

PCCC

Personnel exposure and sampling
methods related to amine-based CO₂
capture technology

Alexander Reyes Andersson

General HSE, chemical management, occupational hygienist and waste
management



Agenda

- Introduction
- Over exposure limit values (OELV)
- Sampling methods
- Results



Testing various
capture
technologies

Joint
venture



Tested 17 different Technologies

 **> 40.000 hrs**
Proprietary Campaigns

Solvent
Technologies

Start 2012



Start 2020

Emerging
Technologies



Sponsored by TCM Owners, DOE, EC and CLIMIT

 **> 23.000 hrs**
Non-proprietary Campaigns

 **> 70**
Scientific publications

2013



During TCM time we have performed work environmental measurements for almost all campaigns.

- What are OELV (Over exposure limits values)
 - Recommended and/or regulatory exposure concentrations limits for different chemical components
 - Normally based on NOAEL (LOAEL/3)
- Why is this of importance?
 - Manage daily work, prepare the industry
 - Miss full evaluation for the majority of CO2 capture related components
- TCM have tested 12 different amines during the last 13 years. 3 of them have established OELV, the 3 that have it are the ones we have tested in open campaign (PZ, MEA and AMP)
- It is possible to estimate OELV based on available toxicological data.
- Estimation can match established OELV, but also be estimated lower than established.
- Limits for the population related to nitrosamines are established by the Norwegian Institute of Public Health (NIPH), but not for amines.

The R8 tool helps derive a **Derived No-Effect Level (DNEL)** for workers, which can function as an internal OEL in the absence of a regulatory limit

$$\text{DNEL (mg/m}^3\text{)} = \frac{\text{NOAEL (mg/m}^3\text{)}}{\text{Interspecies Factor} \times \text{Intraspecies Factor} \times \text{Duration Factor}}$$

Nr. amines	OELV [ppm]			Comments
	Avg	Min	Max	
17-20	0.61	0.01	5	Total in industry
12	0,29	0.01	1	9 estimated and 3 established
3	0.41	0.03	1	Established, MEA (0,2ppm), PZ (0,03ppm) & AMP (1ppm)

Note: Estimation 0.01 ppm can be of concern

Basis for selecting company OELV [ppm]

Component (type)	Norwegian OELV (ppm) ¹	ACGIH TLV's (2019) ¹²	German OELV (ppm) ¹³	BP (°C)	Health Classification. ²
Monoethanolamine (MEA) ³	1	3 6 (S)	0.2	171	Acute Tox. 4(swallow) H302, Acute Tox. 4(skin) H312, Skin Corr. 1B H314, Acute Tox. 4(inhaled) H332
Piperazine (PZ) ³	0.03 0.09 (S)	0.03	0.03 (S)	146	Skin Corr. 1B H314, Skin Sens. 1 H317, Resp. Sens. 1 H334, Repr. 2 H361fd
Aminomethyl propanol (AMP) ³	N/A	N/A	1	166	Skin Irrit. 2 H315, Eye Irrit. 2 H319, Aquatic Chronic 3 (H412)
Ammonia ⁴	15	25 35 (S)	20	-33	Skin Corr. 1B H314, Acute Tox. 3 H331, Aquatic Acute 1 H400
Formaldehyde ⁴	0.5	0.1 0.3 (S)	0.3	-19	Acute Tox. 3(swallow) H301, Acute Tox. 3(skin) H311, Skin Corr. 1B H314, Skin Sens. 1 H317, Acute Tox. 3(inhaled) H331, Muta. 2 H341, Carc. 1B H350
Acetaldehyde ⁴	25	25 (C)	50	20	Eye Irrit. 2 H319, STOT SE 3 H335, Muta. 2 H341, Carc. 1B H350
Acetone ⁴	125	250 500 (S)	500	56	Eye Irrit. 2 H319, STOT SE 3 H336
Dimethylamine (DMA) ⁴	2	5 15 (S)	2	7	Skin Irrit. 2 H315, Eye Dam. 1 H318, Acute Tox. 4 H332, STOT SE 3 H335
Nitrosodimethylamine (NDMA) ⁴		200ng/m³ (Netherlands)		153	Acute Tox. 3(swallowed) H301, Acute Tox (inhaled). 2 H330, Carc. 1B H350 (C ≥ 0,001%), STOT RE 1 H372, Aquatic Chronic 2 H411

