# **SUPPLEMENTAL FILE - 1**

# Limits of Quantitation (LOQ)

Figure S1-1 provides the distribution of the LOQ-values associated with samples marked as "non-detects" (ND) for all sample types. In general, the LOQ was <1 ppb. The average LOQ for ND-samples was 0.26 ppb, the geometric mean, 0.15 ppb.

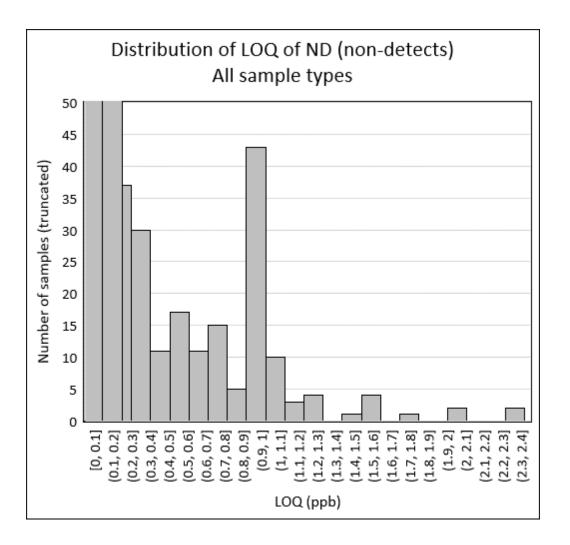
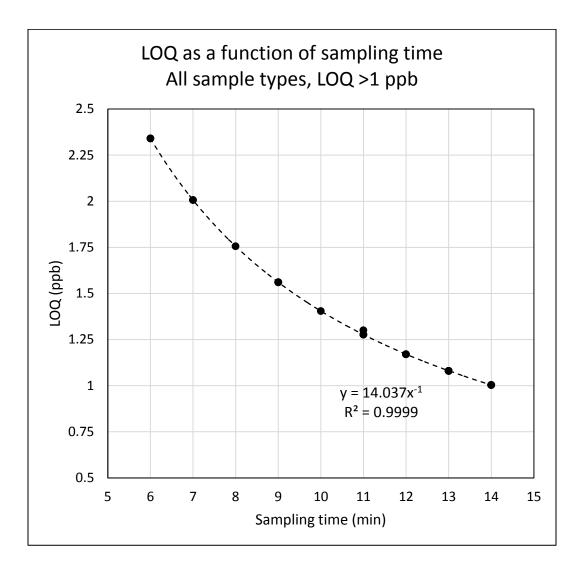


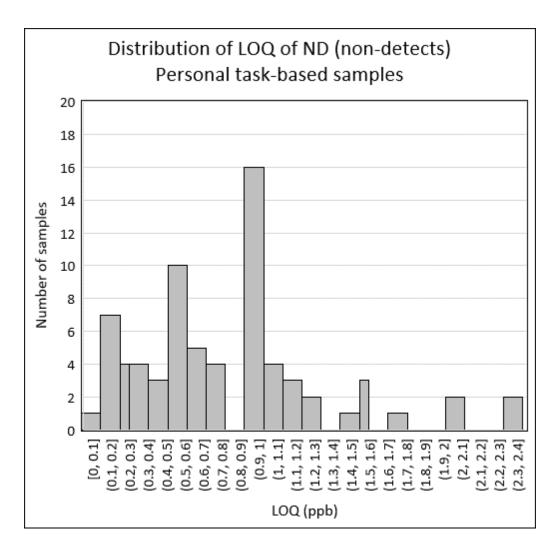
Figure S1-1: Histogram of limit of quantitation (LOQ) values for samples marked as "non-detects" (ND).

The LOQ only exceeded 1 ppb when the sample time was <15 min, as expected from the method used (Figure S1-2).



**Figure S1-2**: Relationship between sampling time and LOQ for samples marked as "non-detects" (ND).

Twenty-seven ND samples (all types) had a LOQ >1 ppb, 18 of which were personal task-based samples (Figure S1-3). The average LOQ for personal task-based ND-samples was 0.81 ppb, the geometric mean, 0.65 ppb.



