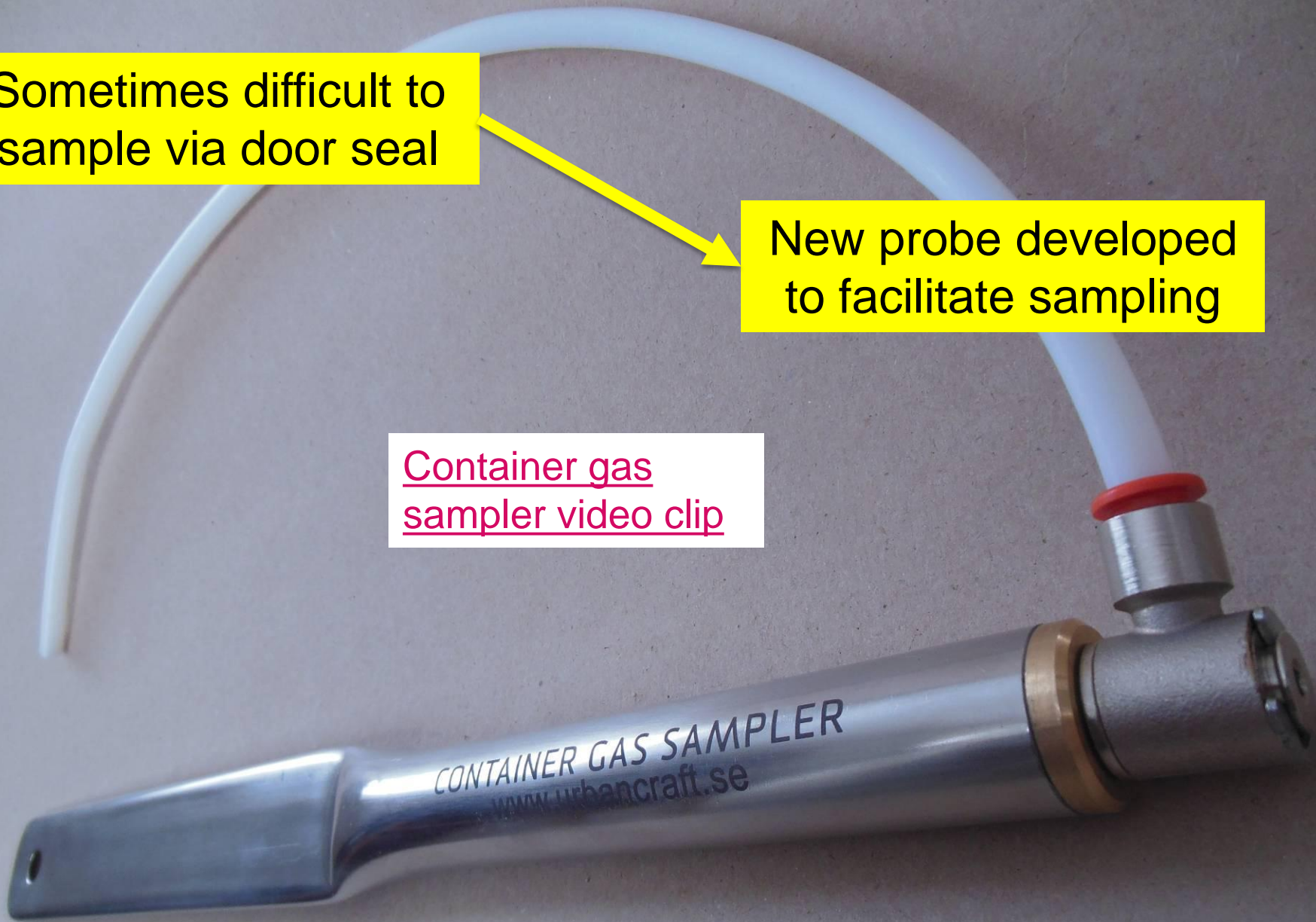
1. Acute intoxication
2. Chronic effects
 - acute exposure
 - repeat exposure

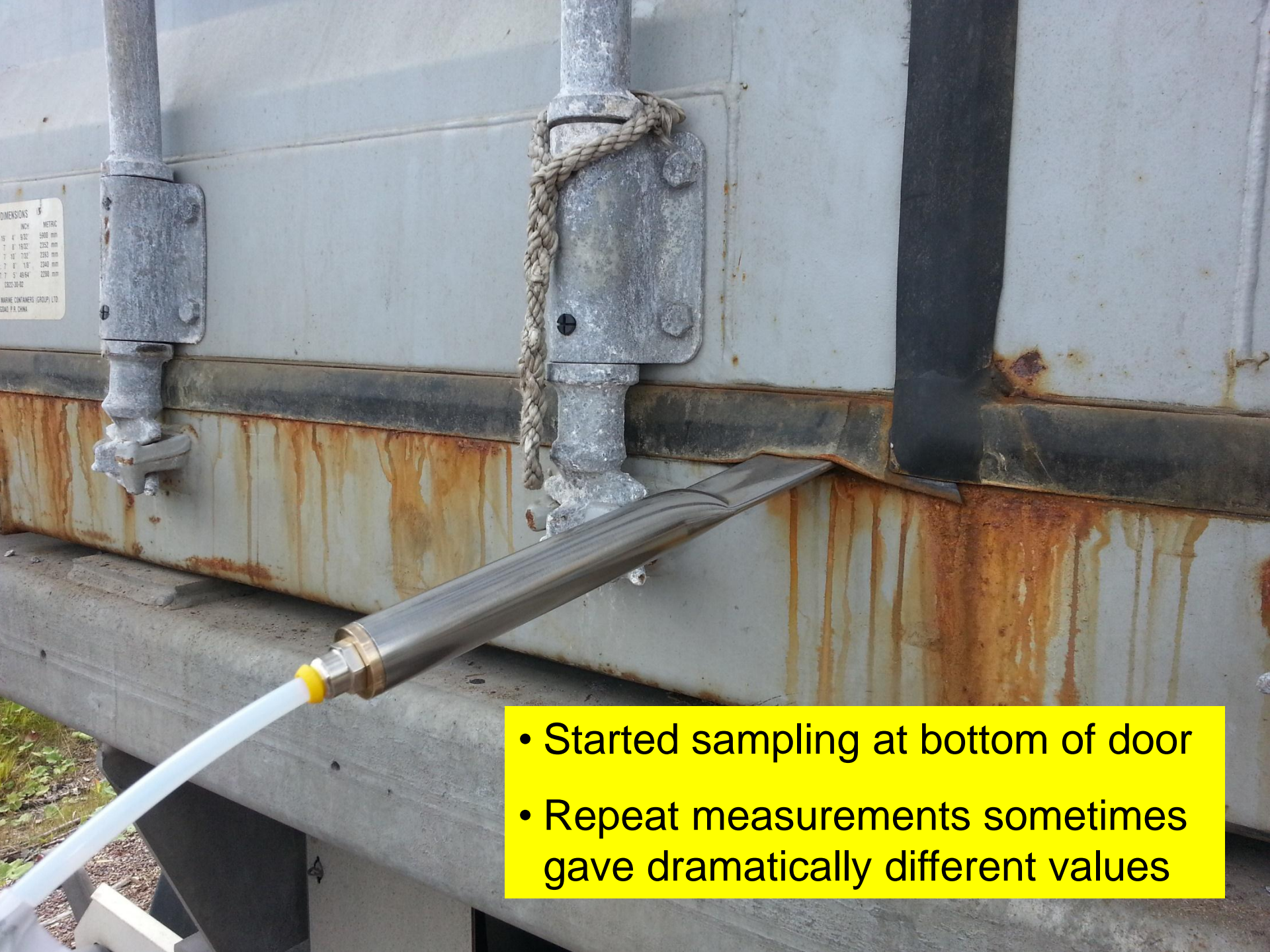
Sometimes difficult to sample via door seal