S = STEL -Short-Term Exposure Limit

C = Ceiling – concentration that should not be exceeded

¹ Norwegian Labour Inspection Authority -8 h OELV

¹² American Conference of Governmental Industrial Hygienists (ACGIH)

² Classification based on ECHA C&L-inventory database

³ Amine

⁴ Degradation components

¹³ German Labour Inspection Authority -8 h OELV

Some of the mayor work related tasks with potential personnel exposure

Location / task	Discipline	Risk / comments	Mitigating action
Analysis house	Inst.tech	Diffuse emission spot	Measure both close and a t
Storage tanks	All	Diffuse emission spot	Measure close to exhaust and at potential exposure height
Sampling cabinets	Ope.Shift	Operators can come in contact with solvent	Measure during sampling, without sampling, maintained and not maintained cabinet.
Emptying and filling of amine plant	Ope.Shift	Dedicated areas. Operators can come in contact with solvent	VOC Measurements during filling and emptying.
Laboratory related work	Lab.tech	Iso-kinetic sampling, indoor laboratory work	Measure during iso-kinetic
Maintenance / Incidents	Ope.Shift, inst.tech & others	Equipment must be opened, potential exposure	Many different scenarios. Normally we use full face mask and chemical gloves adapted to the specific solvent
Top of absorber	All	Emission plume can have local impact	Use VOC meter at the top of the stack

Sampling methods and strategies

Nitrosamines high priority 2012-2020
(carcinogenic)

Sampling strategy:

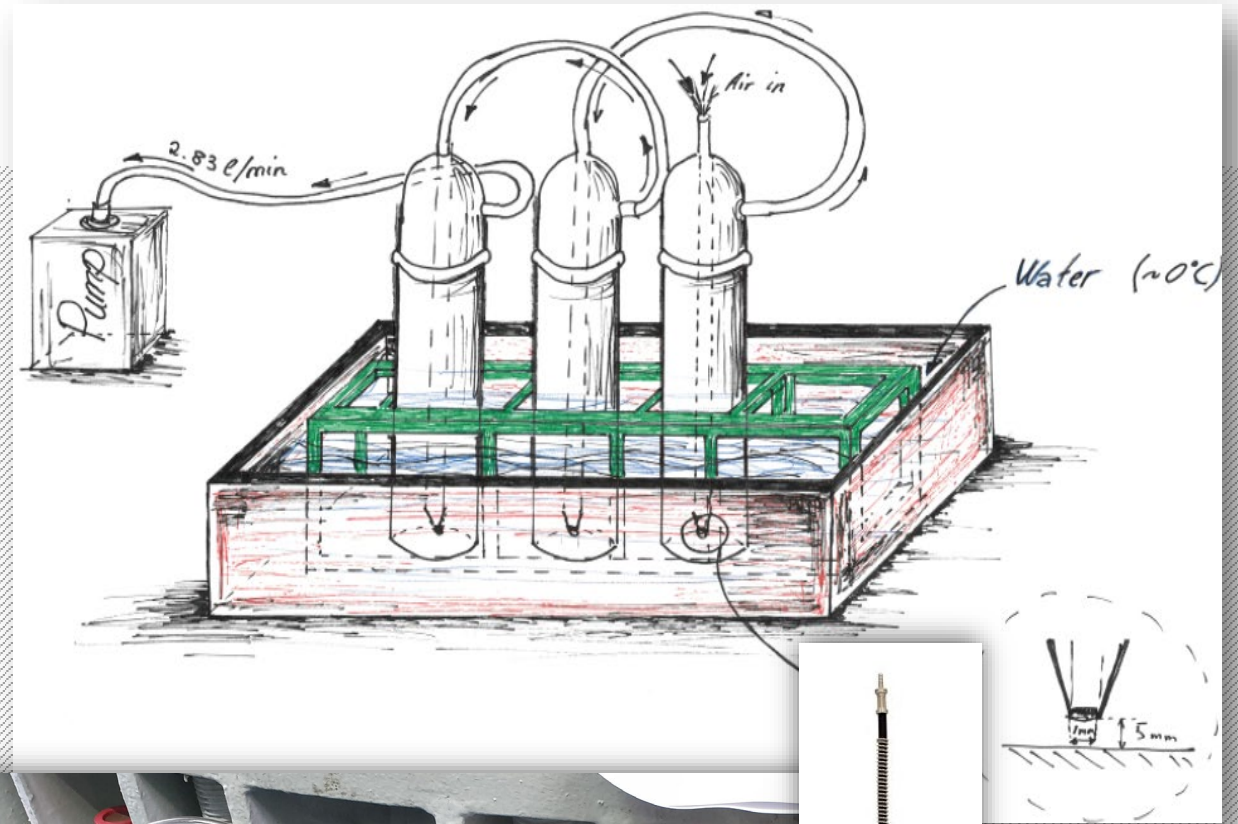
- Focus on nitrosamines and performing measurements during all campaigns
- Majority inside the battery limit of TCM

