

# Understanding Exposures from Volatile Chemicals Emitted from New & Tire-Derived Rubber Flooring

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# Genesis of Current Study - 1

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- CDPH Building Material Emissions Study (BMES, 2003), funded jointly with CalRecycle (IWMB at the time)
  - Tested rubber flooring products, including new and tire-derived rubber (NR and TDR)
  - Many products emit substantial amounts of VOCs, including those with no established reference exposure levels for health protection
  - Unanswered questions about how long VOCs continue to off-gas from these products.

# Genesis of Current Study - 2

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- *“...further refinement and testing of rubber-based...products are necessary before these products can be promoted for wide use in most indoor environments”.*
- OEHHA asked to develop noncancer health values for chemicals that were emitted from TDR flooring.
- CDPH asked to conduct more detailed follow-up emission studies.

# CDPH Study Methods

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- New floor products acquired directly from manufacturers within 1 month of production
- Sample conditioning for 10 days
- Emission testing at 14 days (Section 01350)
- Continuous conditioning till 28-d, 60-d, and 90-d tests
- Analyses for VOCs and aldehydes



# Testing Chambers



**Chamber "A"**



**Chamber "C"**



**Chamber "B"**

# Results

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- VOC emissions at 14-days
- Estimated concentration exposures
- Long-term (28-, 60-, and 90-d)

# 25 Flooring Samples Tested

(32 specimens including replicate lots)

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## Primary Use

- Acoustic Underlayment - 4; Indoor - 16; Exterior - 5

## TDR Content

- TDR (> 60%) - 17; NR (<10%) - 8

## Thickness

- 2 mm - 2; 3 mm - 7; 6 mm - 2; 10 mm - 9; 25 mm - 3; >50 mm - 2

## Form & Composition

- Tile - 13; Roll - 7; Panel - 2; Pavers - 3
- Homogenous - 16; Layered - 9

## Manufacturer

- California - 1; Other states - 6; Canada - 2

# VOC emissions

## **New Rubber (NR)**

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- **Interior-use products:** Acetaldehyde, Acetone, Benzothiazole, Butylated Hydroxytoluene, Carbon disulfide, Cyclohexanone, Decanal, Isopropyl Alcohol, a-Methylstyrene, Nonanal, Phenol, 4-Phenylcyclohexene, Styrene, Toluene, 1,2,4-Trimethylbenzene

## **Tire-derived rubber (TDR)**

- **Interior-use products:** Acetaldehyde, Acetone, Acetophenone, **Benzene**, Benzothiazole, Butylated Hydroxytoluene, Butyraldehyde, Carbon disulfide, Chlorobenzene, Cyclohexanone, Decanal, n-Decane, Ethylbenzene, **Formaldehyde**, Methyl Isobutyl Ketone, a-Methylstyrene, **Naphthalene**, Nonanal, Octanal, Phenol, Styrene, **Toluene**, 1,2,4-Trimethylbenzene, n-Undecane, m/p-Xylene, o-Xylene
- **Exterior-use products:** Acetaldehyde, Acetone, Benzothiazole, Carbon disulfide, Cyclohexanone, n-Decane, Ethylbenzene, 1-Ethyl-4-methylbenzene, **Formaldehyde**, Hexanal, Methyl Isobutyl Ketone, **Naphthalene**, Styrene, **Toluene**, 1,2,4-Trimethylbenzene, n-Undecane, **m/p-Xylene**, **o-Xylene**

