



Assessment of Collection, Handling, and Storage Requirements for Volatile Sulfur Samples

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Executive Summary

Complaints due to odours are a major issue for many industrial as well as agricultural facilities because the repeated release of unpleasant odours can constitute both a public nuisance and a possible regulatory violation. Amongst the most common odorous emissions, volatile sulfur compounds (VSCs) are the most malodorous, having very low odour threshold values, and in many cases can be the dominant odorants.

An effective odour management scheme requires a functional method of sampling/determining/measuring odorants that provides reliable and accurate data. This requirement is especially complicated in the case of VSCs due to the fact that they are unstable and their losses/degradation during sample storage and handling are poorly understood.

Laboratory and field-based experiments were conducted to assess the impact of storage conditions upon 10 VSCs (hydrogen sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, tert-butyl mercaptan, butyl mercaptan, ethyl methyl sulfide, dimethyl disulfide, diethyl disulfide, and dimethyl trisulfide) in order to deliver the following objectives:

- 1) Determine the impacts of factors such as storage time, sample bag materials (Tedlar, Mylar, and Nalophan), temperature, sample relative humidity, light exposure, and the presence of other volatile organic compounds upon the losses of VSC odorants.
- 2) Recommend handling and storage conditions that can be incorporated into industry practices to reduce the losses of VSCs and improve the quality of data used by the industry for design and decision making purposes.

The first component of the work consisted of controlled laboratory experiments to measure the change in relative recovery (or the relative reduction) of VSC samples during storage. The experimental matrix for this work was constructed by indexing all of the possible combinations of impacting factors to ensure a consistent and sufficiently large data set so that reliable sample storage/handling recommendations can be made.

Based upon the laboratory study, the following sample handling and storage conditions were recommended:

- 1) Storage time for VSC samples should not exceed 18 hours.
- 2) Storage temperature for VSC samples should not exceed 20°C.
- 3) Although the results did not indicate any negative impact of light exposure upon the losses of the VSCs, it is recommended that the samples should not be exposed to direct sunlight as sample temperature can increase due to a greenhouse effect.
- 4) In the case of extreme sample relative humidity, sample dilution can be implemented as a mitigation measure, but care must be taken to avoid sample losses.
- 5) With the 24 hour maximum storage time period recommended, Nalophan is the bag material of choice given its performance and its price.

Headspace air samples from two sewer sites in Sydney were collected, handled, stored, and tested using the recommended storage and handling conditions to determine potential losses of VSCs and odour concentrations that could be expected. In general, it was observed that after 24 hours of storage, relative recoveries for VSCs of the field samples were 74.7% – 106.9% for H₂S; 86.8% – 92.8% for MeSH; 91.5% – 94.9% for DMS; 111.7% – 129.4% for DMDS; and 95.0% – 107.8% for DMTS. In terms of the VOC content in the field samples, trichloromethane (16.6 µg/m³ – 188.6µg/m³) was most encountered compound. Other VOCs spotted in the field samples included: toluene (30.1 µg/m³ – 36.5 µg/m³); p-xylene (4.3 µg/m³ – 7.6 µg/m³); and 1,2,3-trimethyl benzene (14.3 µg/m³ – 57.8 µg/m³).

Note that care should be taken when interpreting the above field sample results as they were obtained for only a limited number of sites and conditions. These results might not be representative of all site conditions and sample compositions/matrix effects that could be experienced in sewer headspaces and at wastewater treatment plants.

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1.0 Overview

Odour complaints are a major issue for many waste management, industrial and agricultural facilities because the emission of unpleasant odours can cause both public nuisance and possible regulatory violation (Pandey and Kim, 2009b, Kleeberg et al., 2005). This issue is becoming increasingly important with the shrinkage of the buffer zones between those facilities and surrounding residential areas (Gostelow et al., 2001, Trabue et al., 2006).

In practice, hydrogen sulfide (H_2S) and other volatile organic compounds (VOCs) such as aromatic, aliphatic hydrocarbons; aldehyde; terpenes; ketones etc. are the main subjects of odour assessment. However, other odorants such as volatile sulfur compounds (VSCs) including methyl mercaptan, ethyl mercaptan, dimethyl sulfide, and dimethyl disulfide are also malodorous and can, in many cases, be the dominant odorants emitted due to their very low odour thresholds (Lestremau et al., 2004, Ras et al., 2008a, Ras et al., 2008b, Susaya et al., 2011). **Table 1** lists some of the most common VSCs and their odour threshold values.

Table 1 Odour Threshold Values (OTVs) of Some VSCs

Family	Compounds	CAS No.	Linear Formula	Odour Threshold Value ($\mu\text{g}/\text{m}^3$) ^{1,2}
Basic Sulfur Compound	Hydrogen Sulfide (gas)	7783-06-4	H_2S	0.21 – 270
Thiols	Methyl Mercaptan (gas)	74-93-1	CH_3SH	0.0003 – 38
	Ethyl Mercaptan	75-08-1	C_2H_5SH	0.046 – 21
	2-Methyl-2-Propanethiol	75-66-1	$(CH_3)_3CSH$	0.09 – 3.3
	1-Butanethiol	109-79-5	$CH_3(CH_2)_3SH$	1.5 – 3.0
	Dimethyl Sulfide	75-18-3	$(CH_3)_2S$	0.3 – 160
Sulfides	Ethyl Methyl Sulfide	624-89-5	$CH_3CH_2SCH_3$	62
	Dimethyl Disulfide	624-92-0	CH_3SSCH_3	1.1 – 78
	Diethyl Disulfide	110-81-6	$(C_2H_5)_2S_2$	0.3 – 23
	Dimethyl Trisulfide	3658-80-8	CH_3SSSCH_3	0.06 – 7.5
	Carbon Disulfide	75-15-0	CS_2	70 – 180

¹ van Gemert, L.J. (2003). *Odour Thresholds: Compilations of Odour Threshold Values in Air, Water and Other Media*. Oliemans Punter & Partners BV, The Netherlands.

² Note that there is a high level of variability in reported OTVs and as such they should only be considered as an order of magnitude guide to determine if a compound is likely to be of interest from an odour perspective.

In order to develop an effective odour management scheme, the first step is to have suitable methods of determining/measuring/quantifying odorants. This step is particularly difficult with regards to VSC samples due to (Kim et al., 2006, Pandey and Kim, 2009a, Wardencki, 1998):

- complex sample matrices;
- low concentrations; and
- wide variation of concentrations between compounds.

The most common low-cost practice is to use plastic bags such as Tedlar (preferred in the US) and Nalophan (preferred in Europe and Australia) as the sample container for odorous emission sampling. However, previous studies have indicated that during storage in plastic bags, VSC samples can undergo losses caused by sorption or leakage (Kim et al., 2012); photo/metal catalytic oxidation (Lau, 1989, Mochalski et al., 2009, Nielsen and Jonsson, 2002, Sulyok et al., 2001); and permeation through the bag film (Guillot and Beghi, 2008). Furthermore, there is a lack of standardized sampling protocols and a limited understanding of the degradation/transformation and losses of odorants during the sample handling, transportation, and storage components of the analysis chain.

Existing sample handling procedures are primarily rules of thumb regarding storage time (maximum 30 hours as in European Standard EN 13725:2003; and up to 6 hours as in German VDI 3880:2011). To date, several studies have assessed the stability of VSCs in a range of plastic sample bags (e.g. standard Tedlar bags, black/clear layered Tedlar bags, Nalophan bags) with a large discrepancy in the results (Lau, 1989, Nielsen and Jonsson, 2002, Sulyok et al., 2001). There has, however, not been any study with a comprehensive inspection of the matrix impact of storage conditions (storage time, bag materials, temperature, sample relative humidity, sample light exposure, the presence of VOCs) upon the losses of VSCs in odorous emission samples. The main objectives of this project, therefore, was to address this knowledge gap, providing a better understanding of the influence of sample storage conditions upon the degradation/transformation of the VSCs, along with science based guidance on the handling and storage of whole air samples containing VSCs.

2.0 Methodology

This project identified and focused on six key factors that were most likely to affect the degradation/transformation of odorants:

- storage time;
- temperature;
- sample relative humidity;
- exposure to light;
- sample bag materials (Tedlar, Mylar, and Nalophan); and
- the presence of VOCs.

The influence of the above mentioned factors upon the stability of VSCs were assessed by measuring the time-dependent change of the relative recovery of known amounts of VSCs in 3 bag materials under different combinations of storage temperature, light exposure, sample relative humidity, and VOC content. The results obtained were then assessed to estimate the level of impact each factor had upon the loss of the VSCs, which was then used to recommend handling and storage conditions for VSC samples.

Even under the recommended conditions, the transformations and losses of VSCs cannot be totally negated unless the samples are analysed immediately on site (which is impractical and not cost effective in most of the cases). Field samples were collected, handled, stored in accordance with the recommendations and analysed to assess potential magnitude of changes and the relevant uncertainty results that could be expected in field samples.

2.1 Bag Preparation

Three types of laboratory-made bags with a capacity of 5 litres were prepared (**Table 2**):

Table 2 Bag Materials

Material	Bag Size (cm x cm)	Film Thickness (µm)	Water Vapour Transmission Rate (g)(mil)/(24 hr)(100 in ²) [*]
Tedlar (Polyvinyl Fluoride)	40 x 30	50	3.24
Mylar (Biaxially-oriented Polyethylene Terephthalate)	35 x 35	25	~1.7
Nalophan (Polyethylene Terephthalate)	46 x 26	25	1.2

^{*} Adapted from Manufacturer Product Specifications

All bags were fitted with 1/4" stainless steel Swagelok fitting and heat sealed. After being made, the bags were filled with dry clean air, left for 24 hours to test for leakage, and then vacuumed before used.

2.2 Sample Preparation and Analytical Procedures

2.2.1 Sample Preparation

The work was conducted in a controlled laboratory setting using gas samples prepared with 10 VSCs (

Table 3). The 10 VSCs were chosen because they are commonly encountered in field samples and are readily available as stable standards.

Table 3 List of Sulfur Compounds

Family	Compounds - Abbreviation	In-Bag Sample Concentration ($\mu\text{g}/\text{m}^3$)
Basic Sulfur Compound	Hydrogen Sulfide (gas) – H ₂ S	98.1
Thiols	Methyl Mercaptan (gas) – MeSH	253.8
	Ethyl Mercaptan (liquid) – EtSH	157.3
	2-Methyl-2-Propanethiol (liquid)	150.0
	1-Butanethiol (liquid)	157.9
Sulfides	Dimethyl Sulfide (liquid) – DMS	158.6
	Ethyl Methyl Sulfide (liquid) – EMS	157.9
	Dimethyl Disulfide (liquid) – DMDS	196.1
	Diethyl Disulfide (liquid) – DEDS	186.2
	Dimethyl Trisulfide (liquid) – DMTS	225.4

Samples for stability tests were prepared by dynamic injection of 75 μL of 10 ppmv stock liquid standards as well the gas standards (27 mL of 10 ppmv H₂S; 50 mL of 5 ppmv methyl mercaptan) into the sample bags using a custom-made calibration solution loading apparatus (Figure 1). Dry clean air (generated by a laboratory air/nitrogen generator (Domnick Hunter, US) and filtered using a Big Supelpure HC Trap was supplied to the calibration solution loading apparatus at a flow rate of 400 mL/min for 10 minutes. All samples were prepared in duplicate.



Figure 1 Sample Preparation for Stability Tests

2.2.2 Experimental Matrix

To provide a comprehensive assessment of the impacts of storage conditions (apart from storage time and bag materials) upon the stability of the prepared sulfur samples, experiments were conducted at different combinations of certain designated levels of the key factors (temperature, sample relative humidity, light exposure, and VOC content). The specific conditions evaluated in this study are presented in **Table 4**.

Table 4 Designated Levels for Main Factors

Factors	Designated Levels
Temperature	5°C, 20°C, and 30°C
Sample Relative Humidity	0%, 40%, and 80%
Light Exposure	0%, 100% ¹
VOC content	0%, 100% ²

¹ 0% level indicates tests were conducted under unlit conditions, 100% indicates lit conditions with average light intensity within the environmental chamber of 4338 lux (measured by Testo 545 light meter).

² 0% indicates tests without VOC, 100% indicates a mixture of 17 VOCs (**Table 5**).

Temperature and light exposure were controlled by placing the sample bags inside the environmental chamber (Steridium, Australia) (**Figure 2**). Two other main factors (sample relative humidity and VOC content) were controlled by static injection of calculated amounts of water and mixture of VOCs (**Table 5**) into the bags during the sample preparation processes. From inside of the environmental chamber, the sample bags were connected to the analytical system via $\frac{1}{16}$ " PTFE (Polytetrafluoroethylene) tubes.

Table 5 List of VOCs used in tests

Compound	In-Bag Sample Concentration ($\mu\text{g}/\text{m}^3$)
Dichloromethane	1.3
Benzene	218.5
Toluene	216.3
2-ethyl-1-hexanol	208.3
(+)- α -pinene	214.5
m-xylene	217.0
p-xylene	215.3
o-xylene	219.8
Styrene	226.5
Decane	182.5
Hexane	164.8
(R)-(+)-limonene	210.5
1-butanol	202.5
Butyraldehyde	200.0
2-butanone	201.3
Butyric acid	241.0
Phenol	347.5



Figure 2 Environmental chamber

Based on **Table 4**, an experimental matrix was created by indexing all of the possible combinations of the levels of the factors, giving a total number of 36 tests. With samples being measured at specific time points during each test (0, 3, 6, 9, 12, 15, 18, 21, 24, 30, 36, 42, 48, 54, 60, and 66 hours – 1 initial reference point plus 15 points), each of the 10 compounds would give 576 data points (**measurements**) per bag material, which was a reasonably large number to give a reliable assessment result.

As there is currently no standard storage time recommended in the surveyed literature (e.g. maximum 30 hours as in European Standard EN 13725:2003; and up to 6 hours as in German VDI 3880:2011), a wider range of storage time was assessed (up to 66 hours). As preliminary tests demonstrated that compounds such as H₂S and some mercaptans could lose up to 60% within 66 hours (which would be considered an unacceptable level of loss), the assessment of longer storage periods would not provide additional value to the research.