Sampling methods:

- Direct reading or sampling medium (pump + adsorbent)

Sampling strategies:

- Stationary – local area, background concentrations
- Full shift – represent daily work, 8h shift
- Task – risk assess specific tasks



Sampling methods - Amines

Challenges

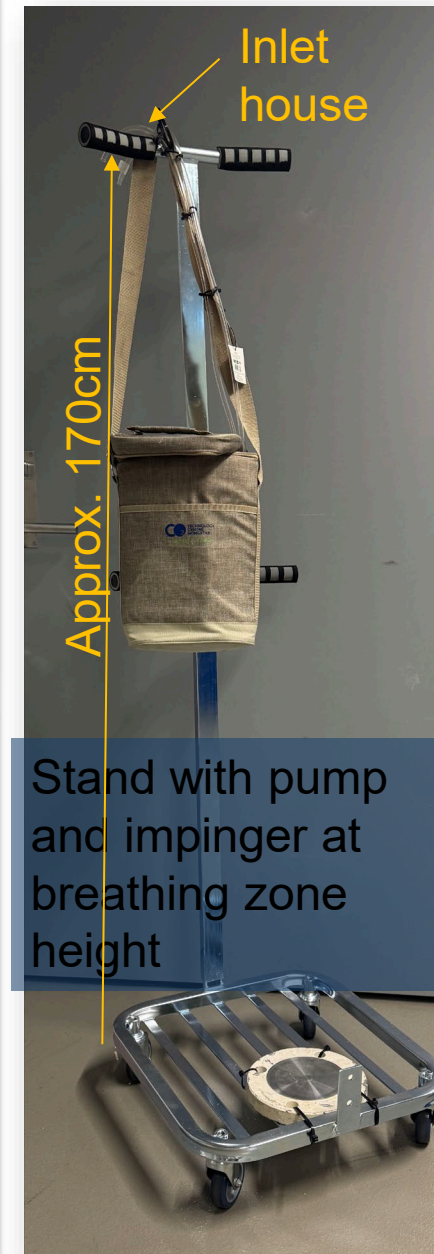
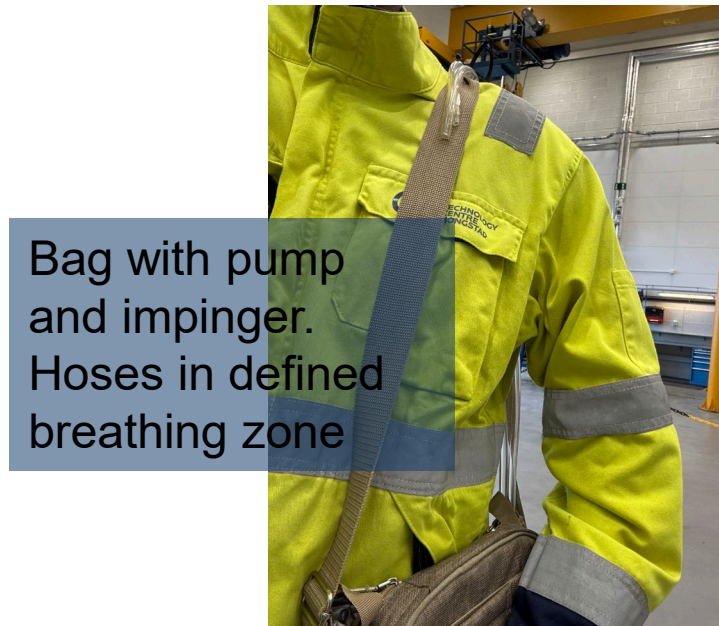
The “industrial” laboratories don’t have established methods and prepared tubes for amine adsorption. NIOSH recommends adsorbent.