**Figure S1-3**: Histogram of limit-of-quantitation (LOQ) values for personal task-based samples marked as "non-detects" (ND).

Since  $\frac{1}{2}$  LOQ was used for sample categorization, only the 4 samples with a LOQ >2 ppb could potentially have been "misclassified" between the categories "x≤1 ppb" and "1<x≤5 ppb", but not between higher concentrations. This is a minimal effect that does not affect the most important conclusions drawn from the analysis that was performed.

# **SUPPLEMENTAL FILE - 2**

#### **Flexible foam production process**

#### Slab stock (refer to Figure S2-1)

Slab foam is made by dispersing the chemical mixture over a plastic or paper-lined conveyer belt on which the foam is produced as the polymerization takes place. While foam machines vary, they share basic operating features. The mix head is located at the head of the line, often called the 'pourhead' or the 'bridge'. As the chemical mixture is dispersed onto the 'laydown' area, the foam begins to flow across the base of the tunnel, rising as it continues on the conveyor, filling the tunnel. The height of the foam blocks (also called buns) typically ranges from 3.5-4 feet. The tunnel is usually 5-8 feet in width and is semi-enclosed, with a few entry/exit points along the line to the cut off saw, where the finished foam block is cut into specified lengths and exits the tunnel. Exhaust ducts are typically installed in the top of the tunnel enclosure to capture vapors that are released during the foaming process. The length of foam blocks varies and can be as long as 200 feet (Cummings and Booth, 2002). Although much of the process is enclosed, several points of exposure are present; they include, but are not limited to: 1) the bridge/pourhead – the control panels and pourline operators are positioned at this location; 2) the ski/flat top operator area, which is usually approximately 5-15 feet down the line from the pourhead -- the worker observes and controls the rise of the top of the foam block; 3) the rewind area, where plastic film or paper is removed from the sides and top of foam blocks, and ; 4) the

saw areas, where workers observe the saw operation, mark (tag) the foam, and clean the saw blade. When the foam passes beyond the saw operation, it moves via conveyor and crane to a foam storage or rapid cure area for further curing and storage. Rapid cure is also referred to as 'cooling bed' in this report. It is known that during startups and shutdowns of a foam run, there is a significant potential for exposure to TDI. During a shift, there may be one startup with one type of foam, there may be a changeover where one foam grade is changed to another without having to stop the line, or there may be several start and stop cycles.

### Molded foam

Molded foams are made by pouring or injecting the chemicals into a mold, allowing the part to 'cure' (i.e. fill the mold with the foam that is formed as the polymerization reaction occurs), and then removing the part from the mold. Two variations of the molded foam process include hotcure and cold-cure molded foam. The hot-cure process involves automated injection of raw materials into a port of a closed mold on a carousel; the molds are then heated, and, upon final rotation on the carousel, the foam fills the mold and the mold is opened either automatically or manually. The part is then removed manually from the mold and moved to an area for final curing. The cold-cure process is similar to hot-cure, differing only in that the mold is not heated as the foam is curing (EUROPUR/EUROMOULDERS, 2019); the reaction is driven by the heat released by the exothermic polymerization process. For both processes, there is potential for exposure upon the opening of the mold and during removal of the article from the mold.

## Job roles and location descriptions

#### Slab stock

<u>Tank Farm Operator/Unloader</u>: includes TDI tanker/truck unloader, tank connector, railcar unloader. This person/position is responsible for a variety of tasks related to the transfer of TDI

products that will later be used production of foam; connecting and disconnecting lines and monitoring unloading activities for TDI are the primary tasks that could contribute to TDI exposure.

<u>Batch Maker/Chem Tech</u>: chemical operator, chemical compounder. This person ensures appropriate material is transferred from the tanks/day tanks, and monitors chemicals for the foam pour.