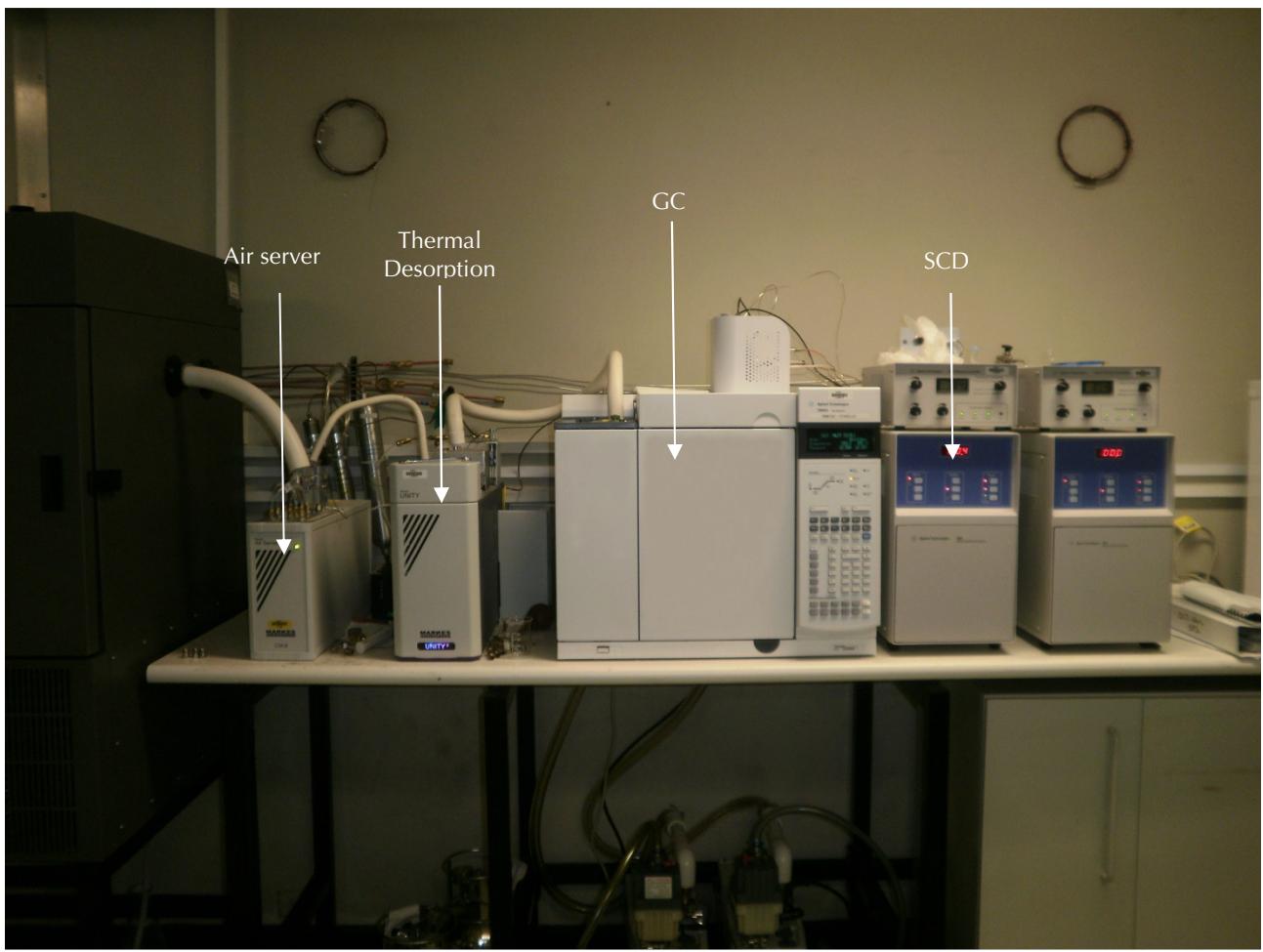


Figure 3 AS-TD-GC-SCD system

2.2.3 VSC Analysis

Samples were analysed at specific time-points (every 3 hours for the first 24 hours and every 6 hours afterward until 66 hours) automatically using an analytical system consisting of an Air Server (AS) equipped with a Nafion gas dryer (CIA8, Markes International, UK) – Thermal Desorber (TD) (Series 2, Markes International, UK) that was coupled to a Gas Chromatograph (GC) (7890A, Agilent Technologies, USA) with a Sulfur Chemiluminescence Detector (SCD 355, Agilent Technologies, USA) (air-server-TD-GC-SCD) (**Figure 3**).

The air server – thermal desorption system utilised a U-T6SUL-2S cold trap (Markes International, UK), flow path temperature 80°C; sampling for 5 minutes at the flow rate of 10 mL/min; outlet split ratio 9.3:1; low trap temperature -30°C; trap heating rate 40°C/sec; high trap temperature 300°C held for 5 minutes. VSCs were separated using a DB-VRX column (30m×0.25mm×1.4 µm) with a temperature program for the GC was set as: 37°C for 2.5 min; 15°C/min to 255°C; held for 3 minutes. The flow rate for carrier gas (high purity helium) was 1.25 mL/min.

The change in the relative recovery of the VSCs (calculated from the peak areas of the compounds) with storage time was used as an indication of storage losses.

2.3 Field Evaluation

Following the above laboratory-based experiments and the development of the recommended storage conditions for VSC samples, field samples from two sewer sites were collected, stored and analysed to assess the relative recovery of VSCs from real sewer headspace air samples.

A simplistic correlation between the losses/degradation of VSCs and the losses/changes of odour quality was evaluated by performing dynamic dilution olfactometry analyses of the samples at 0, 24, and 48 hours of storage. Additional analyses were also conducted for initial VOC content of the sewer headspace air samples to determine whether it was similar to the VOC content used as part of sample matrix in the laboratory-based tests. The VOC content was measured using Tenax TA sorbent tube sampling media, and analysed via Gas Chromatography – Mass Spectrometry (GC-MS). Some adjustments were made to accommodate the complexity of sampling/handling actual samples, including:

- 1) Sample bags for VSC analysis had the capacity of 20 L instead of 5 L and sample bags for dynamic dilution olfactometry test had the capacity of 40 L.
- 2) For one of the 20 L sample bag from each site, 10 L of the sample was pumped out and the bag was refilled with 10 L dry clean air and analysed for stability. This test, combined with the test for original actual field sample, would help reveal the impact of changing initial relative humidity and initial concentrations upon the RR reductions of VSCs.

3.0 Evaluation of the Impacts of Storage Factors

Figure 4 shows the loss trend of 10 VSCs for dry samples (not containing VOCs, unlit) stored at different temperatures in Tedlar bags. The higher the storage temperatures and the longer storage time, the greater the losses of H₂S and mercaptans (except tert-butyl mercaptan). Other sulfides and disulfides were very stable while dimethyl trisulfide experienced losses similar to the mercaptans. The changes of sample composition also increased with storage time due to the differences in the loss behaviour of the VSCs (denoted by the wider spread of loss trend curves at higher storage time) (**Figure 4**).

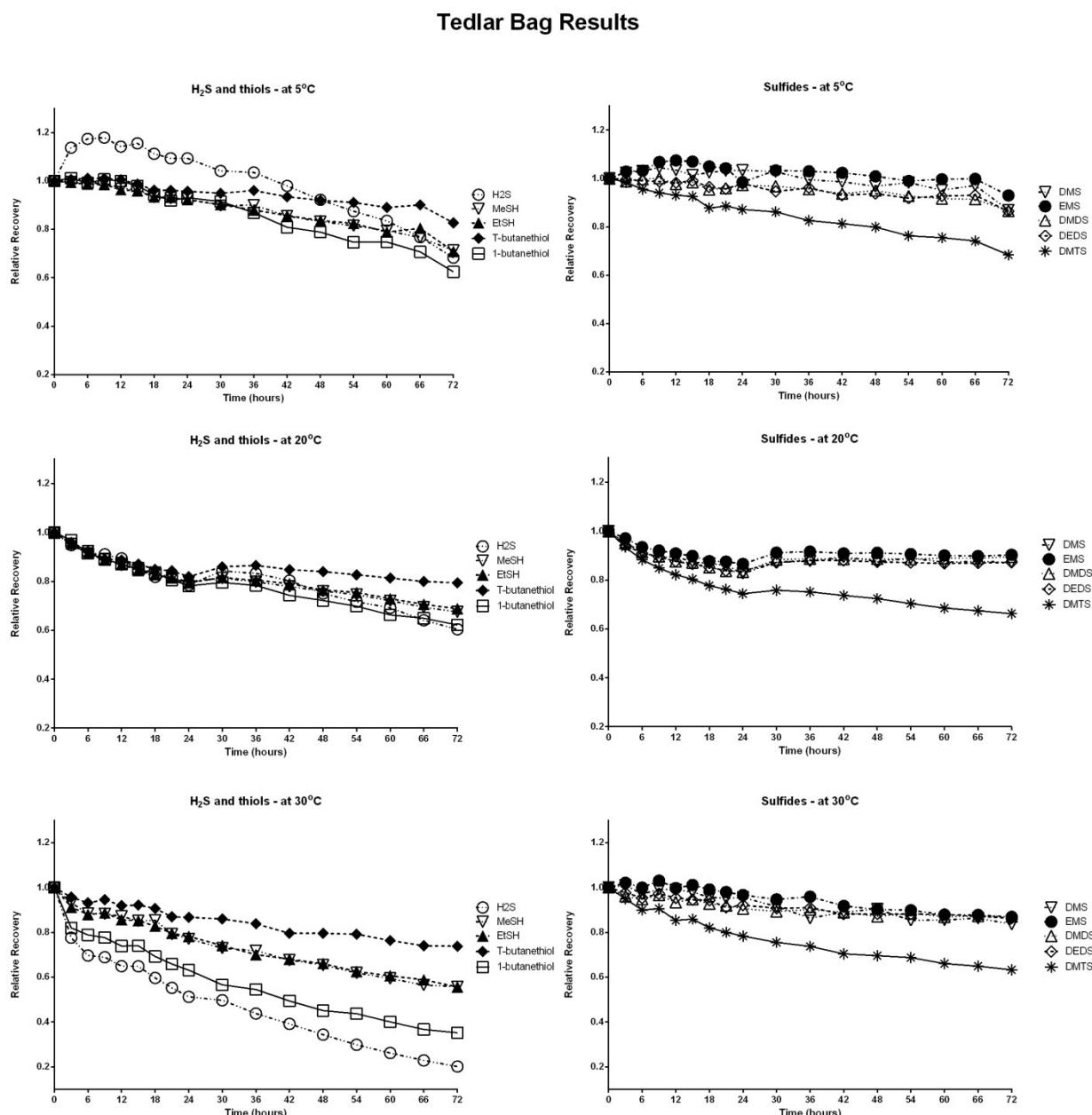


Figure 4 Stability tests for Tedlar bags at 5°C, 20°C, and 30°C, dry, unlit, no VOCs

The impact of storage conditions upon the stability of the VSCs were evaluated based on two key criteria:

- The **relative recovery (RR)** of the VSCs: the RR is used as an indicator of compound losses for the VSCs. The higher the RR, the less loss the VSCs suffer. The RR results of the VSCs was categorised into 4 main levels: high, medium, low, and very low (**Table 6**). The acceptable benchmark for RR of the VSCs was chosen to be $\geq 80\%$ (high and medium).
- The **standard deviation (STDEV)** of the RRs of all the VSCs at each **measurement**: the STDEV of the RRs for all of the VSCs was calculated and also categorised into levels (**Table 6**). As the STDEV indicates the variation (or dispersion) of the RRs around their average, it can be used as a gauge for the change of the composition (or the change in the relative percentages of the VSCs) of the samples during storage. Smaller values of STDEV imply smaller changes in the composition of the VSC mixture. The acceptable benchmark for STDEVs was set at $\leq 10\%$ (small and medium changes in the composition). For the definition of **measurement**, refer to **2.2.2**.

Table 6 Categorisation of the Results

Results	Categorized Levels	Abbreviation	RRs' Values
Relative Recovery (compound loss)	High Relative Recovery	H.	$\geq 90\%$
	Medium Relative Recovery	M.	$\geq 80\%$ and $< 90\%$
	Low Relative Recovery	L.	$\geq 70\%$ and $< 80\%$
	Very Low Relative Recovery	V.L.	$< 70\%$
Standard deviation (composition change)	Small Difference	S.Diff	$\leq 5\%$
	Medium Difference	M.Diff	$\leq 10\%$ and $> 5\%$
	High Difference	H.Diff	$> 10\%$

3.1 Performance of Bag Materials

Among the 10 VSCs studied, the most common compounds that appeared in SCORe field samples were H₂S, MeSH, EtSH, DMS, DMDS, and DMTS. Accordingly, this evaluation focused on the relative recoveries of those compounds.

In order to assess the performance of the 3 bag materials for each of the above 6 VSCs, categorized relative recovery (**Table 6**) for each of the compounds in each of the bag

materials was lumped across all of other factors (temperature, sample relative humidity, light exposure, and the presence of VOCs) for the whole experimental timeframe of 66 hours.

Mosaic plot illustrations of the relative recovery results for H₂S, MeSH, and EtSH are provided as **Figure 5**. In these plots the area of each rectangle (tile) is proportional to the counts/frequency of **measurements** falling into the categories defined vertically (e.g. Tedlar, Mylar, and Nalophan) and horizontally (H., M., L., and V.L.). In terms of the 80% RR benchmark (high and medium RRs), Tedlar bags performed better for H₂S (58.9% of the **measurements** within the $\geq 80\%$ RR benchmark compared to 42% and 39.1% for Mylar and Nalophan respectively), but on par with Mylar and Nalophan for MeSH and EtSH (63.7% relative to 62.2% and 66.3% for MeSH; and 67.8% relative to 71.1 and 72.8% for EtSH correspondingly).

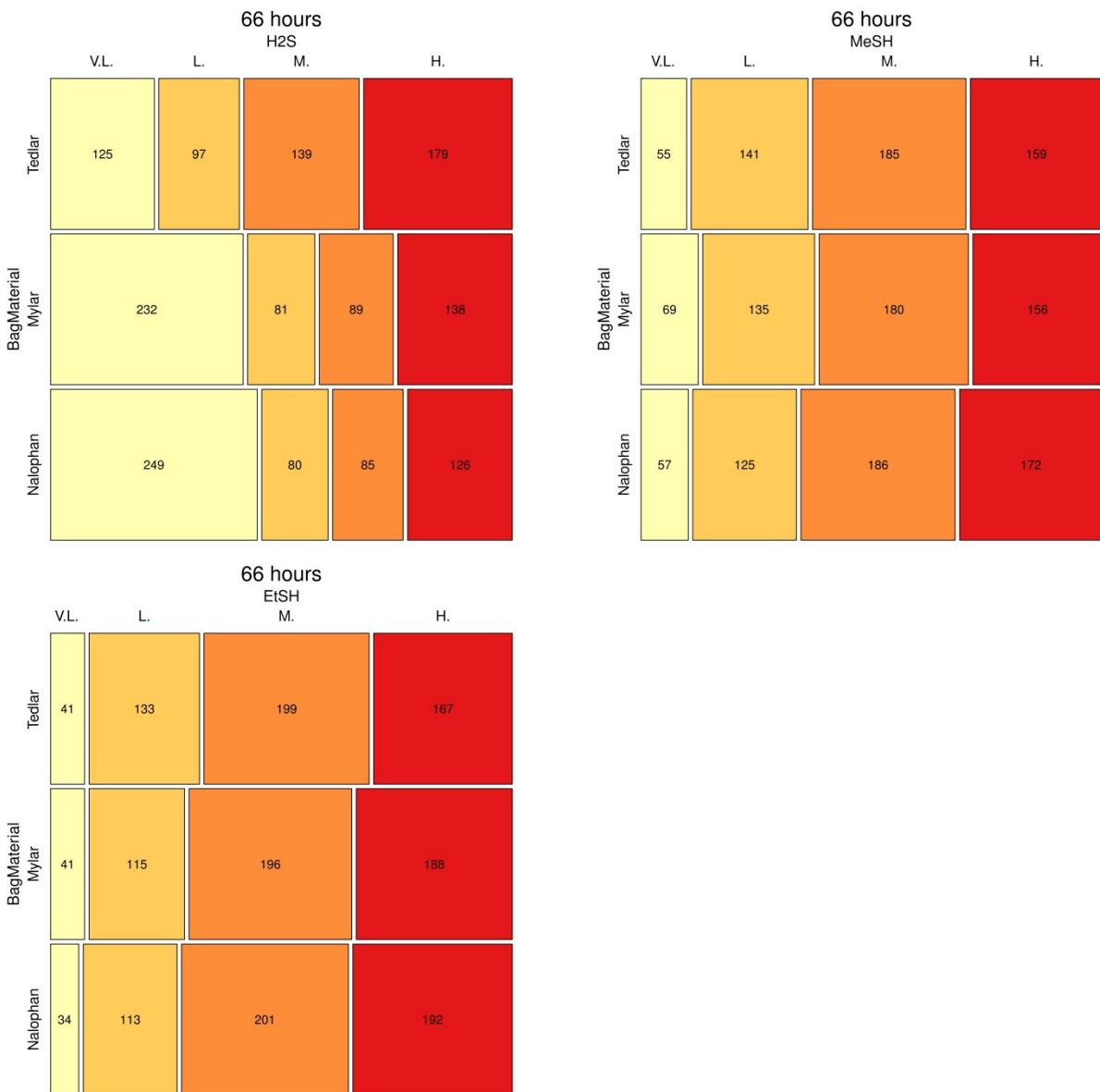


Figure 5 Mosaic Plots - Bag Performance - H₂S and Mercaptans – 66 hours

No significant difference was observed between performance of the 3 bag materials with respect to DMS, DMDS, and DMTS (**Figure 6**). DMS and DMDS were stable in all of the bag materials after 66 hours of storage while considerable losses (up to 31.9% after 24 hours) were observed for DMTS. Due to high level of stability across all conditions, DMS and DMDS stability was not evaluated for the other impact factors (temperature, sample relative humidity, and light exposure).

In terms of standard deviation, Tedlar bags were the best bag type for maintaining the stability of the VSC mixture composition (**Figure 6**).