Direct reading

- Direct reading, UiO, PTR-TOF 4000 analyzer (Ionicon Analytik GmbH, Innsbruck, Austria)
- ION CUB VOC

Full shift and task based sampling

- TCM have been using Aircheck connect pump with impingers and adsorption medium sulfuric acid.
- SKC connect pros: long battery life (>30h) and can achieve sampling flow 2.8L/min
- Challenging to work with pump + impingers
- So far 5 samples, 4 inst.tech 1 lab, all Below Limit Of Detection (BLOD $\approx 0.01\text{mg/m}^3$)



Sampling of nitrosamines

Challenges

- Similar to amines, lack of laboratories. SINTEF have been involved.
- Difficult to extract nitrosamines, especially N-PZ. Impinger is recommended.

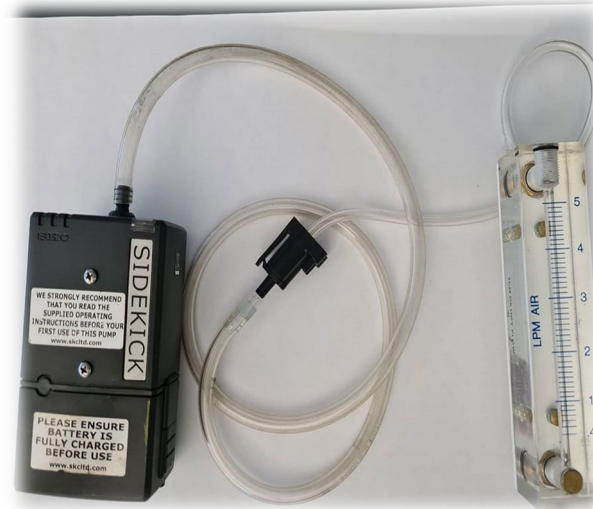
Direct reading

- Direct reading, UiO, PTR-TOF 4000 analyzer (Ionicon Analytik GmbH, Innsbruck, Austria)
- Performed some comparative measurements between PTR-TOF and Thermosorb-N. (+/-150-200%)

Full shift and task

- TCM have been using SKC Sidekick and Aircheck pump together with both impingers and filter.
- Thermosorb-N filters seem to work satisfactory. Laboratory experiments have been setup to verify.
- If we are going of to impinger, also challenging to work with pump + impingers

Thermosorb-N filters



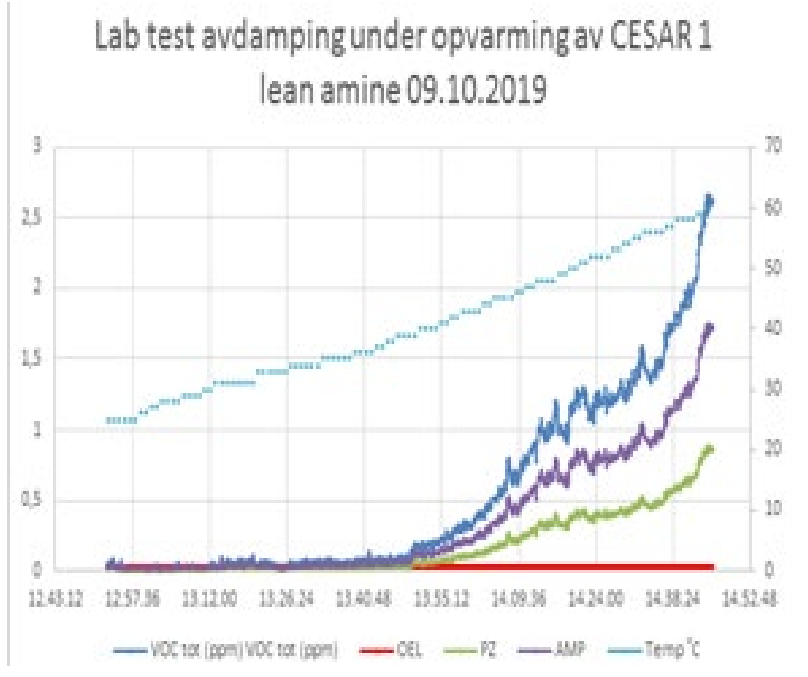
Impinger
Adsorption medium
Sulfamic acid
(H_3NSO_3)