<u>Pourline Operator</u>: other common job titles for this job role category include bridge/ pourline/ pourhead/ foam line/ slabstock operators, helpers, supervisors, foam line assistant, tunnel operator, slabstock tech. The people in these positions are responsible for a variety of activities at the pourhead, including connecting/disconnecting the lines that control the flow of chemicals to the mix head, operating the machine, troubleshooting, startup/shutdown/changeover control for each foam pour.

<u>Ski Operator</u>: also called flat top operator. This person is positioned about 5 to 15 feet from the head, at either side of the tunnel and is responsible for controlling the flat top system. This system applies pressure to the top of the foam as it is formed, ensuring the top of the foam block is flat. The person must have a clear view of the foam in order to effectively perform this duty. Often the person opens the tunnel or sticks his/her head inside.

<u>Rewind Operator</u>: also called side paper operator. Plastic or paper is used on the bottom, sides and/or top of the foam as it's formed. The material is automatically wound off the foam and onto a 'rewind' on either side/top of the tunnel. The operator collects the paper off the rewind machine and disposes of it throughout the production run. The material has fresh and unreacted foam on it when it reaches this area. Often the rewind operator is positioned elsewhere along the line and is only at the rewind for short time periods.

<u>Saw Operator</u>: also called cutoff saw/chop saw operator, foam cutter, knife operator. The buns are automatically cut into specified lengths by a saw. The operator ensures that the blade is clean and working properly by visually observing and troubleshooting as needed.

<u>Bun Tagger</u>: also called tagger, stencil man. This person is positioned after the saw operator on the line and marks or tags each bun with appropriate foam grade or other information as it passes to the bun storage area.

<u>Crane Operator</u>: also includes warehouse helper, swingout conveyor operator, side shift, bun unloader, bun handler, conveyor operator. The person is typically located in the bun storage/warehouse area, and may be inside a crane 'cab'; other common activities include walking around throughout the area, positioning each fresh foam block with a crane into place for cooling.

<u>Cooling Bed Operator</u>: also called vacuum, VCO, table or quick cool table operator. Some slab stock foam facilities employ a cooling bed or chamber to reduce the risk of foam scorching or to achieve certain physical characteristics in the foam. This is achieved by drawing air through the foam to speed the process of cooling.

<u>Material Handler</u>: shuttle operator, tow motor/forklift operator. This person is typically handling smaller foam blocks, taking them from one area to another, such as moving to fabrication or shipping areas.

Note: while no specific position identifies a person inside the tunnel, there are often 1-3 workers from the positions listed above who enter the tunnel at startup to secure and form the end of the bun by holding a large flat object against the foam as it forms. These workers ride the conveyor and exit the tunnel as it approaches the first exit (2-5 minutes inside the tunnel). Respiratory protection is necessary for anyone inside the tunnel during a foam pour.

# Molded foam

<u>Mold Operator</u>: also called carousel operator, demold, repair/demold, trimmer. This person opens the mold and removes the part and trims any extra foam from the molded piece, cleans the mold and sprays a release agent into it as it closes, preparing it for the next injection of foam.

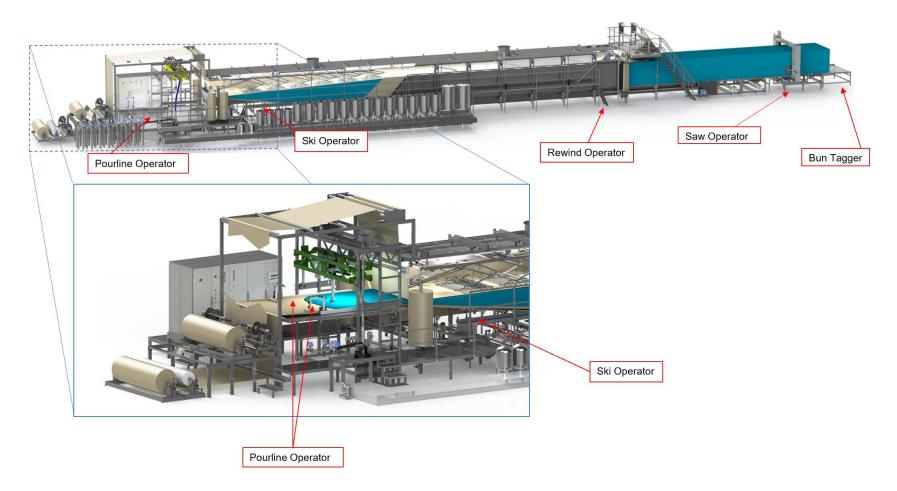
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**Figure S2-1. Location of the various slabstock manufacturing job roles along the slab foam manufacturing line.** Tank farm, batch maker, material handler, and crane operator are located beyond the foam line, hence not shown here. (*Illustrations of slab stock foam line used with kind permission from Laader Berg*)