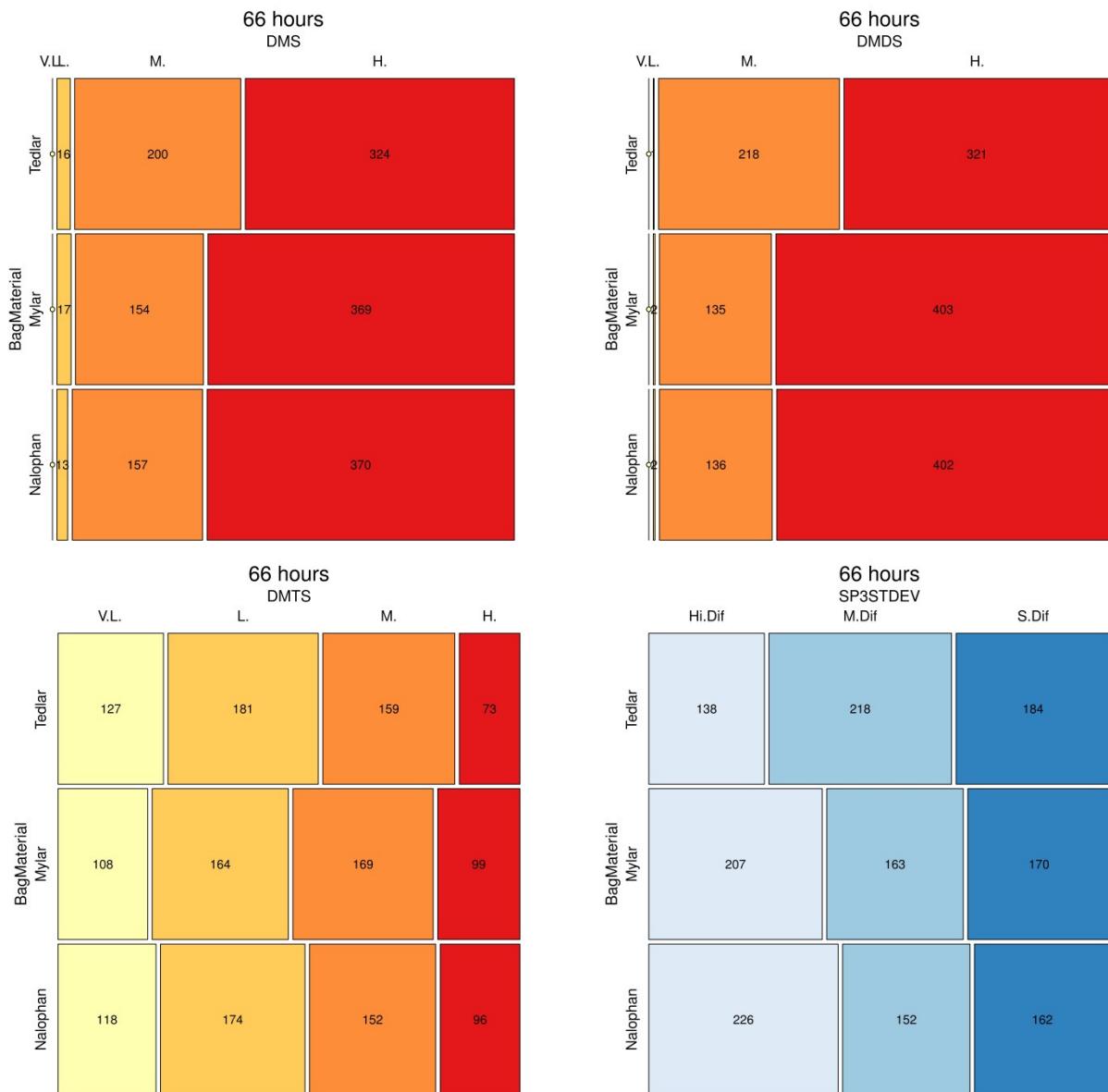


Figure 6 Mosaic plots - bag performance – sulfide, disulfide, and trisulfides – 66 hours

3.2 Impact of Temperature

Relative recovery results for 66 hours of storage indicated a significant temperature impact on the stability of the VSCs of interest. The number of those **measurements** with relative recoveries $\geq 80\%$ as well as with standard deviations (STDEV) $\leq 10\%$ decreased as temperature increased in all 3 bag materials, with the exception of H_2S in Nalophan bags and DMTS in Mylar and Nalophan bags (slight increase as temperature increased). This indicated that the decay of these VSCs was non-uniform and subject to the combined impact of both temperature and bag type.

The 66 hour lumped results were broken down into smaller segments/ranges of storage time (e.g. less than 18 hours, less than 24 hours, and less than 36 hours) to estimate the maximum possible storage time (

Table 7). As seen in

Table 7, the shorter the storage time and the lower the temperature, the higher the percentage of results with $\geq 80\%$ relative recovery was. It could also be seen that reasonable percentages of high and medium relative recovery could be obtained at a storage temperature of 20°C and storage times less than 24 hours, with the exemption of DMTS in Tedlar bags where only 68% of the **measurements** gave relative recoveries $\geq 80\%$. In that case, better results could be achieved by limiting the maximum storage time to 18 hours (**Figure 7**).

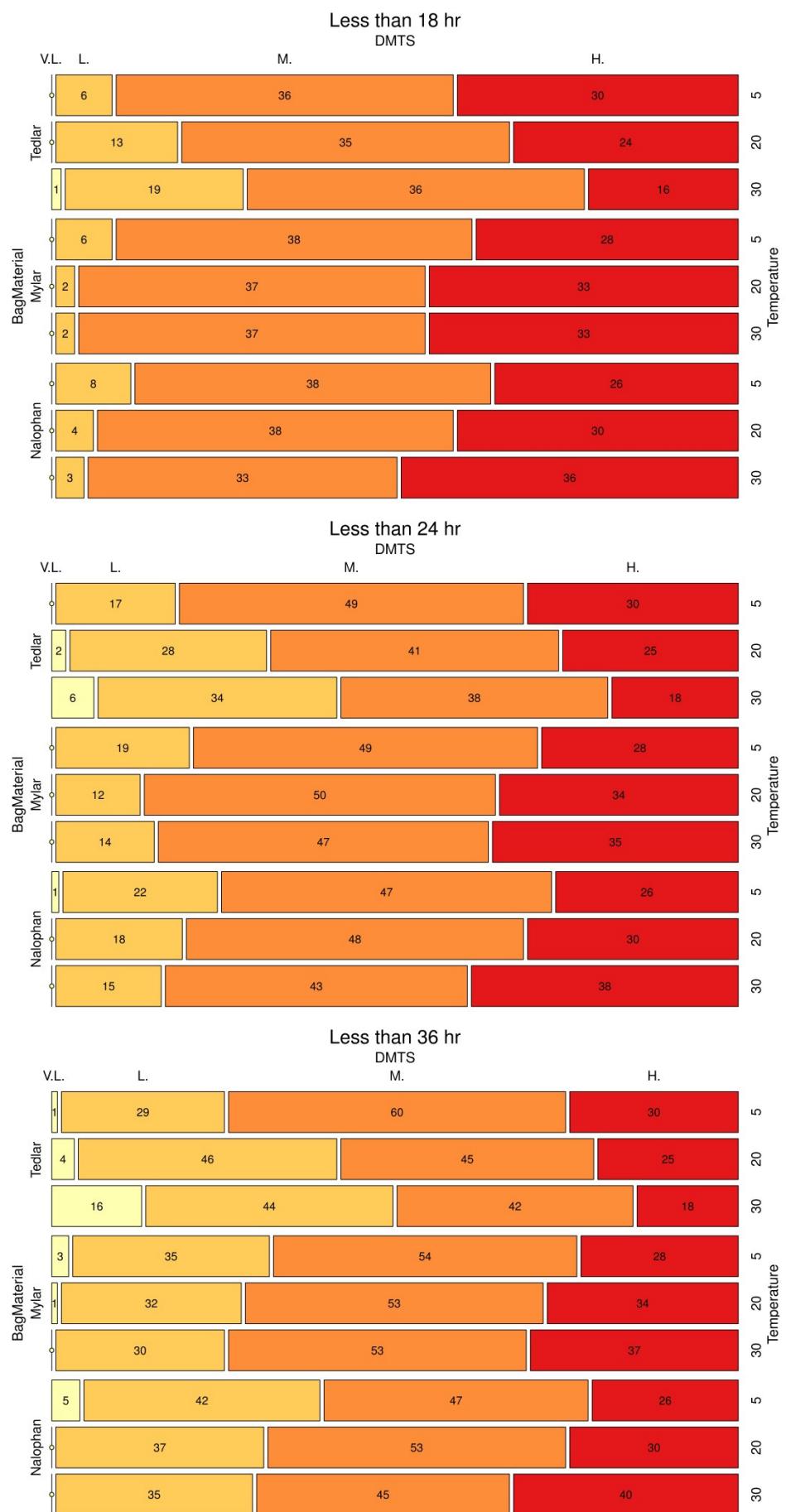


Figure 7 Temperature impacts – DMTS for maximum storage times of 18, 24, and 36 hours

Table 7 Temperature impacts for maximum storage times of 18, 24, and 36 hours

T (°C)	% measurements with high and medium RRs									
	Tedlar			Mylar			Nalophan			
	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs	
H₂S	5	88.9	85.4	84.2	91.7	81.3	68.3	80.6	68.8	56.7
	20	93.1	84.4	80.8	90.3	77.1	62.5	87.5	74.0	59.2
	30	83.3	78.1	75.0	80.6	68.8	58.3	83.3	72.9	60.0
MeSH	5	97.2	95.8	93.3	98.6	95.8	92.5	100.0	97.9	94.2
	20	100.0	93.8	88.3	100.0	94.8	89.2	100.0	95.8	90.0
	30	95.8	85.4	74.2	97.2	89.6	75.0	100.0	94.8	84.2
EtSH	5	100.0	97.9	95.0	100.0	99.0	96.7	100.0	99.0	97.5
	20	100.0	93.8	92.5	100.0	97.9	96.7	100.0	97.9	95.0
	30	94.4	84.4	74.2	97.2	92.7	80.0	100.0	95.8	86.7
DMTS	5	91.7	82.3	75.0	91.7	80.2	68.3	88.9	76.0	60.8
	20	81.9	68.8	58.3	97.2	87.5	72.5	94.4	81.3	69.2
	30	72.2	58.3	50.0	97.2	85.4	75.0	95.8	84.4	70.8

3.3 Impact of Relative Humidity

Three levels of sample relative humidity were evaluated (dry – 0%, 40%, and 80%). Samples with the relative humidity of 40% exhibited the best stability although some exceptions were observed, specifically H₂S in Nalophan bags, and DMTS in Mylar bags were most stable at 80% relative humidity. This suggests a combined impact of both relative humidity and bag material on the decay of the VSCs.

In terms of sample compositions, samples with higher relative humidity were more stable than dry samples. VSC sample compositions in Tedlar bags were most stable at 40% relative humidity while stability in Mylar and Nalophan bags were similar for 40% and 80% relative humidity.

Similar to the above section (3.2), with segmented results (less than 18 hours, less than 24 hours, and less than 36 hours), reasonable percentages ($\geq 80\%$) of **measurements** with high and medium **RRs** were obtained when the storage time was less than 18 hours (**Figure 8**). Mylar and Nalophan bags outperformed Tedlar for DMTS at all three levels of sample relative humidity, while Tedlar bags had better performance from the perspective of H₂S (**Table 8**).

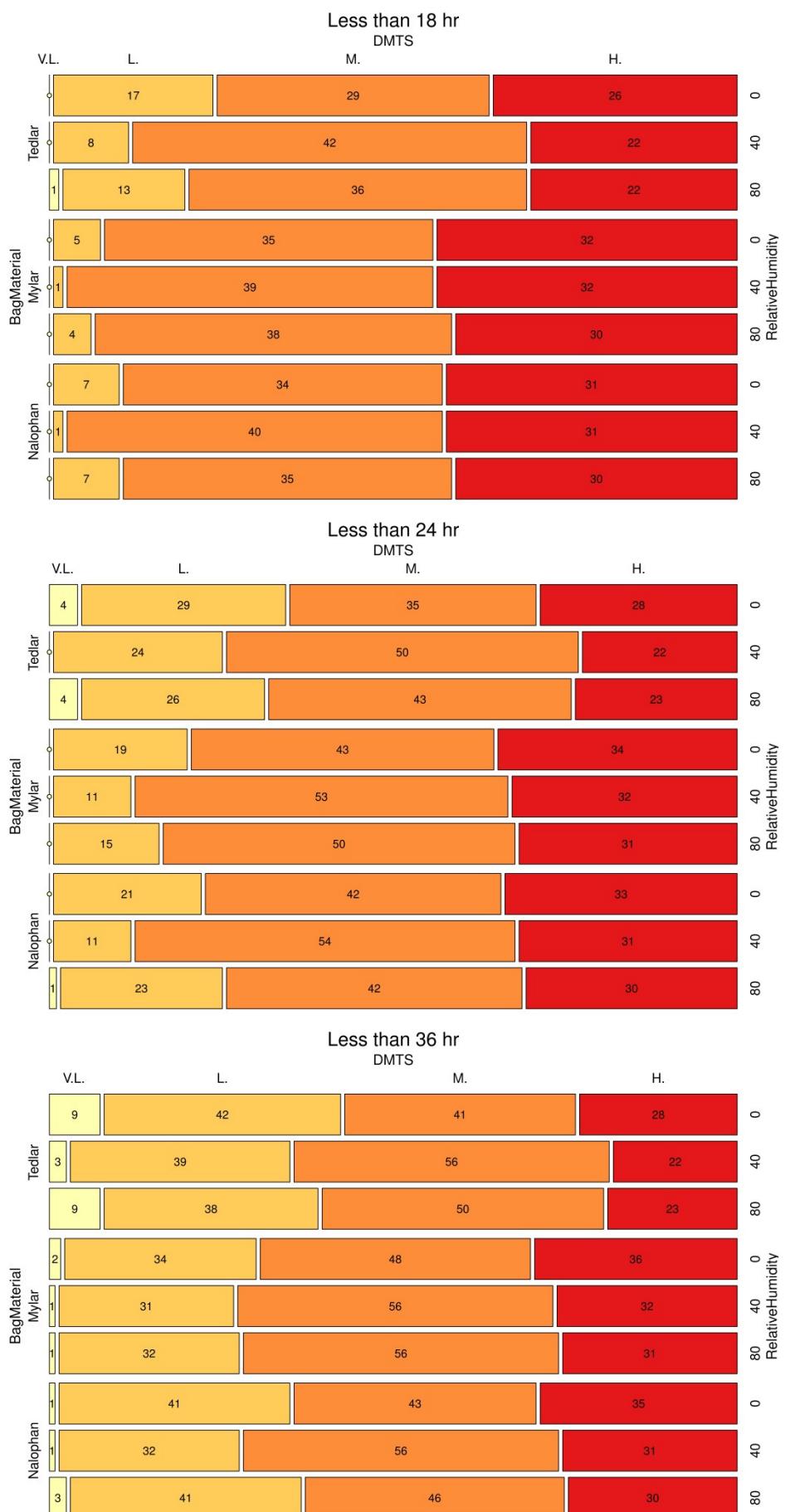


Figure 8 Relative humidity impacts – DMTS for maximum storage times of 18, 24, and 36 hours

Table 8 Relative humidity impacts for maximum storage times 18, 24, and 36 hours

RH (%)	% measurements with high and medium RRs								
	Tedlar			Mylar			Nalophan		
	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs
H₂S	0	79.2	70.8	65.8	80.6	69.8	57.5	72.2	60.4
	40	97.2	92.7	91.7	93.1	80.2	66.7	88.9	77.1
	80	88.9	84.4	82.5	88.9	77.1	65.0	90.3	78.1
MeSH	0	95.8	84.4	76.7	97.2	88.5	81.7	100.0	90.6
	40	100.0	97.9	94.2	100.0	99.0	91.7	100.0	100.0
	80	97.2	92.7	85.0	98.6	92.7	83.3	100.0	97.9
EtSH	0	97.2	84.4	80.0	100.0	93.8	87.5	100.0	93.8
	40	100.0	97.9	95.0	100.0	100.0	95.8	100.0	100.0
	80	97.2	93.8	86.7	97.2	95.8	90.0	100.0	99.0
DMTS	0	76.4	65.6	57.5	93.1	80.2	70.0	90.3	78.1
	40	88.9	75.0	65.0	98.6	88.5	73.3	98.6	88.5
	80	80.6	68.8	60.8	94.4	84.4	72.5	90.3	75.0

3.4 Impact of Light Exposure

There was no conclusive evidence whether VSC samples stored in darkness were more stable than samples stored in light. However, with regard to sample composition, storage in darkness resulted in consistently better results (less change in compositions) than exposure to light during storage (less spreading of the loss trend curves).