Sampling with help of PID



Types of instruments:

- Direct reading, UiO, PTR-TOF 4000 analyzer (Ionicon Analytik GmbH, Innsbruck, Austria)
- PID – Photoionization Detector
- VOC – Volatile Organic Compound
- Mini RAE 3000 and VOC – ION CUB
- Experiments in Laboratory, in sampling cabinets
- ION CUB Pros and cons
 - Pros: Stability/Fast reaction time
 - Reacts to all types of VOC



Factor tables for different components can be used to set OELV and STEL limit on the instrument. Requires sampling effort and is time consuming.



Impinger	Am x	Am x
Impinger	0,19	0,05
PID (VOC)	0,31	0,04
Δ%	160%	80%

Results – for personnel exposure is standard 689
used as standard document

- Standard for comparing results with OELV
- <6 samples use 10, 15, 20% of OELV
- ≥6 samples, statistics, direct comparison with OELV

DS/EN 689:2018

Workplace Exposure - Measurement Of Exposure By Inhalation To Chemical Agents - Strategy For Testing Compliance With Occupational Exposure Limit Values

This European Standard specifies a strategy to perform representative measurements of exposure by inhalation to chemical agents in order to demonstrate the compliance with occupational exposure limit values (OELVs).**This European Standard is not applicable to OELVs with reference periods less than 15 min.

Nitrosamines all concentrations in ng/m3

		Nr. samples	n (%) <IQL	AM [ng/m ³]	Min [ng/m ³]	Max [ng/m ³]	% OELV
Outdoor	Amine plant	24	12 (50%)	5.8	<0.01	39.0	3%
Indoor	Office + laboratory	11	2 (14.3%)	2.4	<0.01	7.4	1%
	Only Laboratory	8	2 (25%)	2.3	<0.01	6.2	1%

	Nr. samples	n (%) <LOD	AM	Min	Max	EUC	% OELV
Full shift	17	0 (0,0%)	3.9	0.8	10.7	11.5	6%
Task all	28	1 (4,5%)	5.1	0.2	12.6	26.3	13%
Task shift	17	1 (5.8%)	3.4	0.1	9.6	19.5	10%
Task lab	8	0 (0.0%)	3.9	0.2	8.7	31.1	16%