New probe developed to facilitate sampling

[Container gas sampler video clip](#)

CONTAINER GAS SAMPLER
www.urbancraft.se





DIMENSIONS
INCH METRIC
L 4' 10.32 5900 mm
W 8' 10.32 2552 mm
H 8' 10.32 2552 mm
T 10' 7.00 3100 mm
T 11' 11.00 3350 mm
T 5' 10.94 1780 mm
C222-10-02
MARINE CONTAINERS GROUP LTD
QINGDAO, P.R. CHINA

- Started sampling at bottom of door
- Repeat measurements sometimes gave dramatically different values

MAX. GROSS 32,500 KGS.
71,650 LBS.

TARE WGT. 3,900 KGS.
8,600 LBS.

MAX. CARGO 28,600 KGS.
63,050 LBS.

CU. CAP. 76.4 CU.M.
2,700 CU.FT.

APPROVED FOR TRANSPORT UNDER CUSTOMS SEAL
1970-2000
C.M.A.
CSC SAFETY APPROVAL

DANGER
No smoking
No fire



3480

Sampling in the middle

CMAU 436438

CMAU

4364
45G1

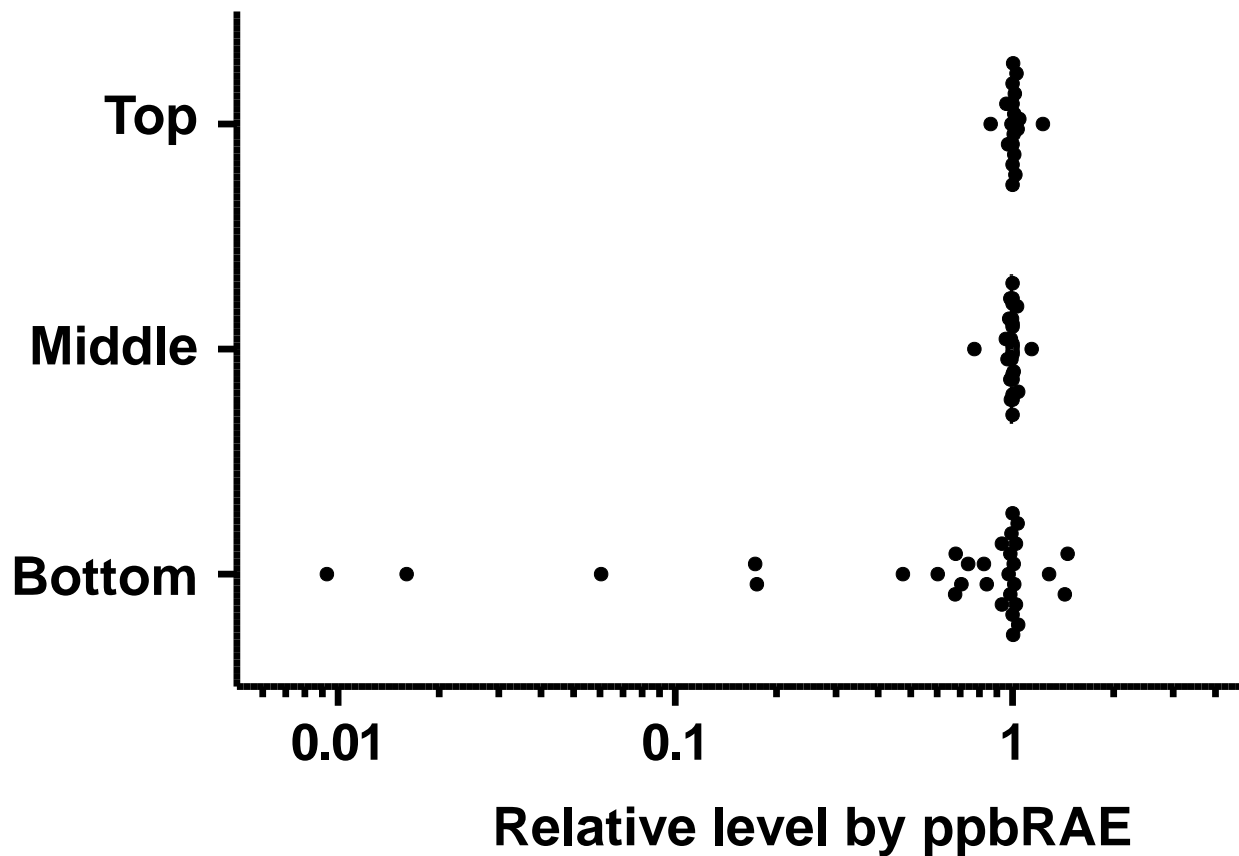
MAX. GROSS
TARE

32.500 KG
71.650 LB
3.860 KG
8.510 LB

NET
CU. CAP.