With regards to bag performance, Tedlar bag gave better stability result for H₂S but its advantage was not clear for the other compounds.

Once again, the smaller time segments of light exposure impact results indicated reasonable percentage of **measurements** with relative recoveries $\geq 80\%$ could be achieved for the storage times less than 18 hours (**Table 9**), especially for DMTS (**Figure 9**).

Table 9 Light exposure impacts for maximum storage times 18, 24, and 36 hours

Light (%)	% measurements with high and medium RRs								
	Tedlar			Mylar			Nalophan		
	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs
H₂S	0	84.3	77.1	73.9	85.2	75.7	65.0	82.4	71.5
	100	92.6	88.2	86.1	89.8	75.7	61.1	85.2	72.2
MeSH	0	97.2	89.6	82.8	98.1	92.4	85.0	100.0	94.4
	100	98.1	93.8	87.8	99.1	94.4	86.1	100.0	97.9
EtSH	0	99.1	91.7	85.6	100.0	96.5	90.0	100.0	96.5
	100	97.2	92.4	88.9	98.1	96.5	92.2	100.0	98.6
DMTS	0	86.1	75.0	67.2	96.3	88.9	77.8	82.6	68.3
	100	77.8	64.6	55.0	94.4	79.9	66.1	78.5	65.6

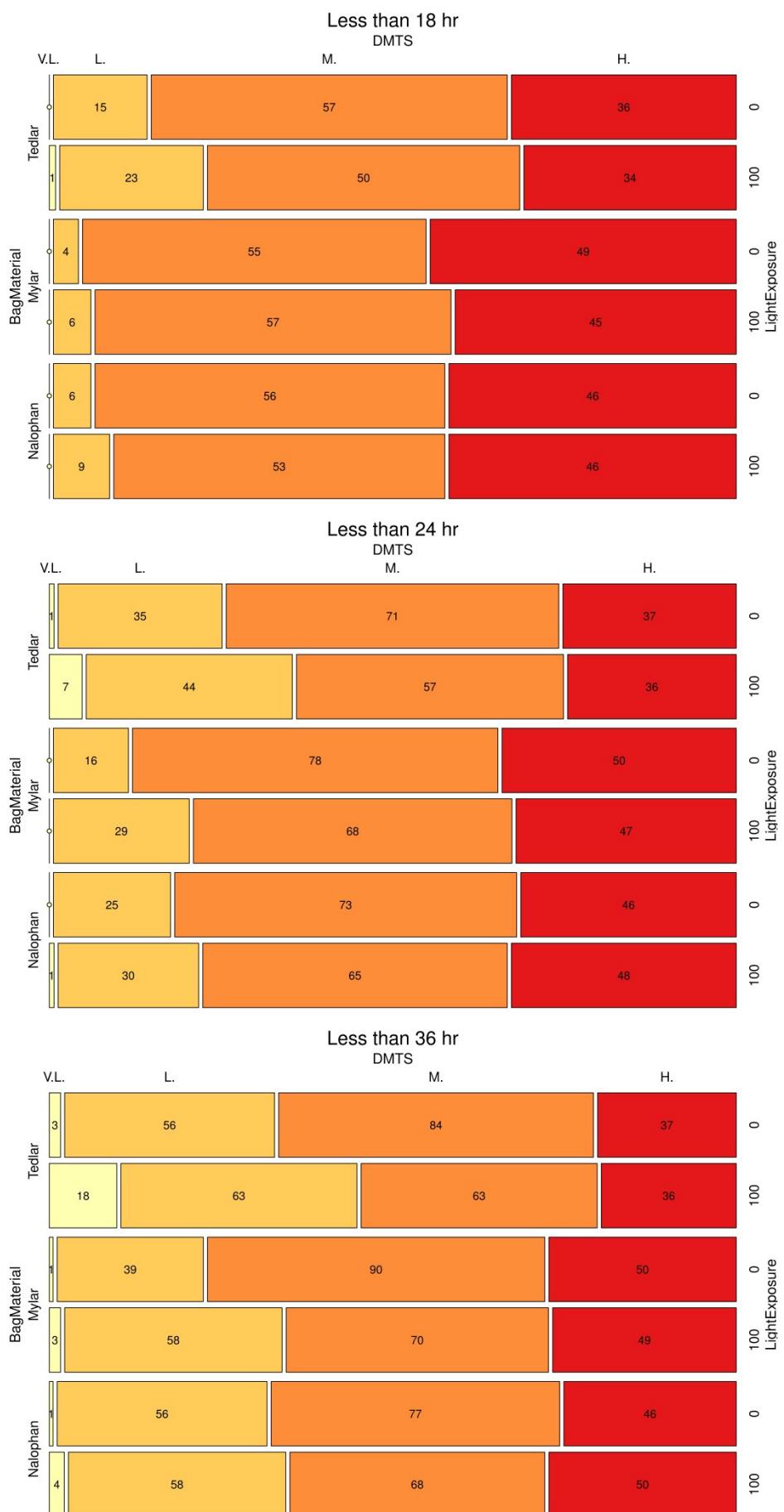


Figure 9 Light exposure impacts – DMTS at less than 18 hrs, 24 hs and 36 hrs

3.5 Impact of VOC presence

66-hour storage data for the presence of VOCs showed consistent decline in the number of results with high and medium relative recoveries for all of the compounds in all 3 bag materials. This indicated that the presence of VOCs had negative impact on the stability of the VSCs. However, VOC in sample bags appeared to help curtail the spreading of the loss trend curves of the 10 VSCs, and had a positive impact on the samples in terms of composition stability (less change in percent composition).

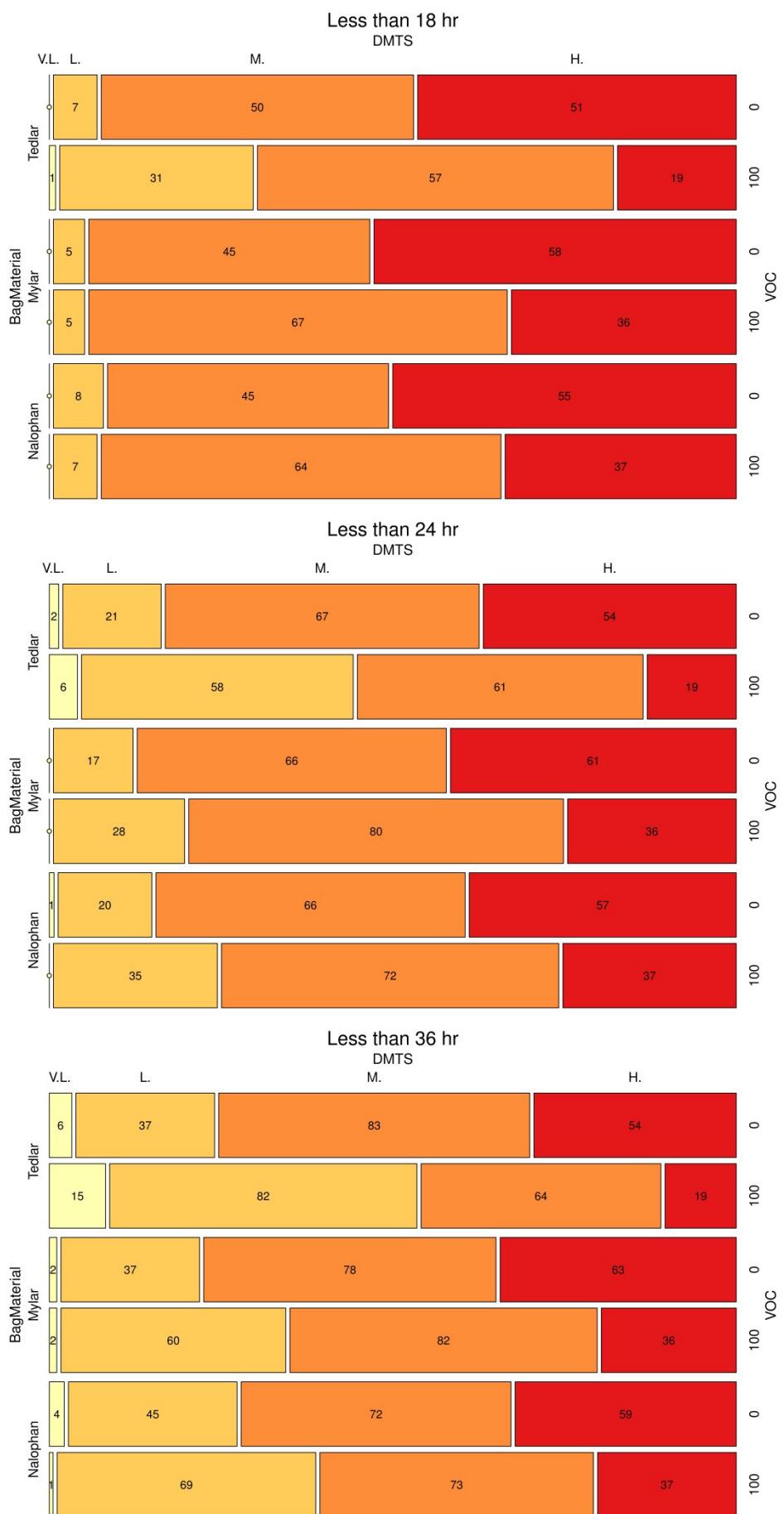


Figure 10 VOC presence impacts - DMTS at less than 18 hrs, 24 hs and 36 hrs

With regards to bag performance, in the presence of VOCs, H₂S was most stable in Tedlar bags while other compounds were more stable in Mylar and Nalophan bags.

Table 10 VOC impacts for maximum storage times 18, 24, and 36 hours

VOC (%)	% measurements with high and medium RRs								
	Tedlar			Mylar			Nalophan		
	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs	18 hrs	24 hrs	36 hrs
H₂S	0	94.4	93.1	92.2	93.5	84.7	70.6	89.8	81.9
	100	82.4	72.2	67.8	81.5	66.7	55.6	77.8	61.8
MeSH	0	100.0	96.5	93.3	99.1	95.8	88.9	100.0	97.9
	100	95.4	86.8	77.2	98.1	91.0	82.2	100.0	94.4
EtSH	0	100.0	96.5	93.3	98.1	96.5	92.2	100.0	97.9
	100	96.3	87.5	81.1	100.0	96.5	90.0	100.0	91.1
DMTS	0	93.5	84.0	76.1	95.4	88.2	78.3	92.6	85.4
	100	70.4	55.6	46.1	95.4	80.6	65.6	93.5	75.7

Similar to the results for other impact factors, acceptable percentages of the **measurements** with relative recoveries $\geq 80\%$ could also be accomplished for less than 24 hours of storage (**Table 10**). However, if the sample matrix contains VOCs, which is the case for sample collection from sewers and wastewater treatment plants, a maximum storage time of 18 hours is recommended.

3.6 Impact verification - field sample testing results

Tests were conducted for sewer headspace air samples collected from two SCORe project monitoring sites including: two tests for site AC1 (test AC1-1 and test AC1-2); and 1 test for site S1 (test S1). The relative recovery results after 18 and 24 hours of sample storage are shown in **Table 11**.

Table 11 Field sample relative recovery results

Site/Test	Relative Recovery (%)									
	H ₂ S		MeSH		DMS		DMDS		DMTS	
	18 hrs	24 hrs	18 hrs	24 hrs	18 hrs	24 hrs	18 hrs	24 hrs	18 hrs	24 hrs
AC1 - 1	-	106.9	-	86.8	-	91.5	-	129.4	-	95.0
AC1 - 2	102.7	103.1	90.2	92.8	90.5	94.9	113.0	111.7	105.4	107.8
S1	74.5	74.7	86.7	87.5	-	-	-	-	-	-

In **Table 11**, it can be seen that most of the VSCs detected in field samples had relative recoveries of more than 80% within the 24 hour timeframe. The only exception was the results of H₂S from site S1 with the relative recovery of 74.5% and 74.7% after 18 and 24 hours of storage respectively.

Relative recoveries greater than 100% were observed for DMS, DMTS, and DMDS for tests AC1-1 and AC1-2. The source of these apparent increases of the relative recovery of DMS and DMTS were not clear, but the increase in the relative recovery of DMDS was probably because of the dimerisation of MeSH. Nevertheless, inspection of the initial percent composition of the VSCs in AC1-1 (40% H₂S, 50.9% MeSH, 3.6% DMS, 3.2% DMDS, 2.3% DMTS) and in AC1-2 (41.8% H₂S, 49.2% MeSH, 4.1% DMS, 2.7% DMDS, 2.1% DMTS) indicates that the absolute increase in concentrations of the VSCs were relatively small (**Table 11**).

Initial VOC concentrations in the field samples are presented in **Table 12**. These results demonstrate the complexity of field samples, most of the detected and quantifiable VOCs were not part of the VOC matrix used in the laboratory based experiments. Even for the same sampling location, samples taken at different time provided significantly different results (test AC1-1 and AC1-2, **Table 12**).

Table 12 Initial VOC contents for field samples

Tests	Quantifiable VOCs (µg/m ³)	Other detected VOCs
AC1-1	Trichloromethane (45.6); toluene (36.5); p-xylene (5.1); 1,23-trimethyl-bezene (15.8)	1,3-dimethyl benzene
AC1-2	Trichloromethane (188.6); toluene (35.3); p-xylene (7.6); 1,23-trimethyl-bezene (57.8); 1-methyl-2-(1-methylethyl)-benzene (56.2); 1,2,3,5-tetramethyl-benzene (62.3); 1,2,3,4-tetramethyl-benzene (38.9); D-limonene (36.1); tetrachloroethylene (21,5); trichloroethylene (12.1)	camphene; 1,2-dichloro-benzene; 1-methyl-4-(1-methylethylidene)-cyclohexene;
S1	Trichloromethane (20.1); tetrachloroethylene(27.3)	

Odour concentrations were measured by dynamic dilution olfactometry at 0, 24, and 48 hours in parallel with the chemical speciation in tests AC1-1 and S1. Relative recovery results (relative to the odour concentration at time 0) are presented in **Table 13**.

Table 13 Odorant relative recovery vs odour concentration recovery

Test	Time	Odorant relative recovery (%)	Odour concentration recovery (%)
AC1-1	24	H ₂ S (106.9%); MeSH (86.8%); DMS (91.5%); DMDS (129.4%); DMTS (95.0%)	94.7%
	48	H ₂ S (86.0%); MeSH (78.5%); DMS (87.7%); DMDS (141.4%); DMTS (109.8%)	86.8
S1	24	H ₂ S (67.3%); MeSH (82.3%)	99.4
	48	H ₂ S (59.9%); MeSH (75.8%)	73.7

As seen in **Table 13**, there is no clear correlation between the loss of VSCs and reduction in measured odour concentration for test AC1-1. However, the results for test S1 did suggest greater dependence of odour concentration on the amount of MeSH in comparison with the amount of H₂S. In addition, both tests indicated very little losses of odour concentrations after 24 hours of storage, supporting the current practice of analysing odour concentrations samples within 24 hours.

4.0 Closure

Laboratory controlled stability tests of VSCs were conducted to provide science based guidance to industry on the handling and storage of whole air samples containing VSCs.

The results indicated that, in terms of bag performance, Tedlar was the most robust material as it had better durability and provided better stability for H₂S and similar stability for other VSCs in comparison with the other two materials. Depending on the application, Nalophan or Mylar could be used as a cheaper alternative to Tedlar. However, care must be taken while handling these two materials since they tended to crumple and form small cracks that caused leakage.

With respect to the impact of temperature, the lower the storage temperatures were, the better the stability of the compounds. Based on the results, acceptable sample stability can be obtained by storing the samples at an ambient temperature of 20°C. Further cooling provides small benefit in terms of VSC stability but increases the possibility of condensation that, in turn, could create the losses of H₂S due to absorption.