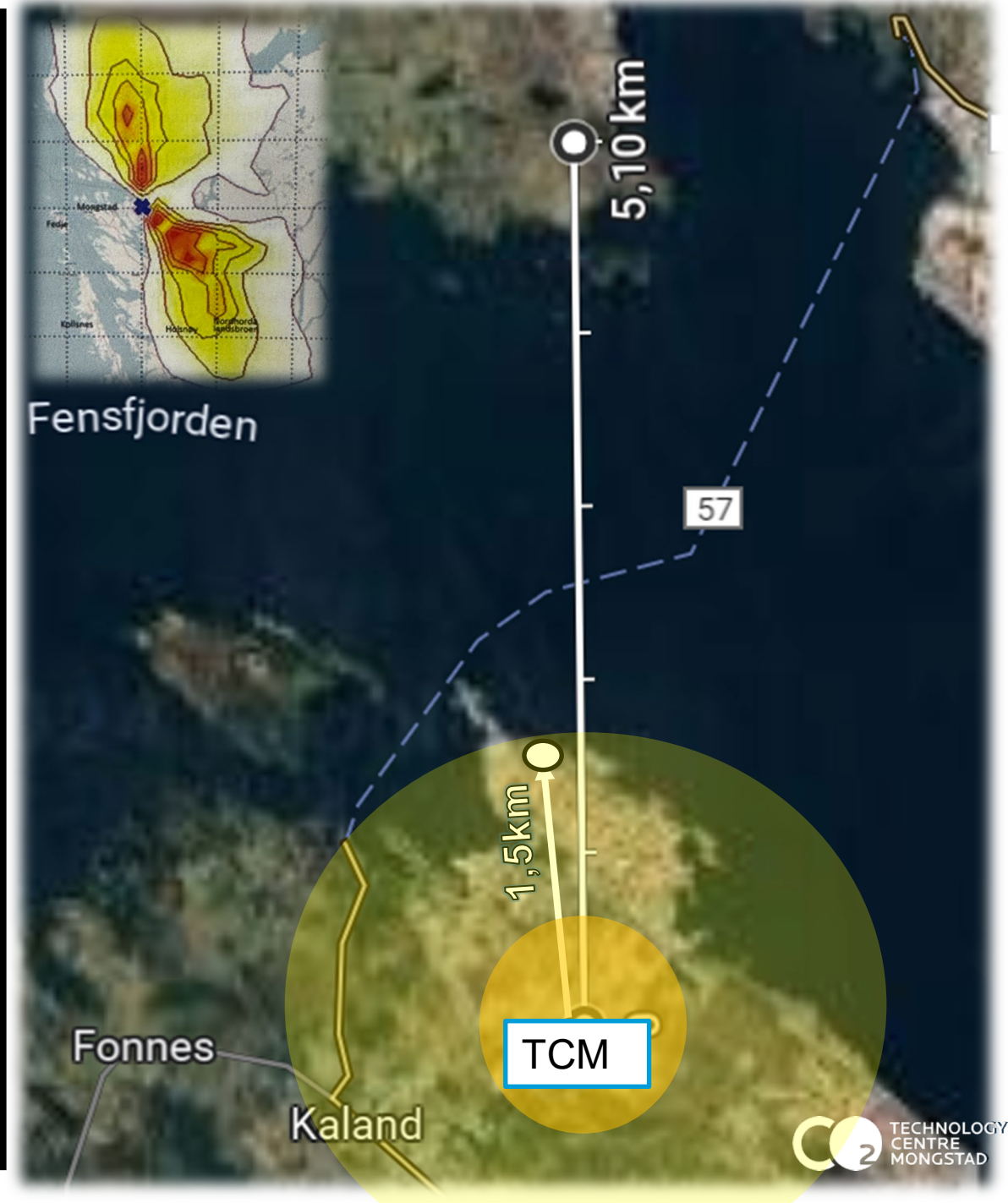
EUC: Estimated upper concentration

Notes: OELV for nitrosamines [200ng/m3]