Sampling at the
top of the door

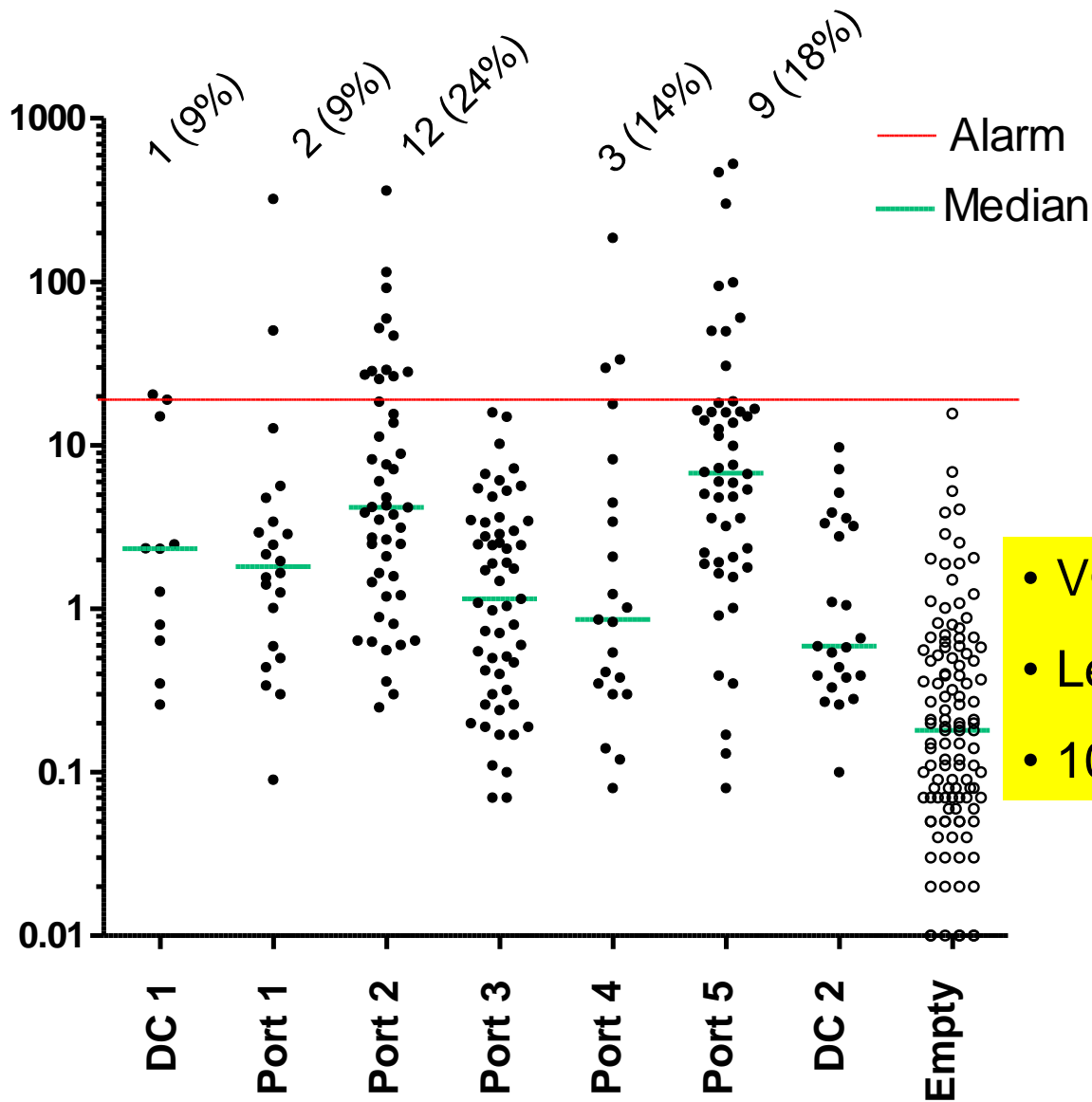
COR-TEN STEEL
CONTAINER



Sampling at bottom of door may result in severe underestimate

Due to leaking door + chimney effect ?

ppbRAE (ppm)



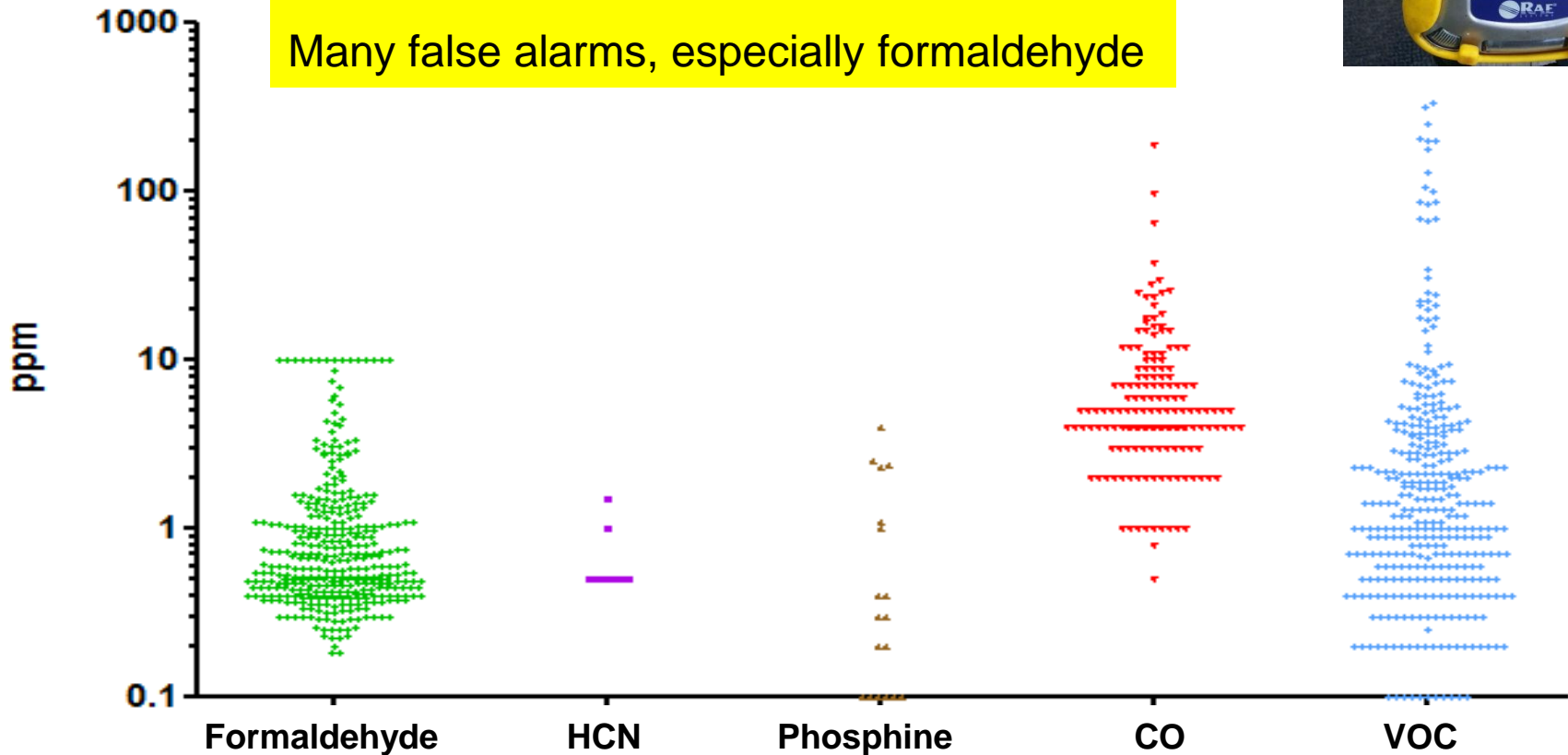
- VOC levels vary 10,000-fold
- Levels differ between sites
- 10-20% exceed 20 ppm