Although there was not clear evidence of any negative impact of lighting on samples, it is recommended that the VSC sample should be kept unlit (if possible), as the lighting intensity studied was rather low (~ 4300 lux – ranged between overcast day/typical TV studio lighting to full daylight without direct exposure to sunlight) in comparison with the real exterior daylight intensity in Australia. More importantly, the exposure to direct sunlight will lead to a greenhouse effect and heat up the sample inside the bag, increasing sample loss due to high temperature.

Experimental results indicated that VSC samples were most stable at medium relative humidity (40%) without the presence of VOCs. However, controlling the sample relative humidity and VOC content is not generally practical and instead we need to be aware of the potential impacts of these factors as the underlying results.

In terms of sample storage time, the results suggested that the sample should not be stored for more than 18 hours to maintain an acceptable level of stability for all of the 10 VSCs. However, given such a small window of time, the implementation of this storage time is

often not practical, as it imposes considerable strain on scheduling the process of remote VSC sampling, which includes taking samples, dispatching the samples to a courier, transporting the samples to the laboratory, accepting the sample delivery, and preparing the samples for analyses. If the storage time is extended from 18 to 24 hours, slightly higher losses were observed for DMTS while other 9 VSCs still retained good stability. For that reason, a maximum storage time of 24 hours is recommended considering the trade-offs between practicalities and the stability of the VSCs.

For the purpose of verification, field samples collected and stored under the above recommended conditions were tested. The obtained results signified that relative recovery of more than 80% for all of the VSCs can be achieved by storing the samples for less than 18 – 24 hours. The only exception is H₂S with low initial concentration, which could lose 25.5% after 24 hours. However, even in that case more than 90% recovery of odour concentration can still be obtained.

Based on the above assessments/analyses of the results, it is recommended that:

- 1) **The storage for the VSC sample should not exceed a maximum time of 24 hours**, at which a reasonably high number of the results had acceptable relative recoveries ($\geq 80\%$) and good composition stability (standard deviations of relative recoveries $\leq 10\%$).
- 2) For samples with high relative humidity (e.g. saturated samples), mitigation measures such as diluting the sample with dry clean air are recommended to reduce the relative humidity to the medium level (~40%).
- 3) **Storage temperature should not exceed 20°C.**
- 4) Although Tedlar is the robust material, within the recommended 24 hour storage timeframe, **Nalophan is the material of choice**, given its acceptable performance and lower cost.