# **SUPPLEMENTAL FILE – 3**

# Overview of TDI exposure information from other studies

 Table S3-1. Additional peer reviewed studies summarizing TDI air monitoring. References are also included in the main article.

Reference	Ν	Min	Max	Mean	Geometric	Median	Notes
	(count)	(ppb)	(ppb)	(ppb)	Mean	(ppb)	
					(ppb)		
Kääriä et al. (2001)	96	< 0.1	32	11			Molders in Plant 1
				1.7			Assistants in Plant 1
		< 0.1	5.7	2.2			Molders in Plant 2
Sennbro et al. (2004)	21	0.1	0.3	0.2		0.2	Molding plant 6
	7	0.4	1.1	0.7		0.7	Molding plant 7
	6	0.1	3.0	1.0		0.6	Continuous foaming plant 1
	4	3.1	5.2	4.1		4.1	Continuous foaming plant 2
Fairfax and Porter (2006)			89				Max value shown only
Austin (2007)	26	<1.0	2.4	0.8			(1) (2)
Broberg et al. (2008)				0.3/0.5		0.3/0.3	2,4-TDI/2,6-TDI
Tinnerberg and Mattsson (2008)	6	6.5	11				

Reference	N	Min	Max	Mean	Geometric	Median	Notes
	(count)	(ppb)	(ppb)	(ppb)	Mean	(ppb)	
					(ppb)		
Rühl and Kersting (2011)	43		1.1				Wood flooring glue application
Säkkinen et al. (2011)							(3)
Gui et al. (2014)			10				(4) (5)
Brzeznicki and Bonczarowska	6	1.0	1.8			1.4	
(2015)							
	20	< 0.1	8.2			0.6	
	6	0.3	1.8			0.7	
Swierczynska-Machura et al.	10	0.1	1.6	0.5	0.3		Foam head
(2015)							
	3	< 0.1	0.9	0.5	0.3		Cutting
	2	1.4	5.8	3.6	2.8		Maintenance
	5	< 0.1	8.2	3.7	1.3		Paper fold (rewind)
Jones et al. (2017)			0.9				(1)

Reference	Ν	Min	Max	Mean	Geometric	Median	Notes
	(count)	(ppb)	(ppb)	(ppb)	Mean	(ppb)	
					(ppb)		
Rother and Schlüter (2021)		0.1	8.9				Values from Chemical Safety
							Reports
	110	0.2	10	0.7			IFA – 90% range – foam
							production
	14	< 0.1	1.3				HSE – long-term
	13	0.2	6.3				HSE – short term

HSE: UK Health and Safety Executive; IFA: Institut für Arbeitsschutz der Deutschen gesetzlichen Unfallversicherung, N: number of samples.

(1): values reported were interpreted as being  $\mu$ gNCO/m<sup>3</sup>, not  $\mu$ gTDI/m<sup>3</sup>; (2): it would appear that 1 ppb was the detection limit, otherwise the mean could not be lower than the minimum; (3): values were reported per time unit, not in concentrations; (4): limited personal samples all non-detectable (for comments, see Spence and Plehiers, 2021); (5): area monitoring generally <5 ppb.

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