Measurements with multiRAE at DC 2

1302 measurements May-Aug 2013

85 alarms (7%)

Many false alarms, especially formaldehyde

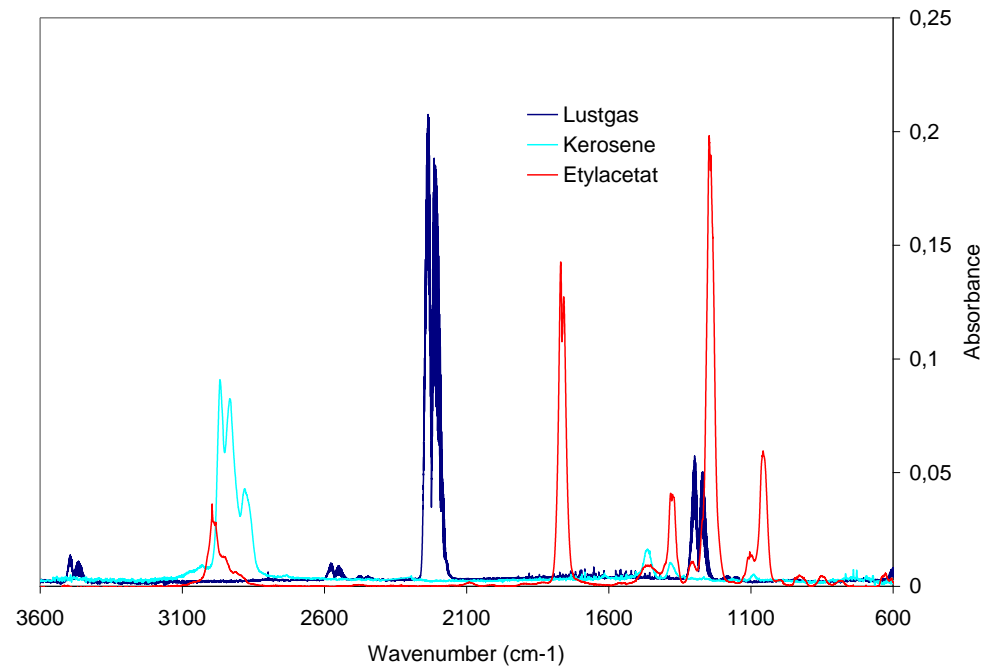


FTIR

Fourier-Transform InfraRed spectroscopy



- Bomem MB 3000
- Resolution 1 cm^{-1}
- 10-m gas cell
- Identification and quantification with library spectra from Infrared Analysis Inc.



Institutet för miljömedicin - IMM

IMM-Rapport nr 1/2011

**Förekomst av gasformiga
bekämpningsmedel och
kemikalier i containrar:
pilotstudie vid import-
kontrollen i Göteborgs hamn**

Urban Svedberg
Gunnar Johanson

46 chemicals detected by FTIR in 256 containers		Can also be detected by				
		ppbRAE	multiRAE	Hapsite GCMS	Airsense GDA2	
Acetaldehyde	Carbonyl sulfide: Carcinogen, fumigant 2 containers 0,1-15.1 ppm No Sw OEL ≈1000 ppm is lethal		Yes	Yes	Yes	
Acetone			Yes	Yes	Yes	
Ammonia			No	Yes	Yes	
Butanone (MEK) 2-			Yes	Yes	Yes	
Butylacetate			Yes	Yes	Yes	
Carbon dioxide		No	No	No	Yes	
Carbon monoxide		No	Yes	No	Yes	
Carbonyl sulfide	Chloroethanol: Carcinogen Residue in ethylene oxide 1 container 6.3 ppm Sw 8h OEL 1 ppm		Yes	Yes	Yes	
Chloroethanol			No	Yes	?	
Chloroform			No	Yes	?	
Cyclohexane				Yes	Yes	Yes
Dichloro-1-fluoroethane 1, (HCFC-141b)				Yes	Yes	Yes
Dichloroethane 1,2-	1,2-Dichloroethane: Carcinogen Used to produce vinyl chloride 2 containers 10 – 30 ppm Sw 8h OEL 1 ppm			Yes	?	
Dichlorometane				Yes	Yes	
Dimethoxymethane (formal)				Yes	Yes?	
Dimethyl ether				Yes	Yes	
Ethanol				Yes	Yes	
Ethyl acetate			Yes	Yes		