Appendix A Temperature Impact for H₂S, MeSH, EtSH, and STDEV

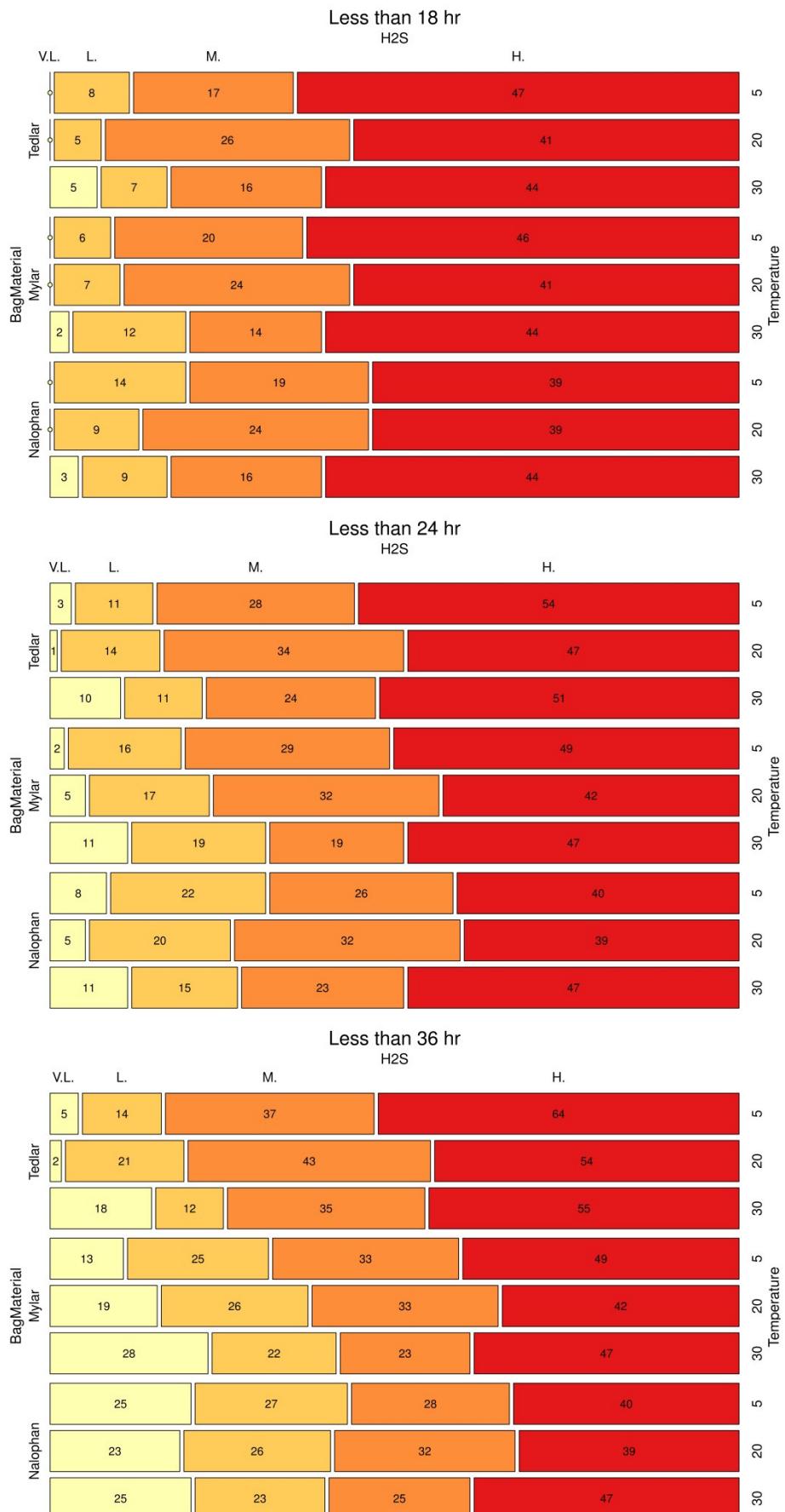


Figure 11 Temperature impacts - H₂S at less than 18 hrs, 24 hs and 36 hrs

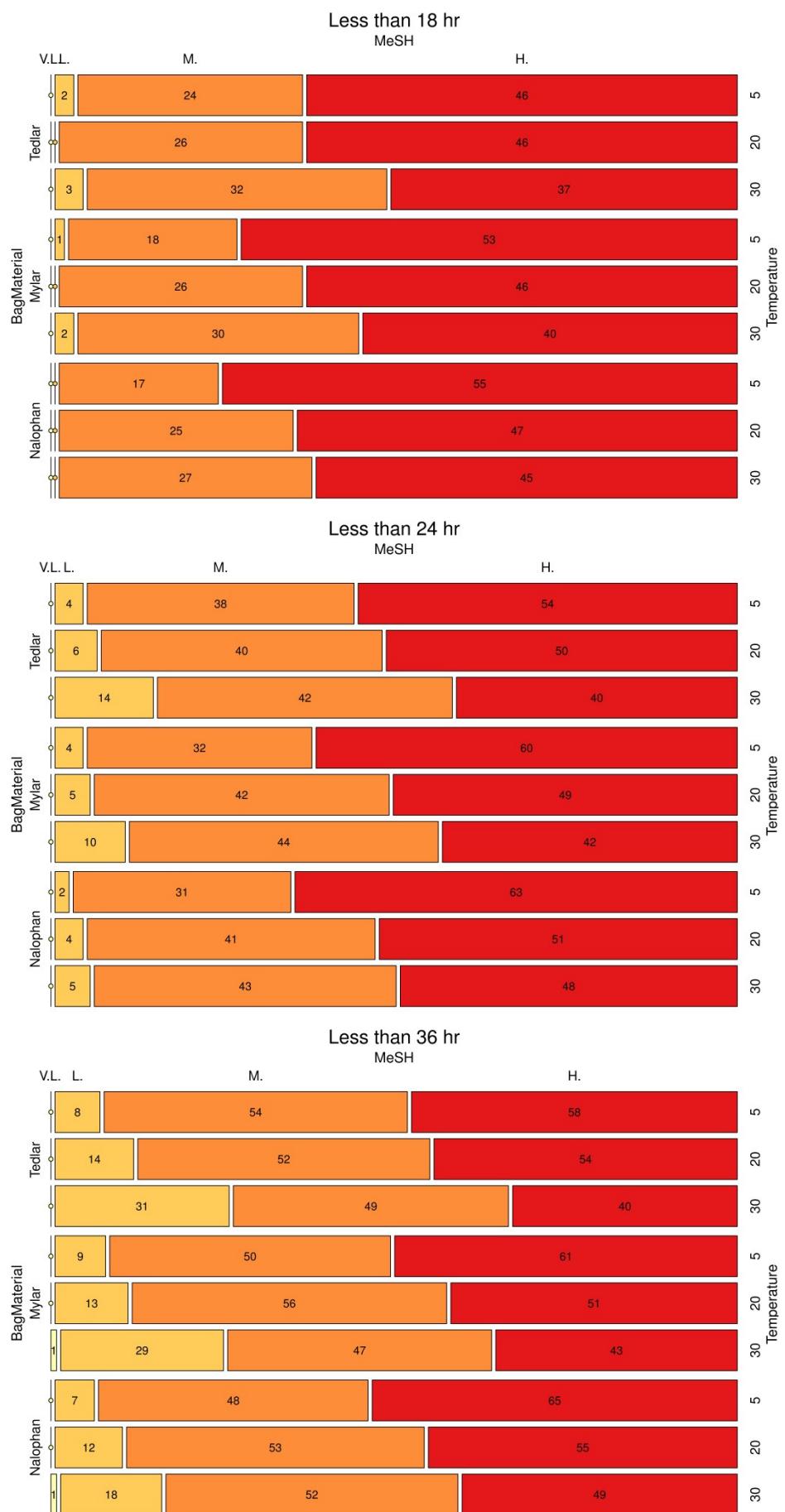


Figure 12 Temperature impacts - MeSH at less than 18 hrs, 24 hs and 36 hrs

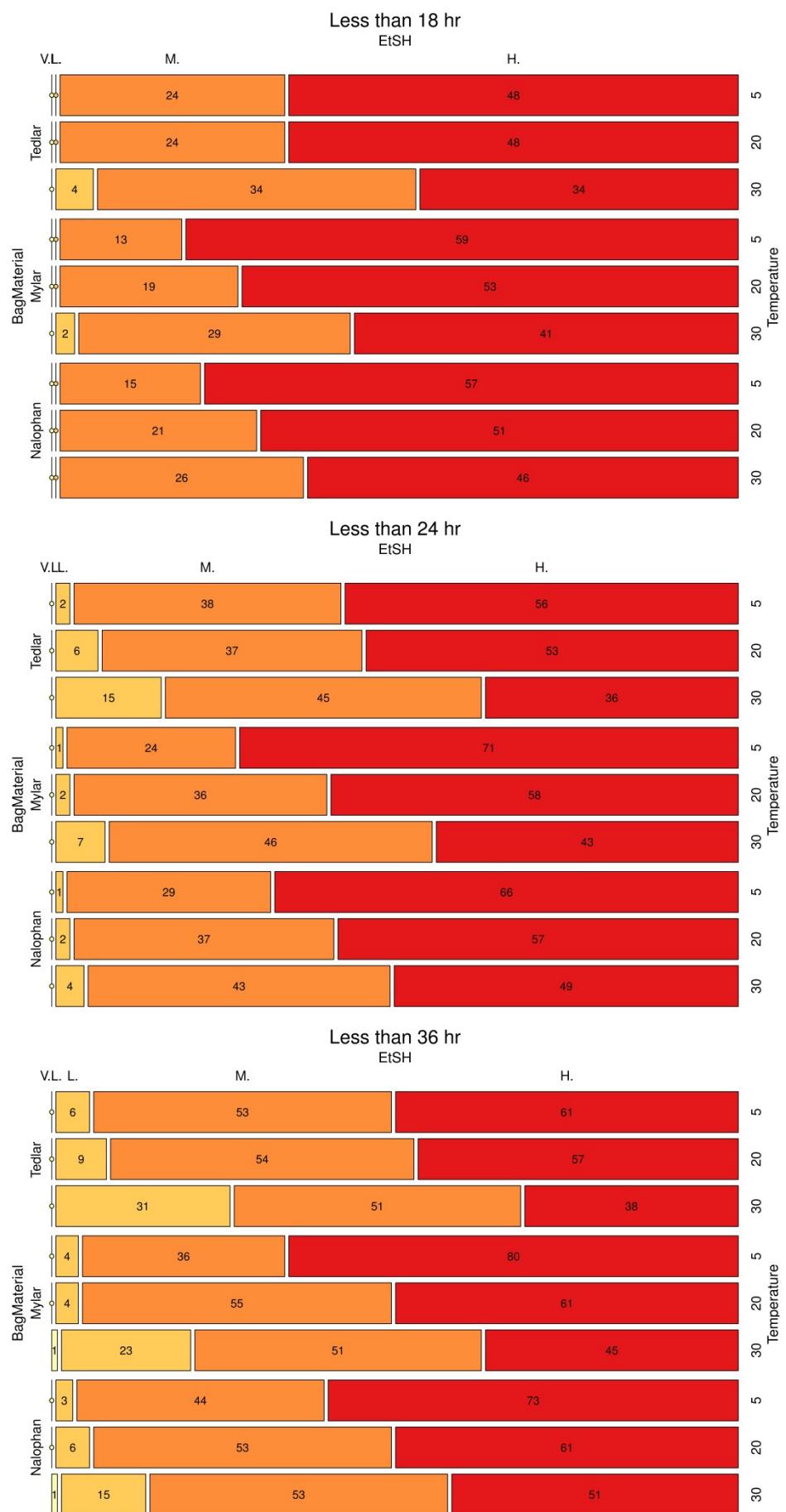


Figure 13 Temperature impacts - EtSH at less than 18 hrs, 24 hs and 36 hrs

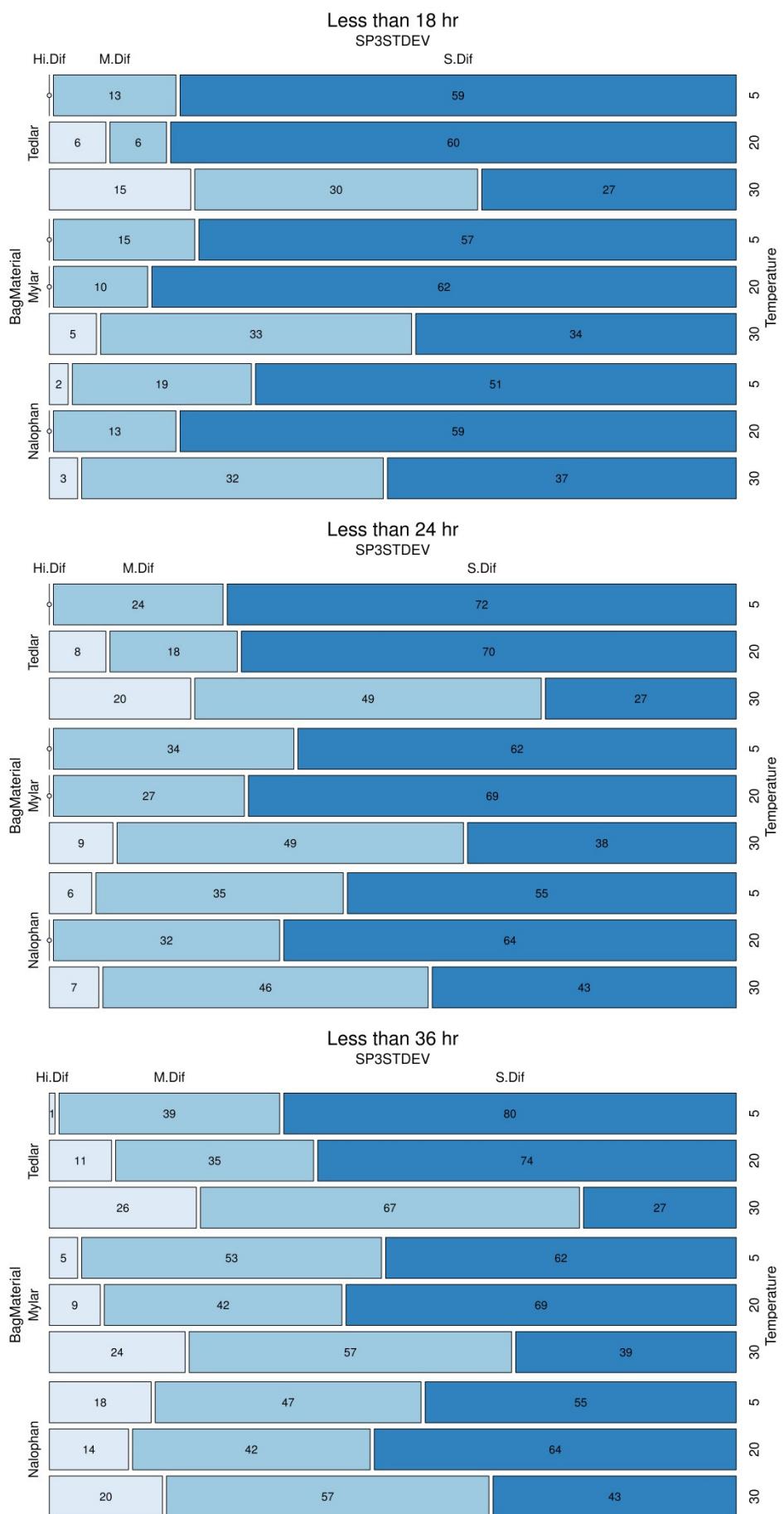


Figure 14 Temperature impacts - STDEV at less than 18 hrs, 24 hs and 36 hrs

Appendix B - RH Impact for H₂S, MeSH, EtSH, and STDEV

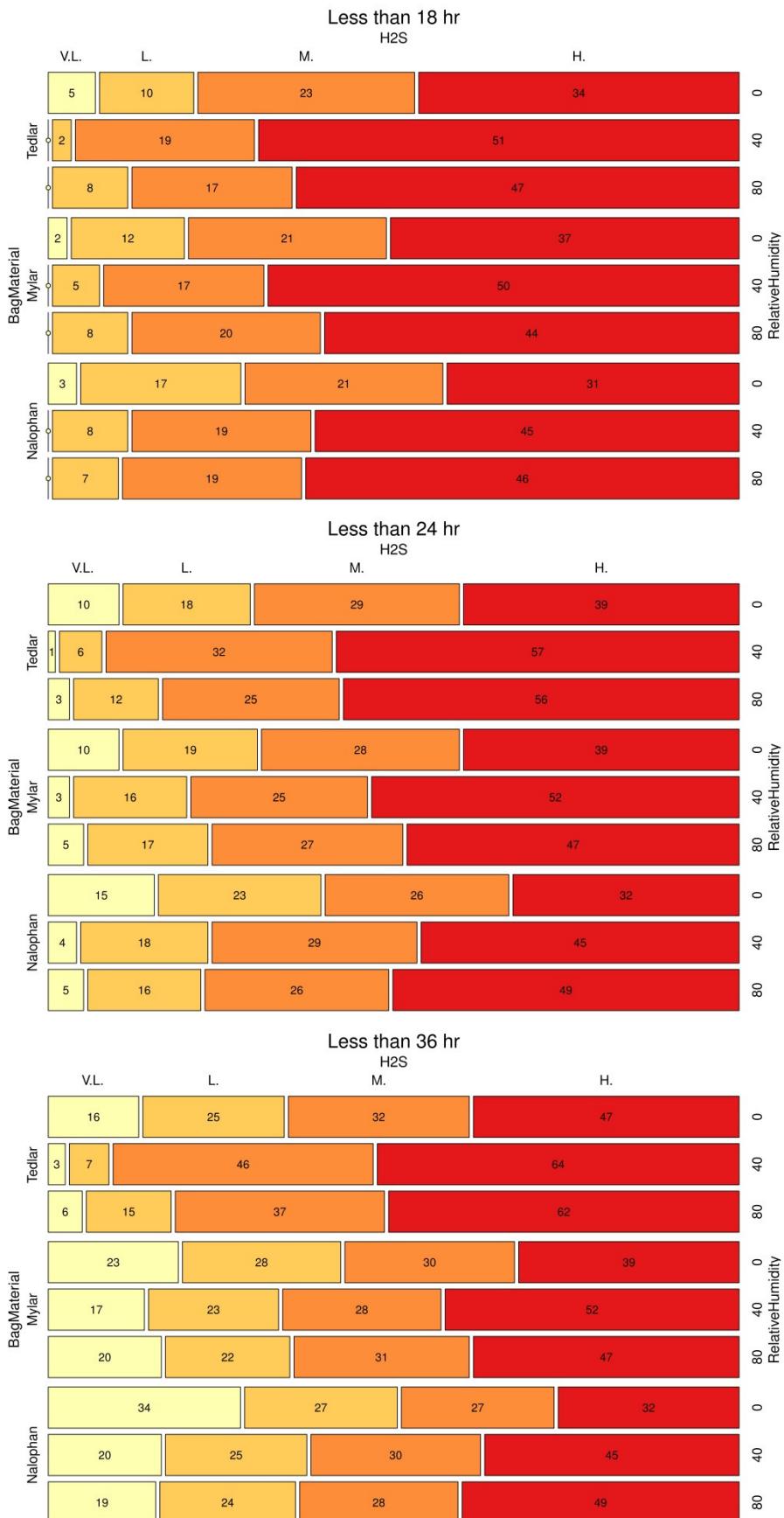


Figure 15 RH impacts - H₂S at less than 18 hrs, 24 hs and 36 hrs