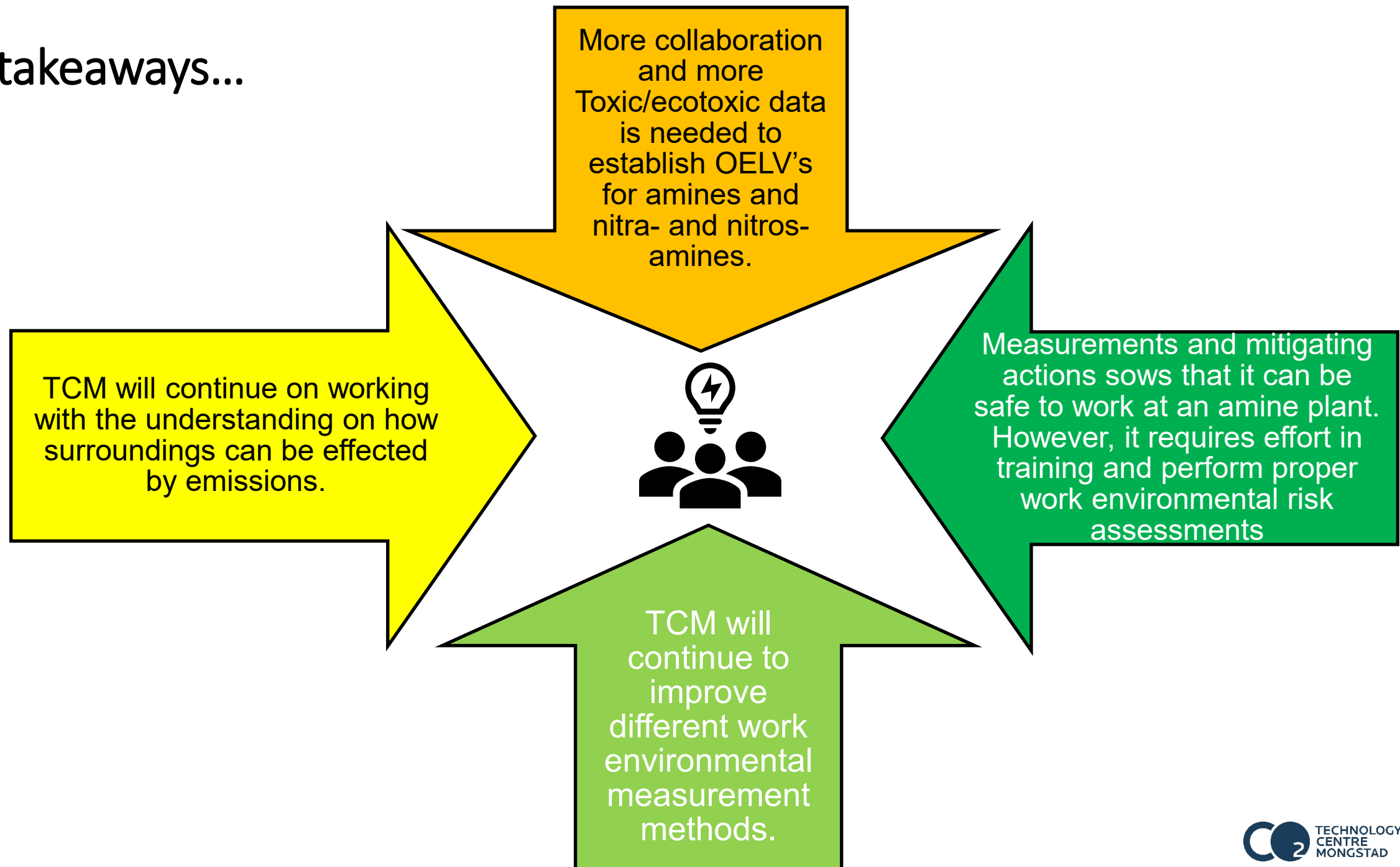
*Reference for outdoor and indoor data: Reyes-Lingjerde et al. 2021. *CO₂ Capture and work environmental sampling at TCM - lessons learned*

In the pipeline...

- Continue with work environmental measurements related to amines, due to that we are in the starting and have been focusing on nitrosamines.
 - Continue to provide both internal and external services:
 - Preparation and quality check of SDS
 - Perform measurements and prepare occupational hygiene reports
 - Work environmental related training for personnel
 - Classification and evaluation of chemicals
 - Facilitate work environmental health risk assessments
 - Waste management and reduce environmental footprint.
-
- Understand emission effects in near surrounding 500-1500m radius.
 - Can be used for validation both environmental and work environmental



Key takeaways...





Connect with TCM

Partnering for CCS Deployment

Why TCM?

- ❖ +60,000 operational hours → proven, bankable performance
- ❖ 17 post-combustion capture technologies tested and derisked for commercial deployment → unmatched track record
- ❖ Neutral, independent test center → trusted by industry, investors & policy makers

What We Offer:

- ❖ **Advisory services:** technology screening, selection & scale-up
- ❖ **Project support:** from feasibility through FID
- ❖ **CO₂ quality expertise:** Characterization, specifications & impurity impacts on compression, Liquefaction, transport & storage
- ❖ Open for new test campaigns, Tailored **advisory services**, Strategic **partnerships & joint projects**

post@tcmda.com