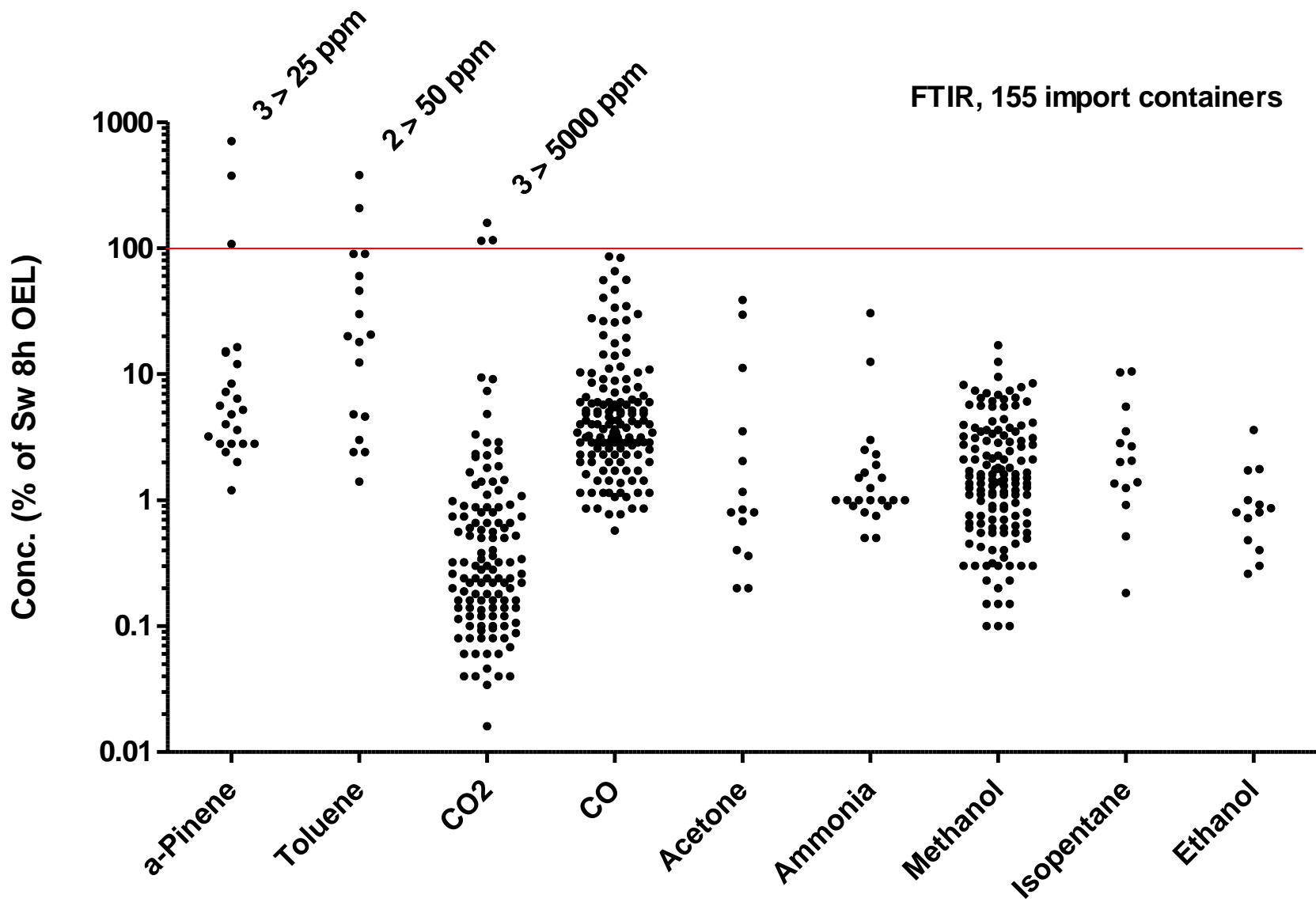
46 chemicals detected by FTIR in 256 containers		Can also be detected by			
		ppbRAE	multiRAE	Hapsite GCMS	Airsense GDA2
Ethylene oxide		No	No	No	?
Ethylene		Yes	Yes	No	Yes
Formaldehyde		No	Yes?	No	Yes
Gasoline		Yes	Yes	Yes	Yes
Heptane, n-		Yes	Yes	Yes	Yes
Hexyl acetate		Yes	Yes	Yes	Yes
Isobutane	Ethylene oxide: Carcinogen, fumigant 1 container 1.7 ppm Sw 8h OEL 1 ppm	Yes	Yes	Yes	Yes
Isobutane		Formaldehyde: Carcinogen, fumigant 9 containers 0.2 – 2 ppm Sw 8h OEL 0.3 ppm	Yes		Yes
Isobutanol			Yes		Yes
Isobutylene			Yes		Yes
Isopentane			Yes		Yes
Isopropanol		Yes	Yes	Yes	Yes
Kerosene / white spirit		Yes	Yes	Yes	Yes
Methane		Yes	Yes	No	Yes
Methanol		Yes	Yes	No	Yes
Methyl formiate		Yes	Yes	Yes	Yes
Methyl metacrylate		Yes	Yes	Yes	Yes
Octamethylcyclotetra-siloxane		Yes	Yes	Yes	Yes
Phosphine		No	Yes	No	Yes

46 chemicals detected by FTIR in 256 containers		Can also be detected by			
		ppbRAE	multiRAE	Hapsite GCMS	Airsense GDA2
Phosphine	Phosphine: Fumigant 1 container 3 ppm Sw 8h OEL 0.3 ppm	No	Yes	No	Yes
Pinene, β-		Yes	Yes	Yes	Yes
Pinene, α-		Yes	Yes	Yes	Yes
Propylbenzene		Yes	Yes	Yes	Yes
Styrene		Yes	Yes	Yes	Yes
Tetrafluorethane (HFC-134a) 1,1,1,2-		Yes	Yes	Yes	Yes
Toluene		Yes	Yes	Yes	Yes
Trichloroethane 1,1,1-		Yes	Yes	Yes	Yes
Trichloroethylene		Yes	Yes	Yes	Yes
Xylenes		Yes	Yes	Yes	Yes

Measurements by FTIR Sept 2013 (n=155)

Most common chemicals

	n	Interval (ppm)	Median (ppm)	8h OEL (ppm)	ppbRAE	multiRAE	Hapsite GCMS	Airsense GDA2
Carbon monoxide	141	0,2 – 30	1,4	35	No	Yes	No	Yes
Methanol	138	0,2 – 25	2,9	200	Yes	Yes	No	Yes
Carbon dioxide	123 (>400)	400 - 8350	540	5000	No	No	No	Yes
Ammoniak	23	0,1 – 6,1	0,2	20	No	No	Yes	Yes
a-Pinene	22	0,3 – 176	1,3	25	Yes	Yes	Yes	Yes
Toluene	14	0,7 - 190	10	50	Yes	Yes	Yes	Yes
Acetone	13	0,4 – 97	2,1	250	Yes	Yes	Yes	Yes
Ethanol	12	1,3 – 18	4,0	500	Yes	Yes	Yes	Yes
Isopentane	10	5,5 – 63	12	600	Yes	Yes	Yes	Yes