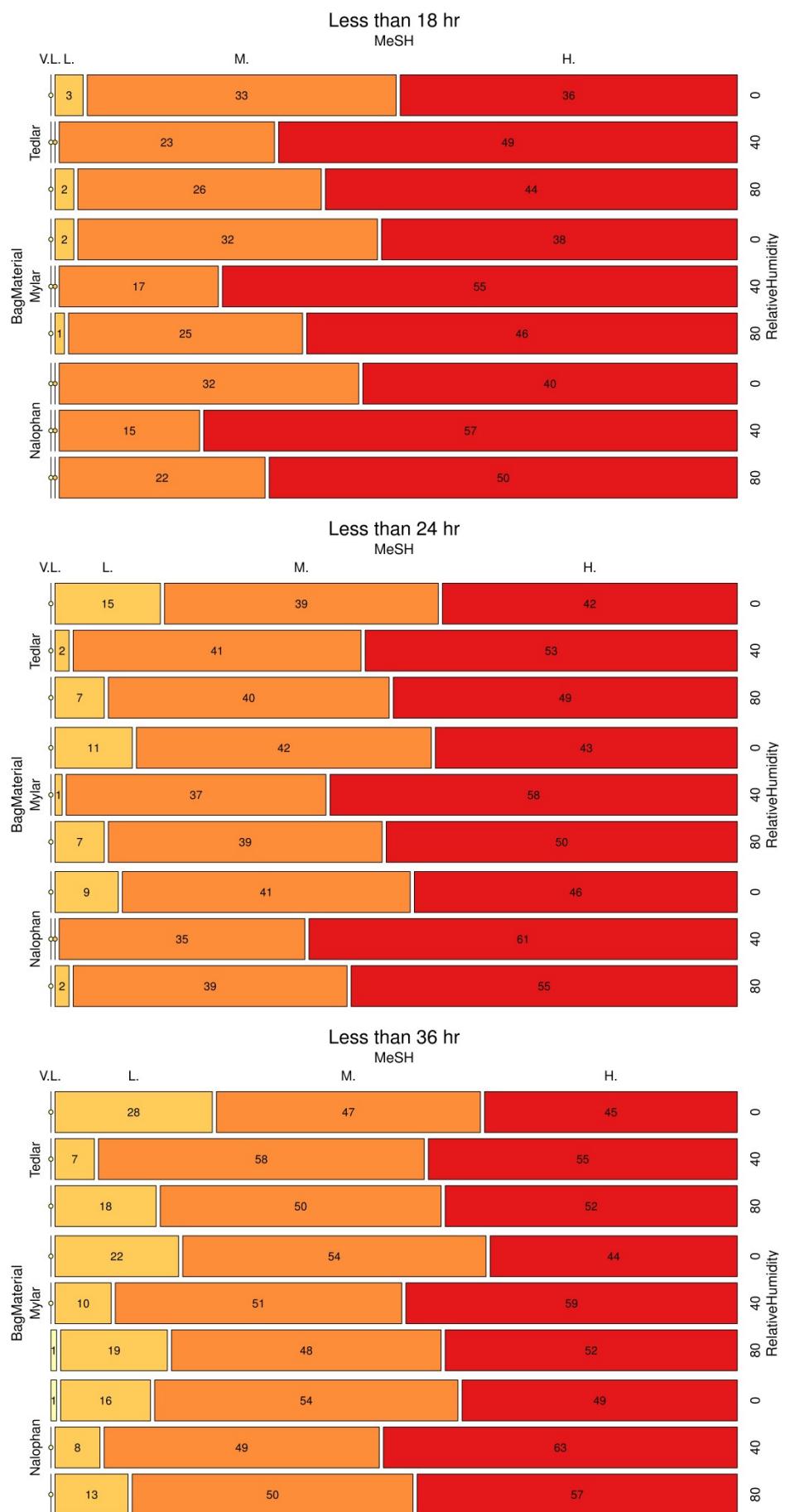


Figure 16 RH impacts - MeSH at less than 18 hrs, 24 hs and 36 hrs

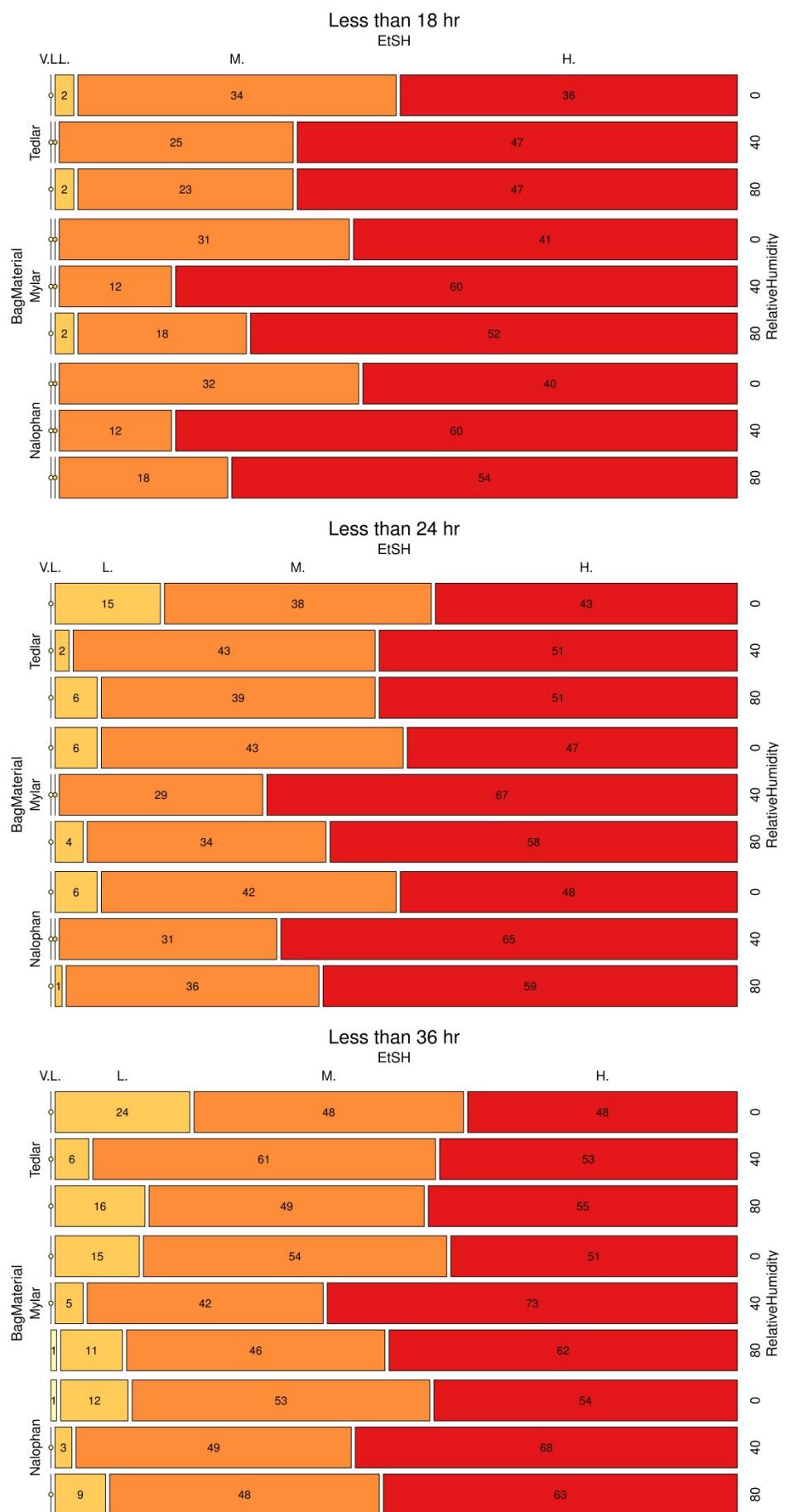


Figure 17 RH impacts - EtSH at less than 18 hrs, 24 hs and 36 hrs

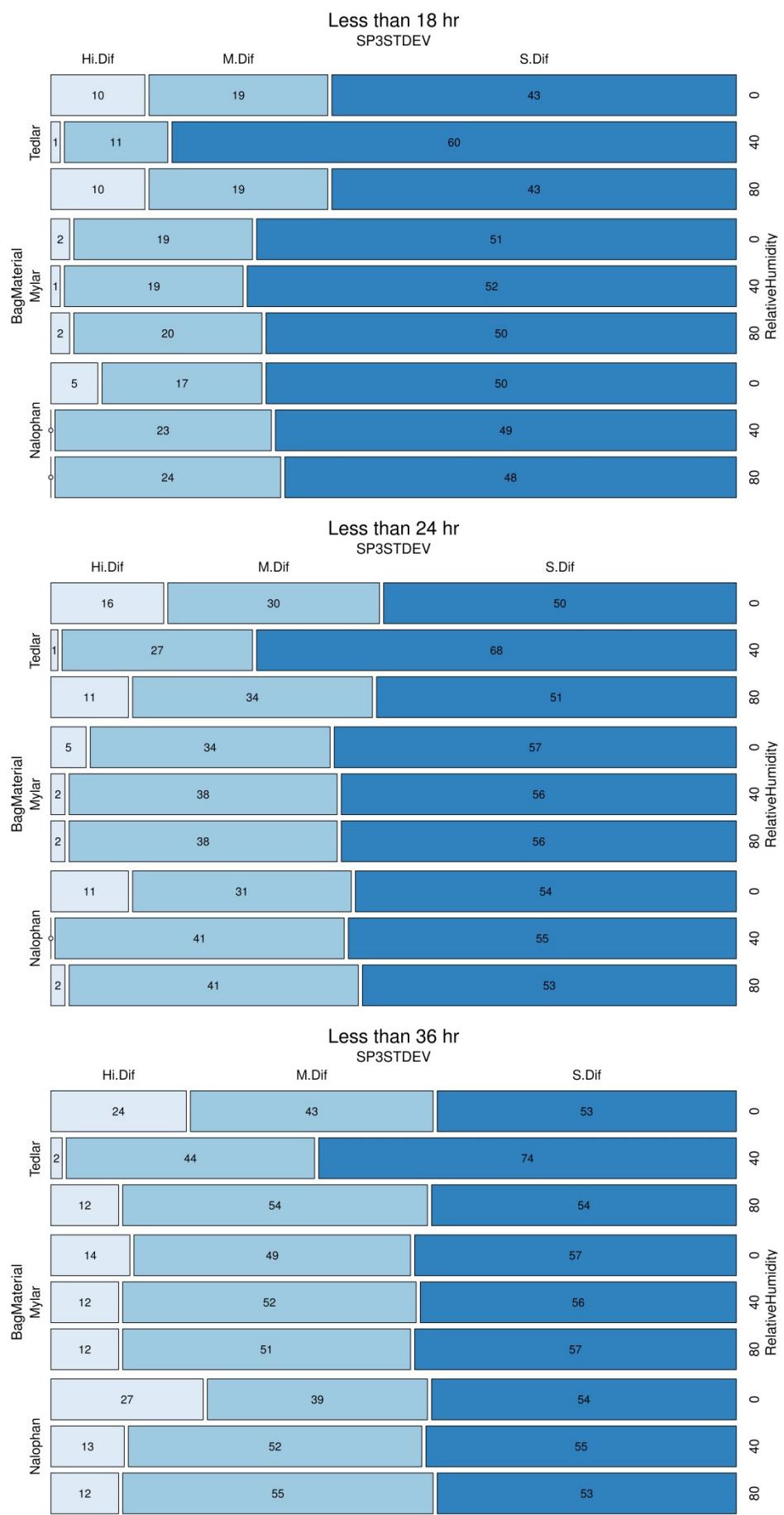


Figure 18 RH impacts - STDEV at less than 18 hrs, 24 hrs and 36 hrs

Appendix C - Light Impact for H₂S, MeSH, EtSH, and STDEV

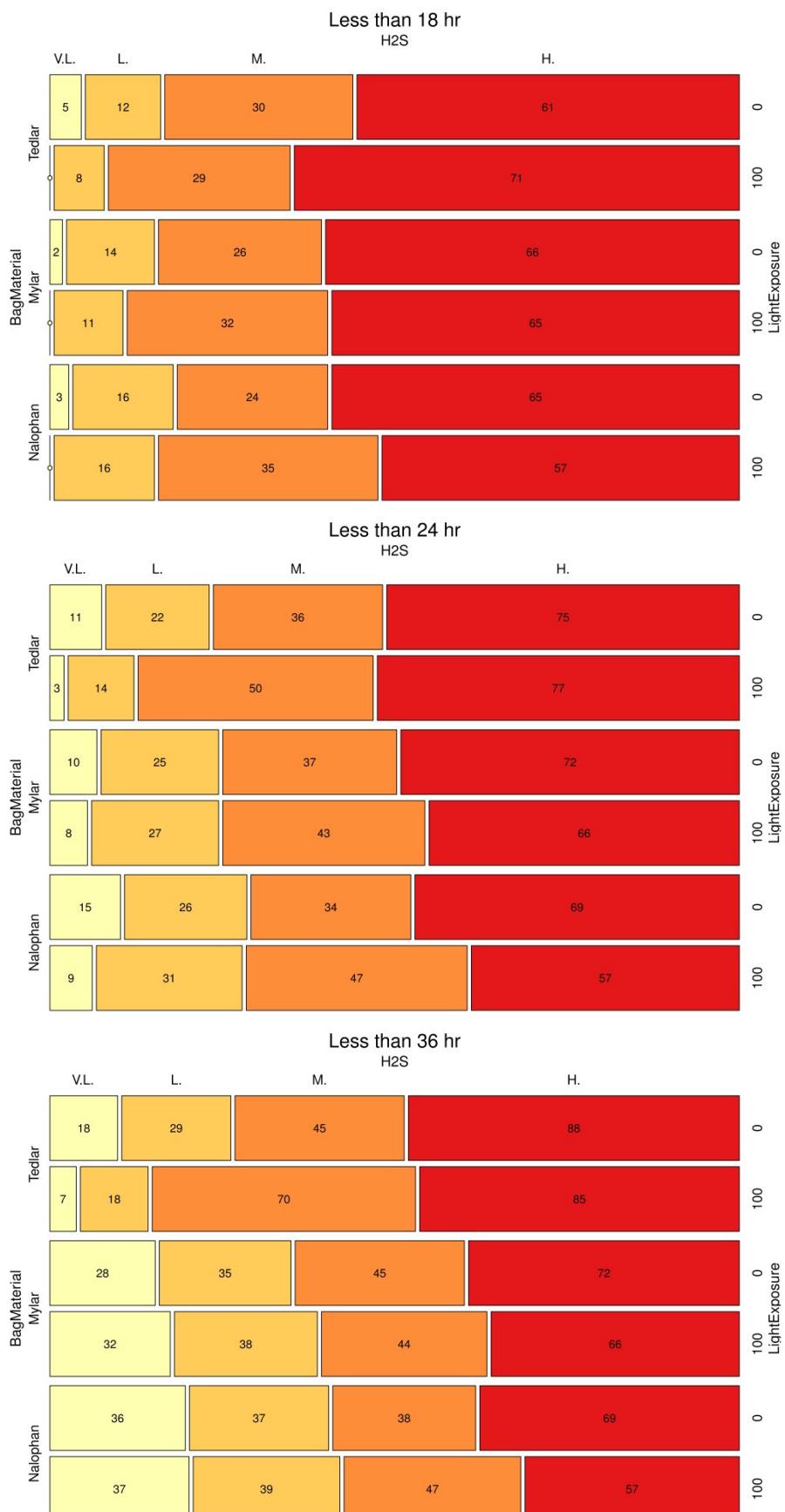


Figure 19 Light impacts - H₂S at less than 18 hrs, 24 hs and 36 hrs

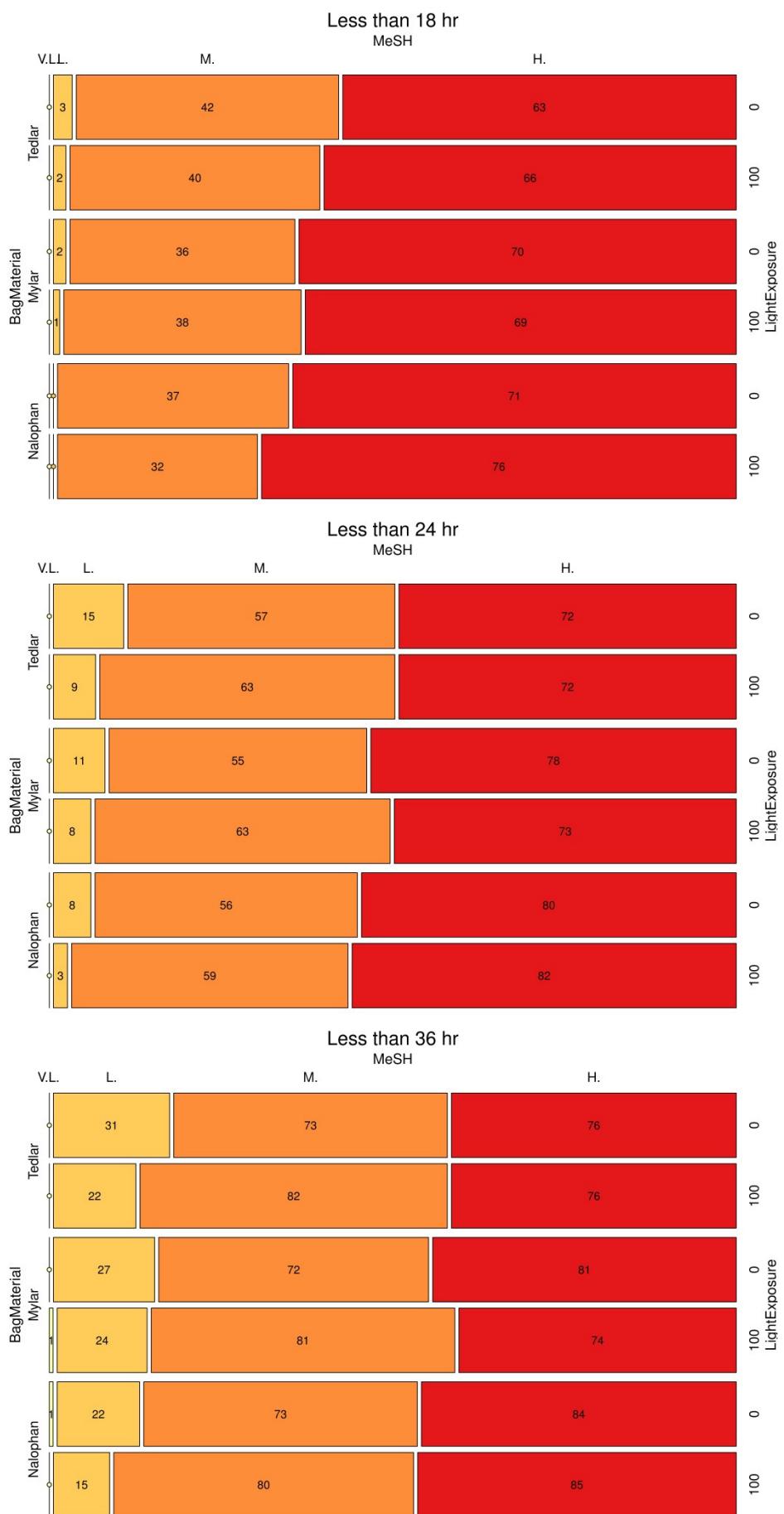


Figure 20 Light impacts - MeSH at less than 18 hrs, 24 hs and 36 hrs

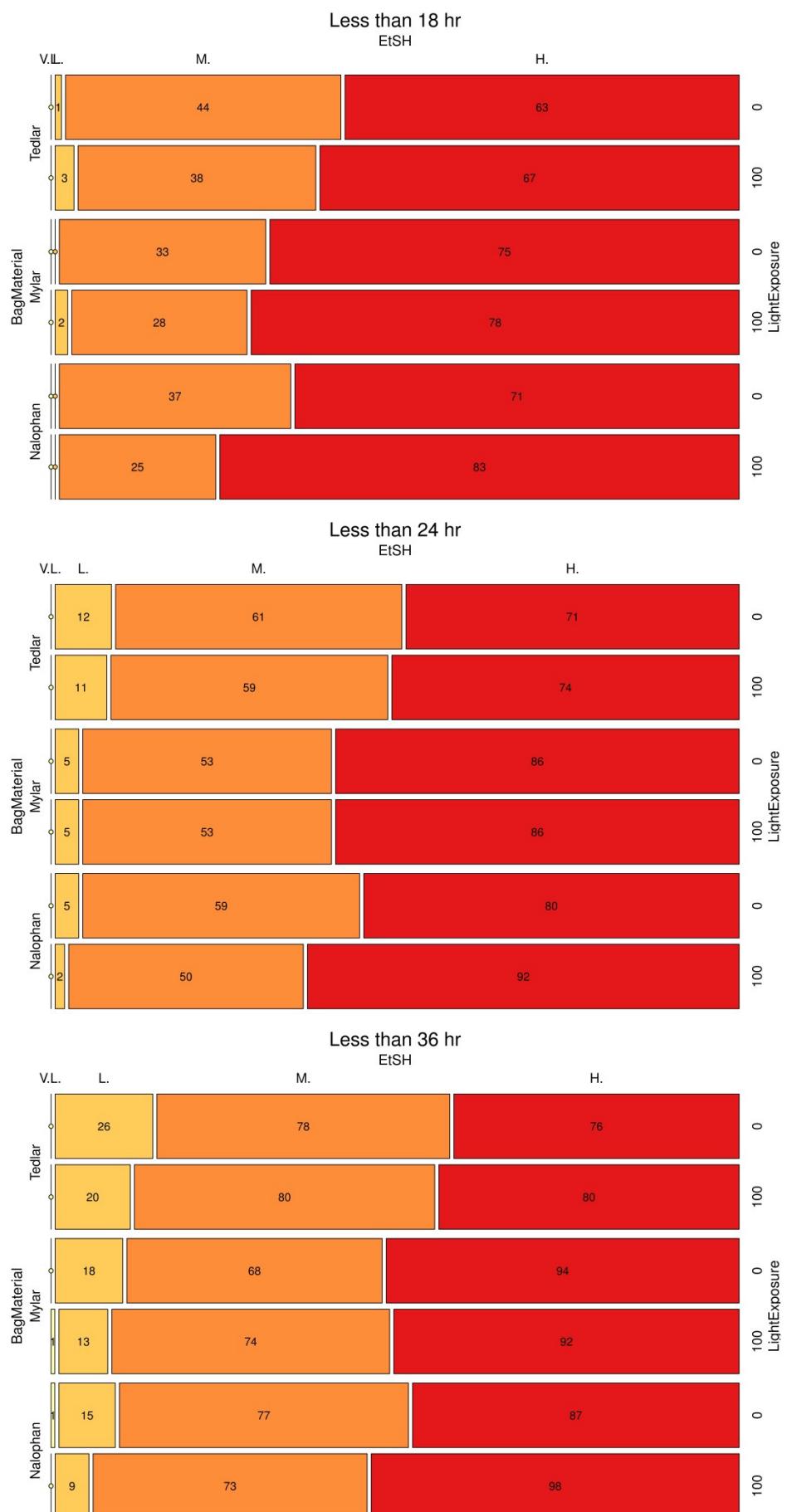


Figure 21 Light impacts - EtSH at less than 18 hrs, 24 hs and 36 hrs