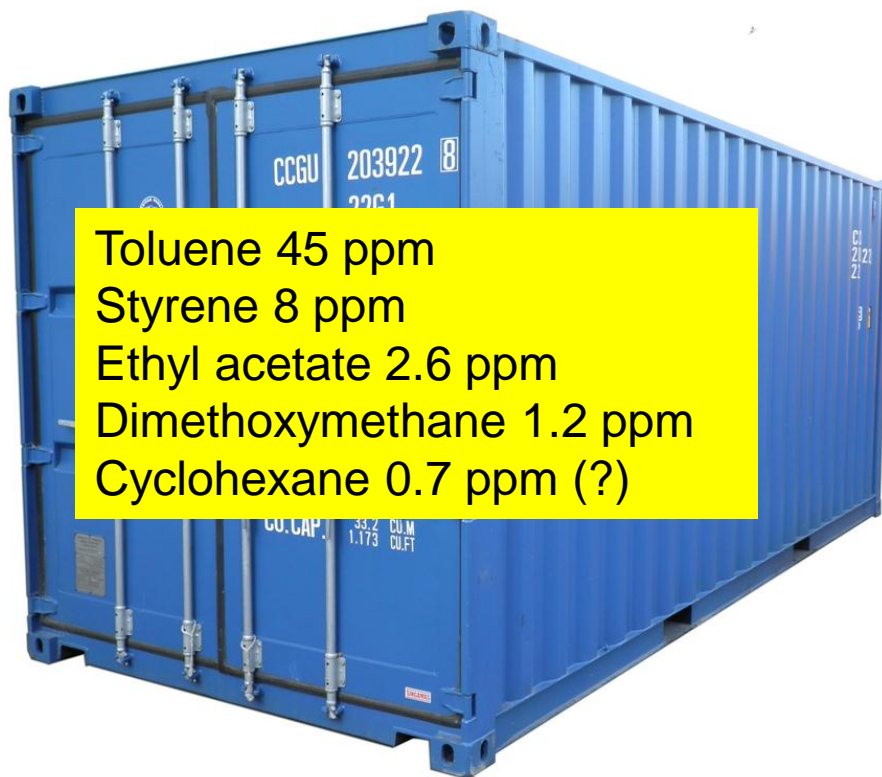


Comparison with OEL

- 16 different chemicals found at levels above half the Swedish 8h OEL
- 10% of containers
- 5% had formaldehyde > 0.3 ppm
- 10 – 20% had VOC > 20 ppm
- Highest exceedance:
1,2-dichloroethanol
30 times the OEL



Shoe containers



Work Inside Ocean Freight Containers—Personal Exposure to Off-Gassing Chemicals

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More than 500 million ocean freight container units are shipped annually between countries and continents. Residual levels of fumigants, as well as naturally occurring off-gassing chemicals emanating from the goods, constitute safety risks, which may affect uniformed workers upon entering the containers. The aim of this study was to assess workers' exposure during stripping of containers and

Personal exposure during stripping

- VOC level unknown prior to stripping and mostly low
- Therefore, prepare container by injecting nitrous oxide (N_2O) as tracer gas. Equilibration for at least 24 h
- Pre-open measurement of “natural” VOC and added N_2O at 0, 6 and 12 m
- Work zone monitoring (arm length's distance) of VOC and N_2O during stripping
 - FTIR continuous – VOC and N_2O
- Breathing zone monitoring during stripping
 - FTIR bag – VOC and N_2O
 - PID continuous and bag – VOC
 - Adsorbent tube
 - (N_2O handheld detector)



COR-TEN STEEL CONTAINER

1

2

CLAS OHLSON
ORDER NO.: 8285
ITEM NO.: 40-785
GOTHEBORG

CLAS OHLSON
ORDER NO.: 8285
ITEM NO.: 40-785
GOTHEBORG

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ITEM NO.: 40-785
GOTHEBORG



CCLU 727332 8
4561

FOR RENT BY
CCLU or its member companies



MAX. GROSS 32,500 KG
71,550 LBS

TARE 3,890 KG
8,575 LBS

NET 28,610 KG
63,075 LBS

CU. CAP. 76.4 CU.M.
2,698 CU.FT.

001 727454
4261



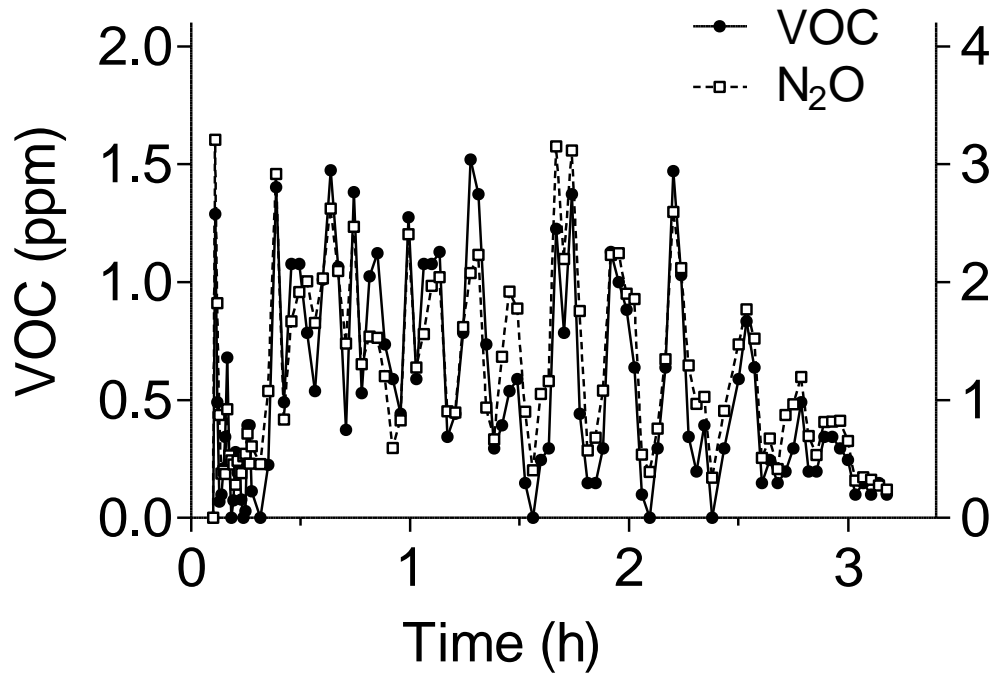
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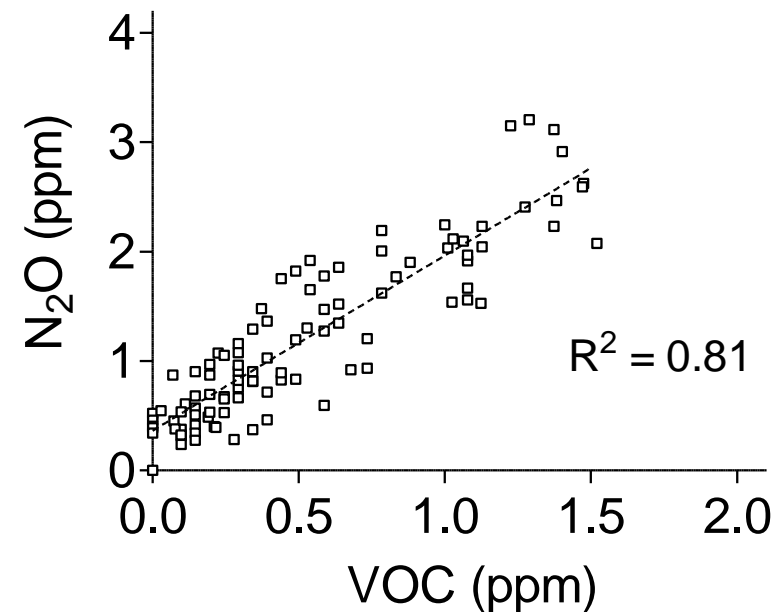




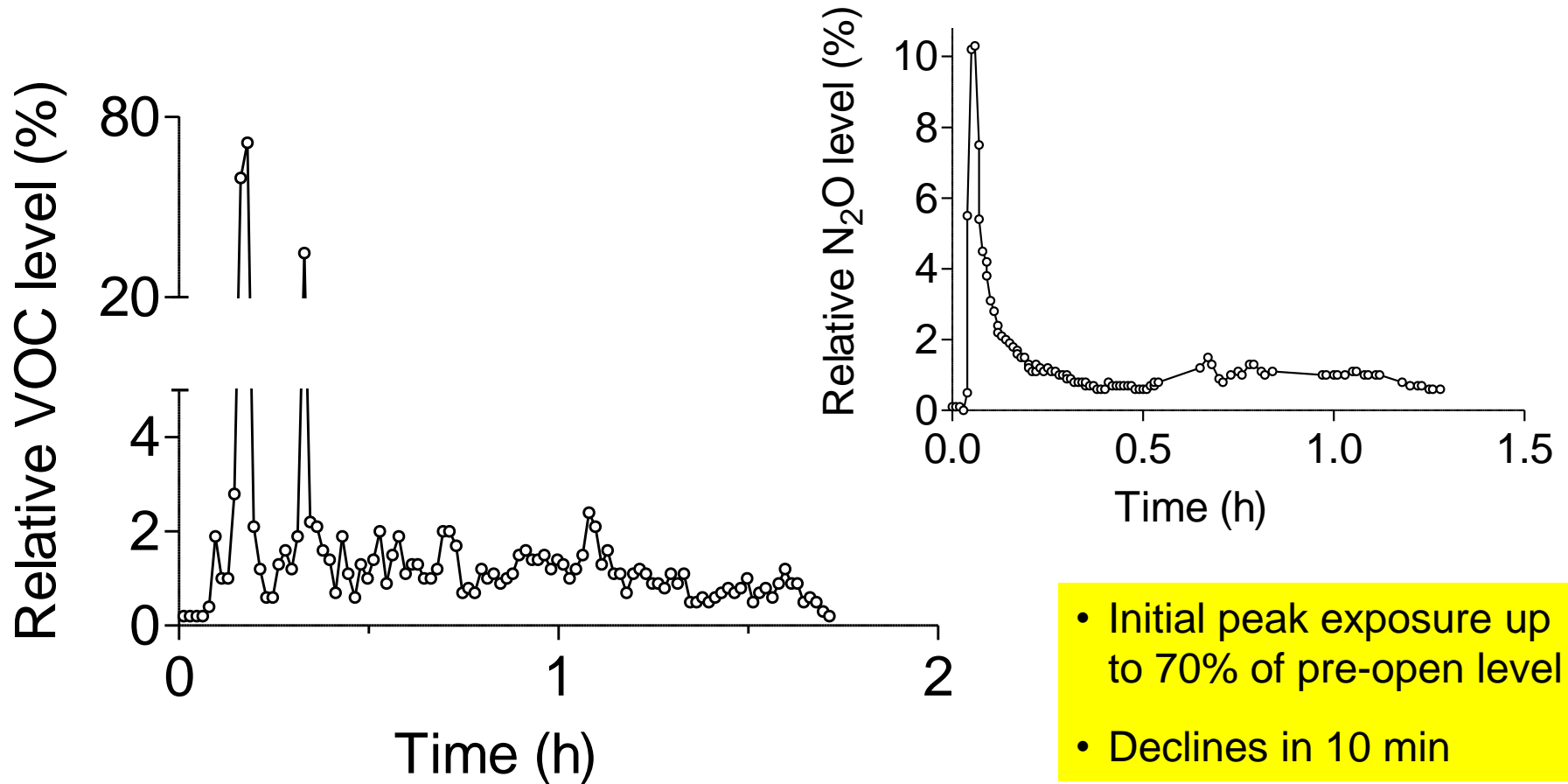
Correlation between VOCs and tracer gas during stripping (work zone)



Good agreement between “natural” VOCs and tracer gas



Personal exposure during stripping (40-ft, natural ventilation)



U Svedberg, G Johanson. Ann Occup Hyg (2013)

Personal exposure during stripping, % of pre-open level (40-ft, natural ventilation)

		Container					
		A	B	C	D	E	F
<i>Breath zone</i>							
VOC	Adsorbent tube	4.7	6.7	5.4	-	-	-
VOC	FTIR bag sample	2.1	1.4	2.8	-	-	-
N ₂ O	FTIR bag sample	2.2	1.3	3.4	1.2	1.6	2.3
VOC	PID bag sample	-	1.1	2.1	-	-	-
VOC	PID continuous	1.7	2.7	3.1	-	-	-
<i>Work zone</i>							
VOC	FTIR continuous	0.7	1.2	-	-	-	-
N ₂ O	FTIR continuous	1.4	0.7	-	1.3	1.7	1.5

U Svedberg, G Johanson. Ann Occup Hyg (2013)