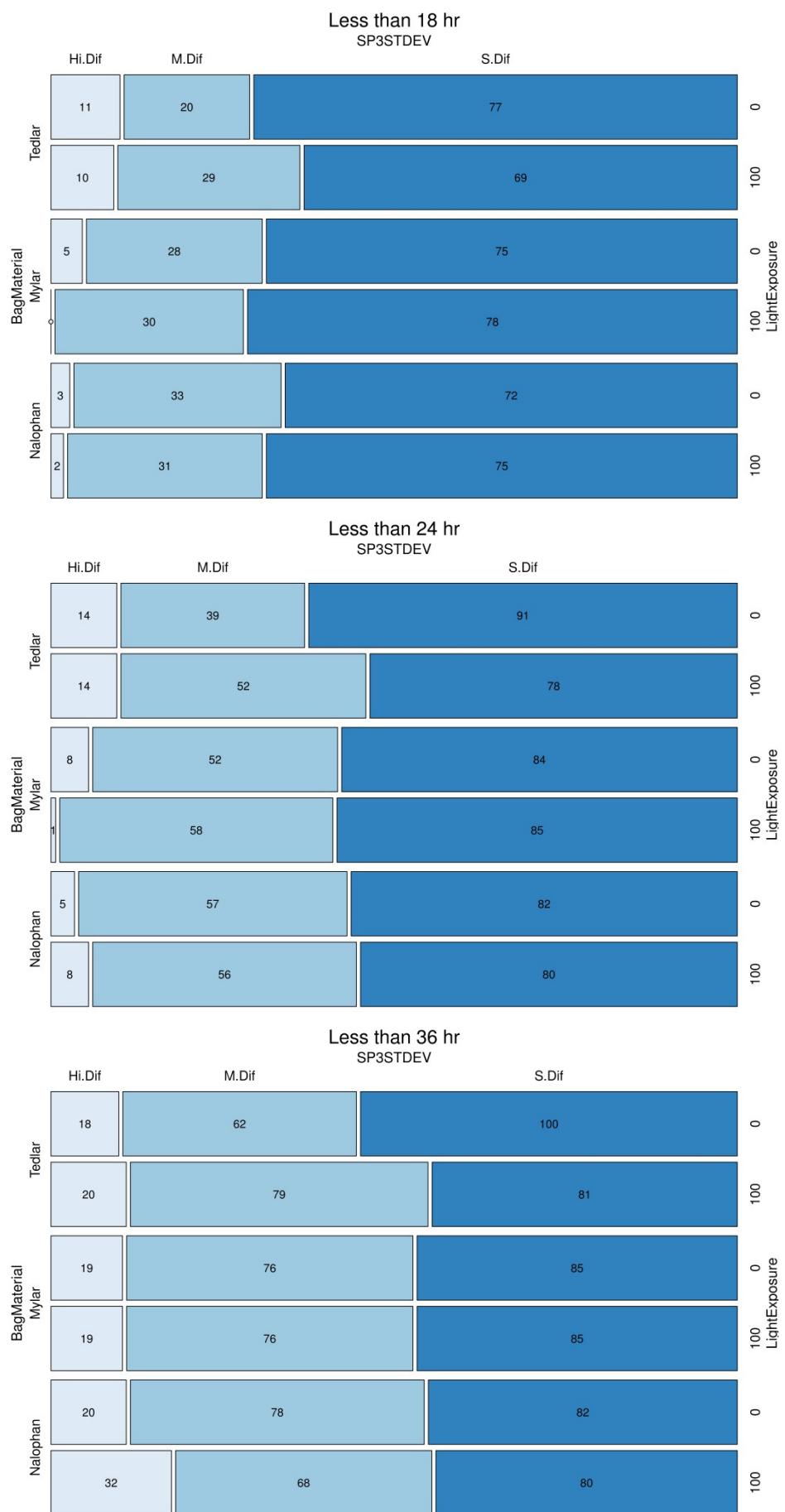


Figure 22 Light impacts - STDEV at less than 18 hrs, 24 hrs and 36 hrs

Appendix D - VOC Impact for H₂S, MeSH, EtSH, and STDEV

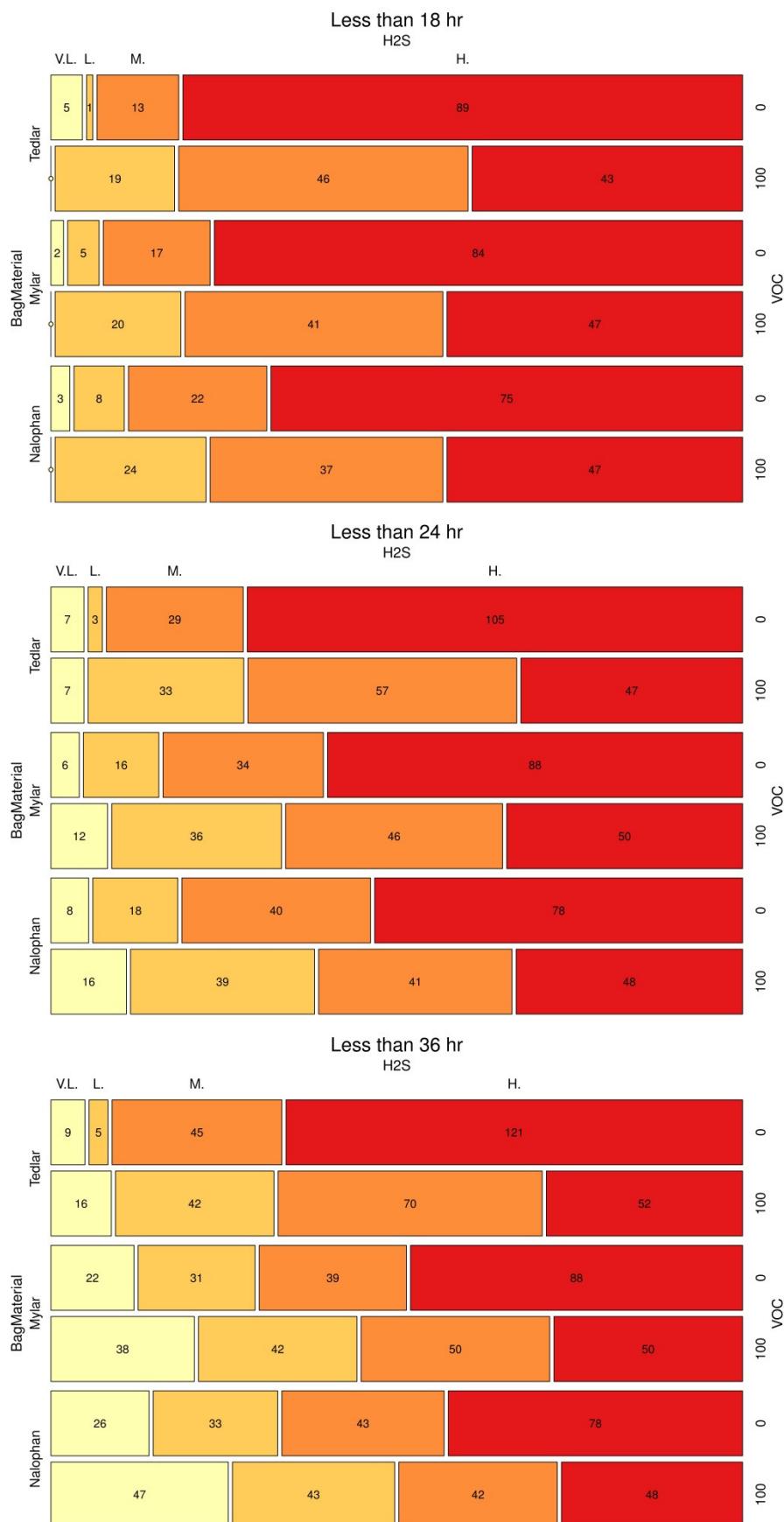


Figure 23 VOC impacts - H₂S at less than 18 hrs, 24 hs and 36 hrs

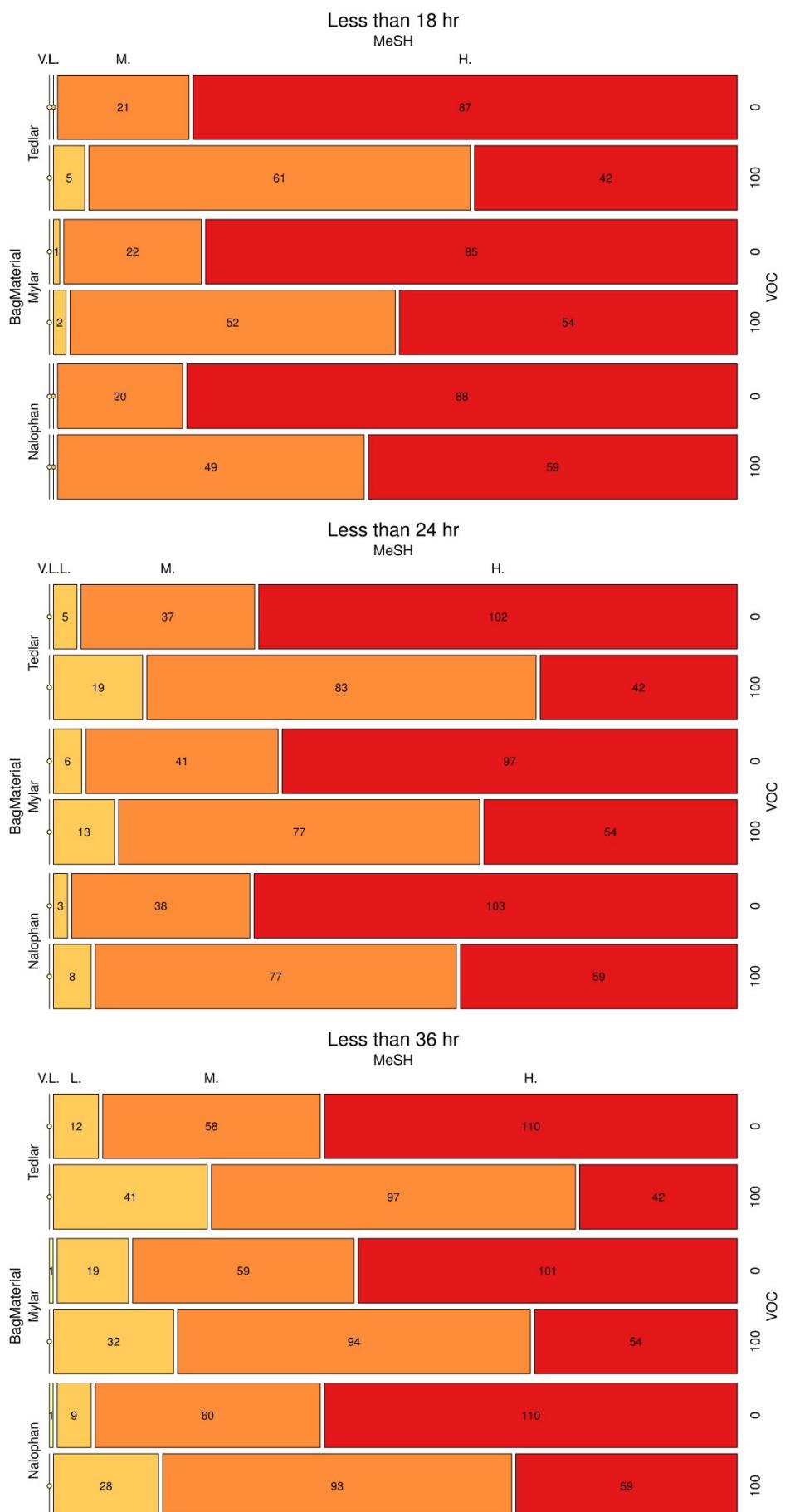


Figure 24 VOC impacts - MeSH at less than 18 hrs, 24 hs and 36 hrs

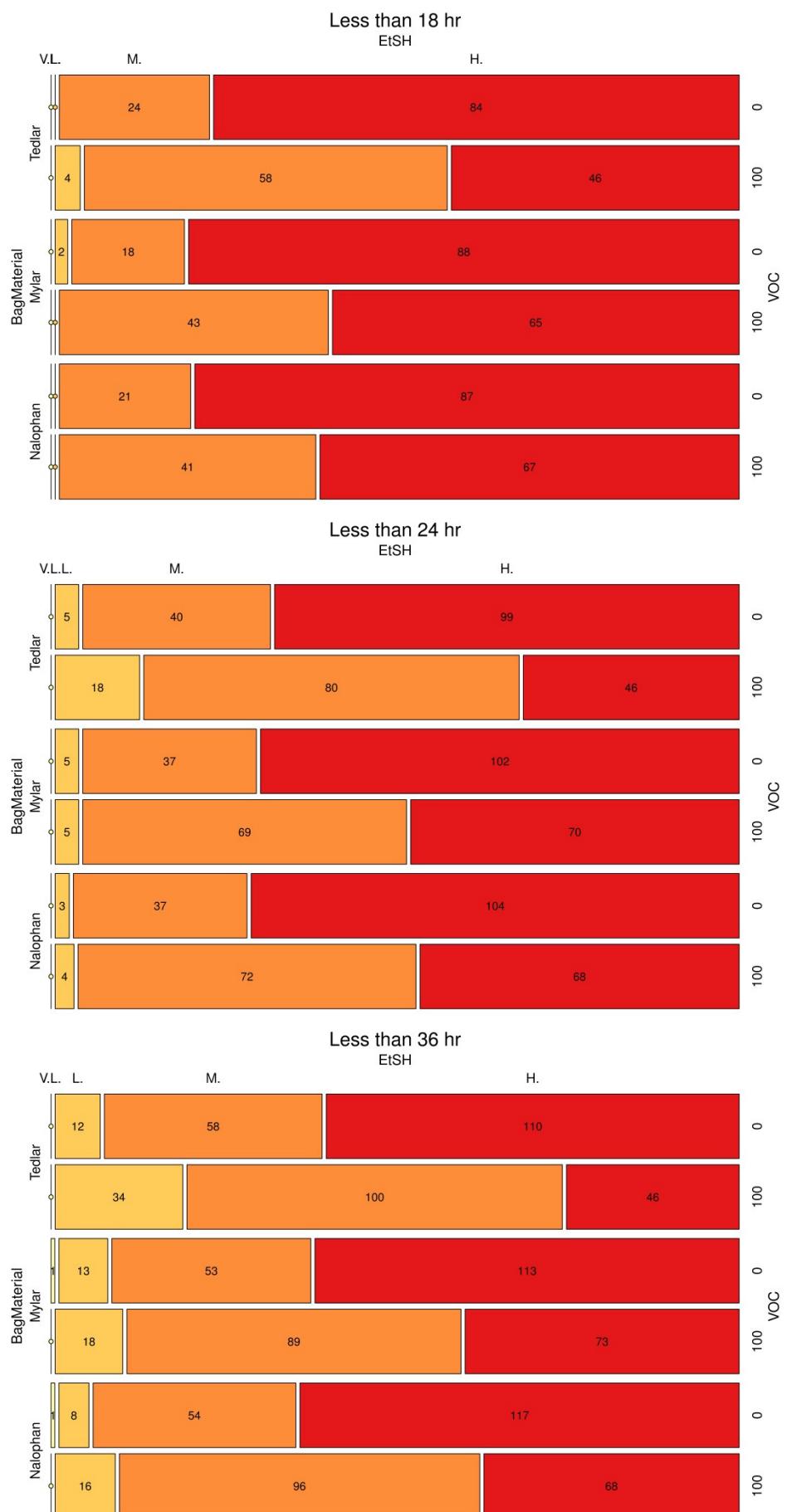


Figure 25 VOC impacts - EtSH at less than 18 hrs, 24 hs and 36 hrs

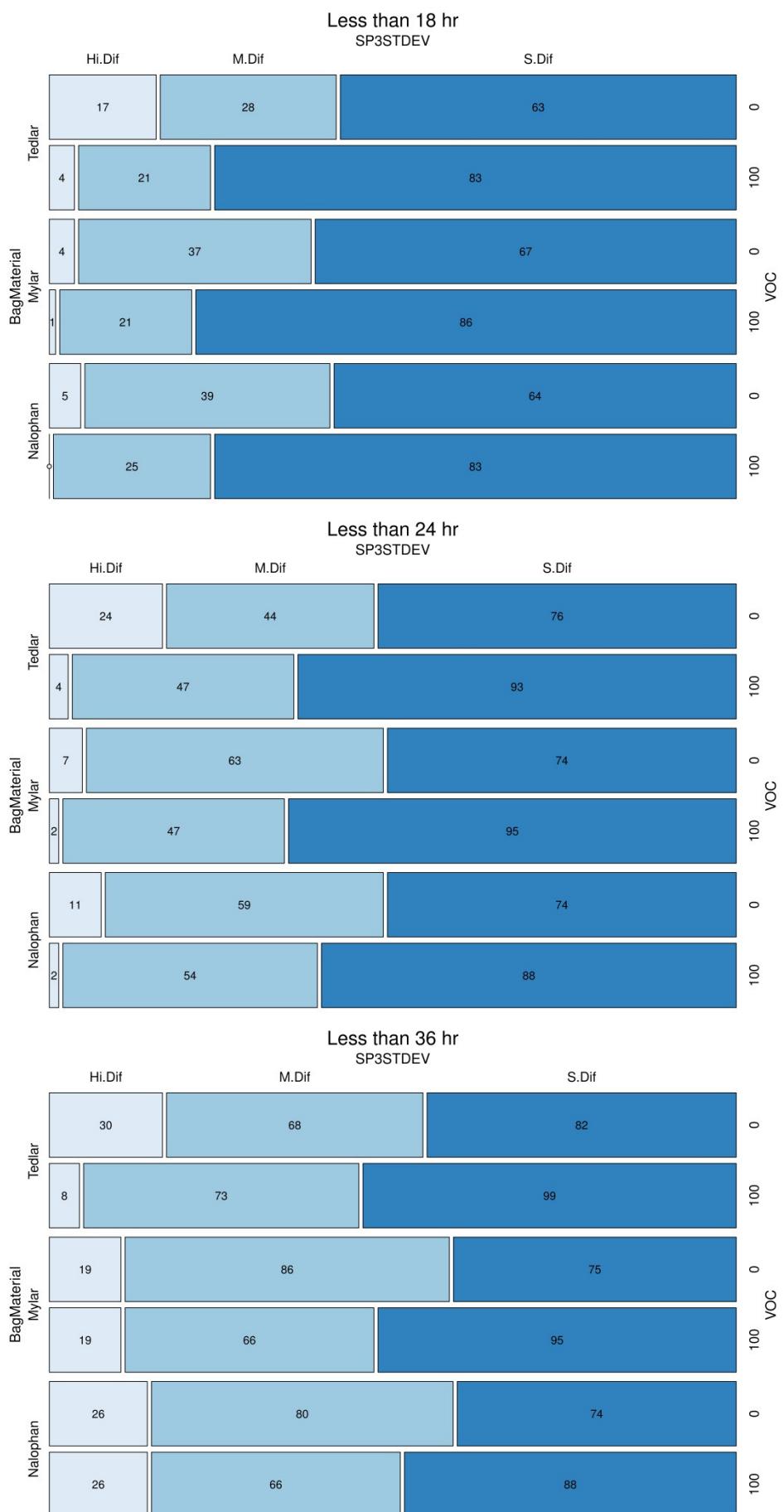


Figure 26 VOC impacts - STDEV at less than 18 hrs, 24 hs and 36 hrs

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