**Workers' average exposure
1-7 % of pre-open level**

Ventilation – preliminary data



Natural ventilation

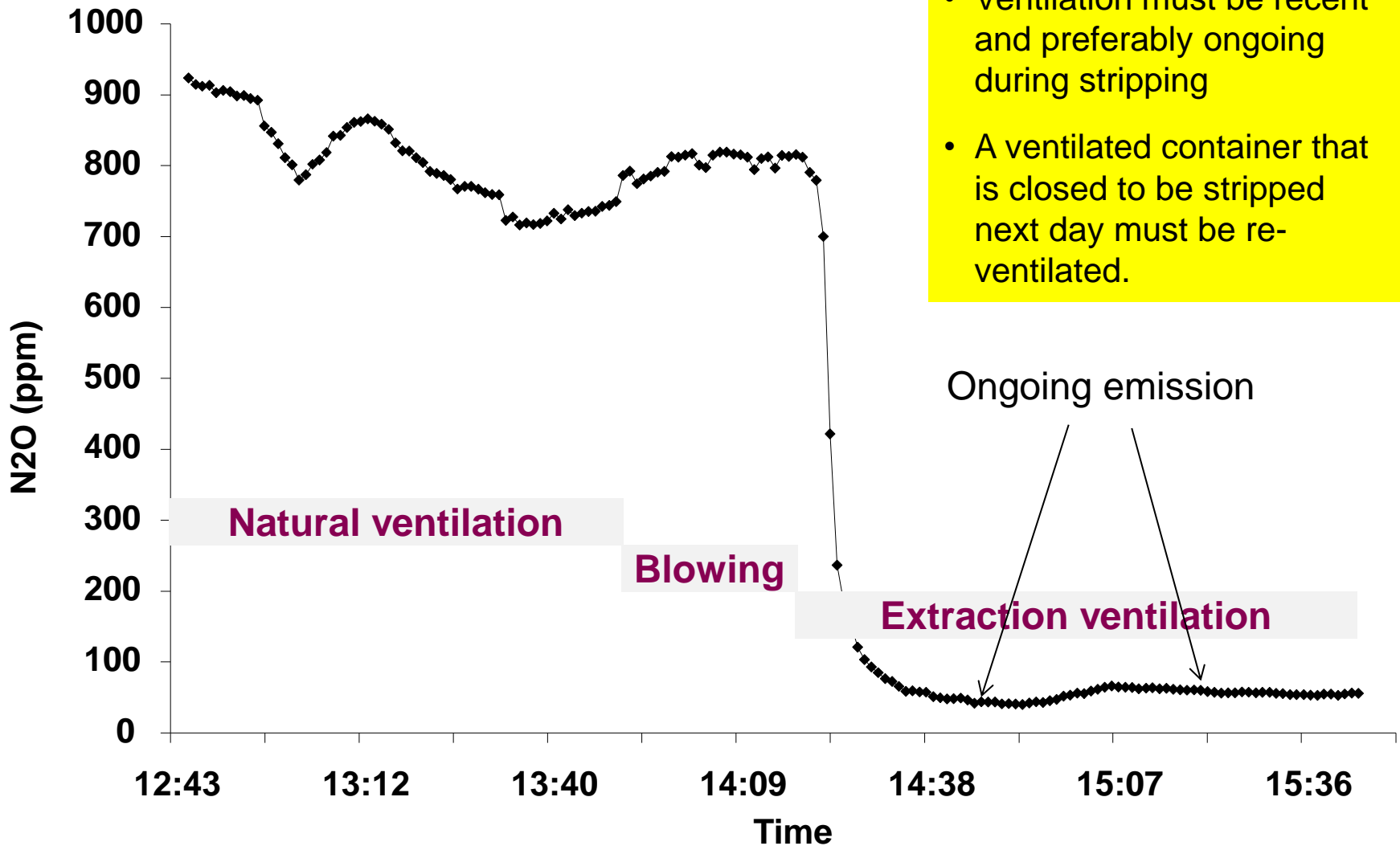


Blowing ventilation

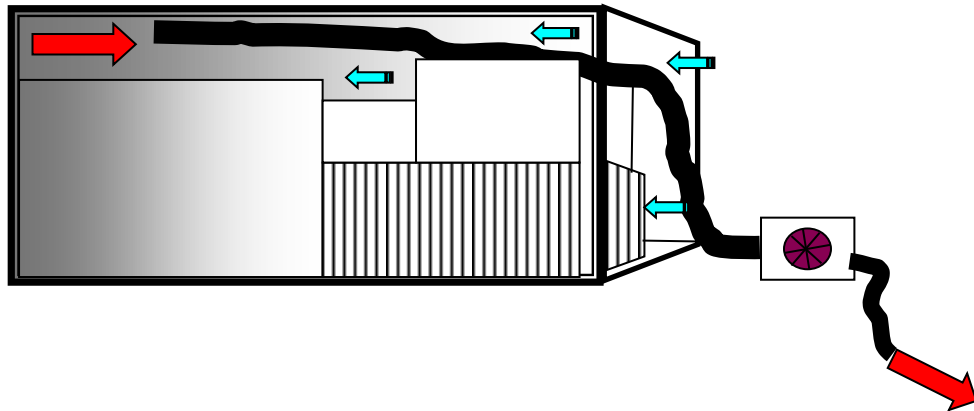


Extraction ventilation

Tracer gas decay 12 m from open doors

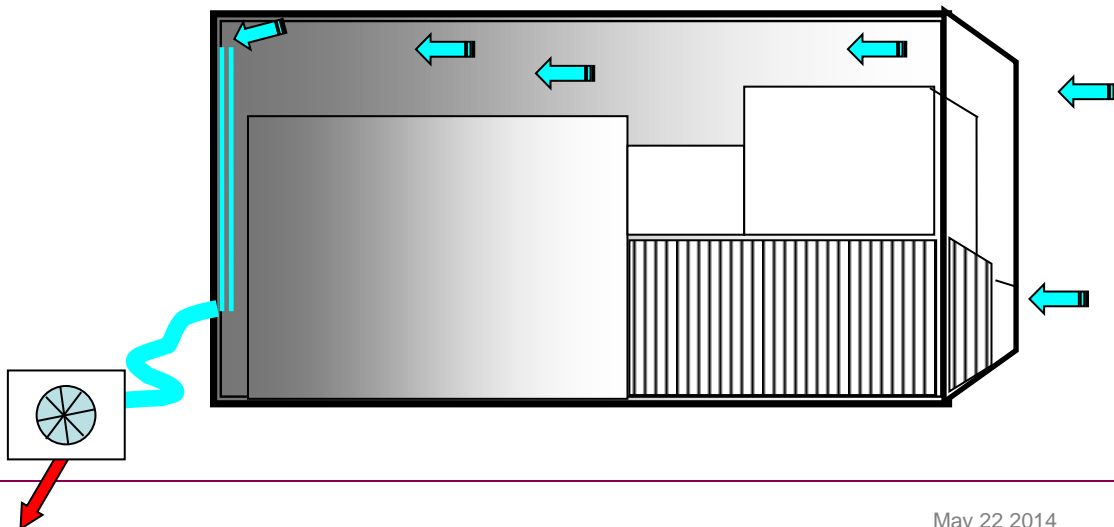


- Extraction ventilation much more efficient
- Ventilation must be recent and preferably ongoing during stripping
- A ventilated container that is closed to be stripped next day must be re-ventilated.



Our tests:
 100-mm pipe inserted above
 goods and connected to 24-V fan

Better solution:
 Extraction ventilation via
 pre-installed ventilation
 port in front of container.



Conclusions

1. Residual harmful levels of fumigants can be found in unmarked containers (but not common)
2. Highly variable content, no handheld instrument covers all chemicals
3. Volatiles around or above the OELs were found in 5 – 20% of the containers
4. Workers' exposures were 1-7 % of arrival (pre-open) concentrations, initial peaks up to 70% were seen.
5. Repeated and prolonged exposure may constitute health risk to those working inside containers



Conclusions

6. Tracer gas method useful for experimental studies of exposure
7. Measure before opening container (middle or top – not bottom). If not, always ventilate, preferably with forced extraction ventilation
8. Extraction ventilation of container seems superior to natural or blowing ventilation (preliminary data)
9. Initiate petition from transportation industry and scientific communities for the redesign of containers to facilitate sampling and ventilation
WHO: Evidence-based informed policy making.
EOM: ...supports translation of scientific findings to regulations and rules...



Thank you!

Acknowledgements

- AFA Insurance
- Västernorrland County Council
- Staff and workers at study sites
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