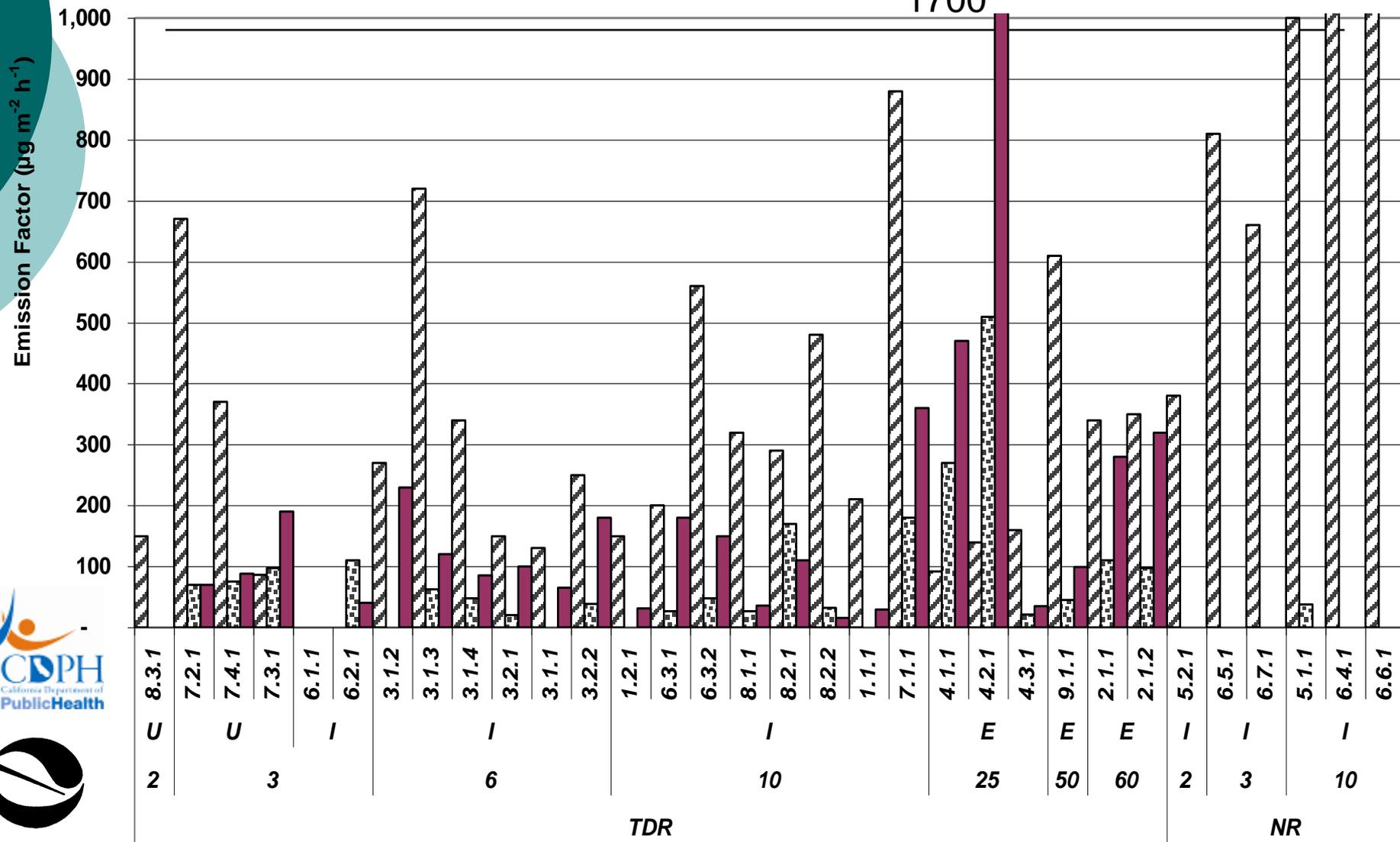
# Chemicals associated with tire production

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<u>Material</u>	<u>Chemical Compound</u>
Polymers	Natural rubber; Styrene-butadiene rubber
Accelerators	<i>Benzothiazole</i>
Activators	<i>Cyclohexanone,</i>
Antioxidants	<i>Methyl isobutyl ketone;</i> <i>Butylated hydroxytoluene</i>
Extender	Silica gel; Carbon black
Plasticizer	Aliphatic and Aromatic oils; Di-(2-ethylhexyl)-phthalate
Retarders	n-Cyclohexylthiophthalimide
Vulcanizers	Tetra-methyl thiurame sulfide

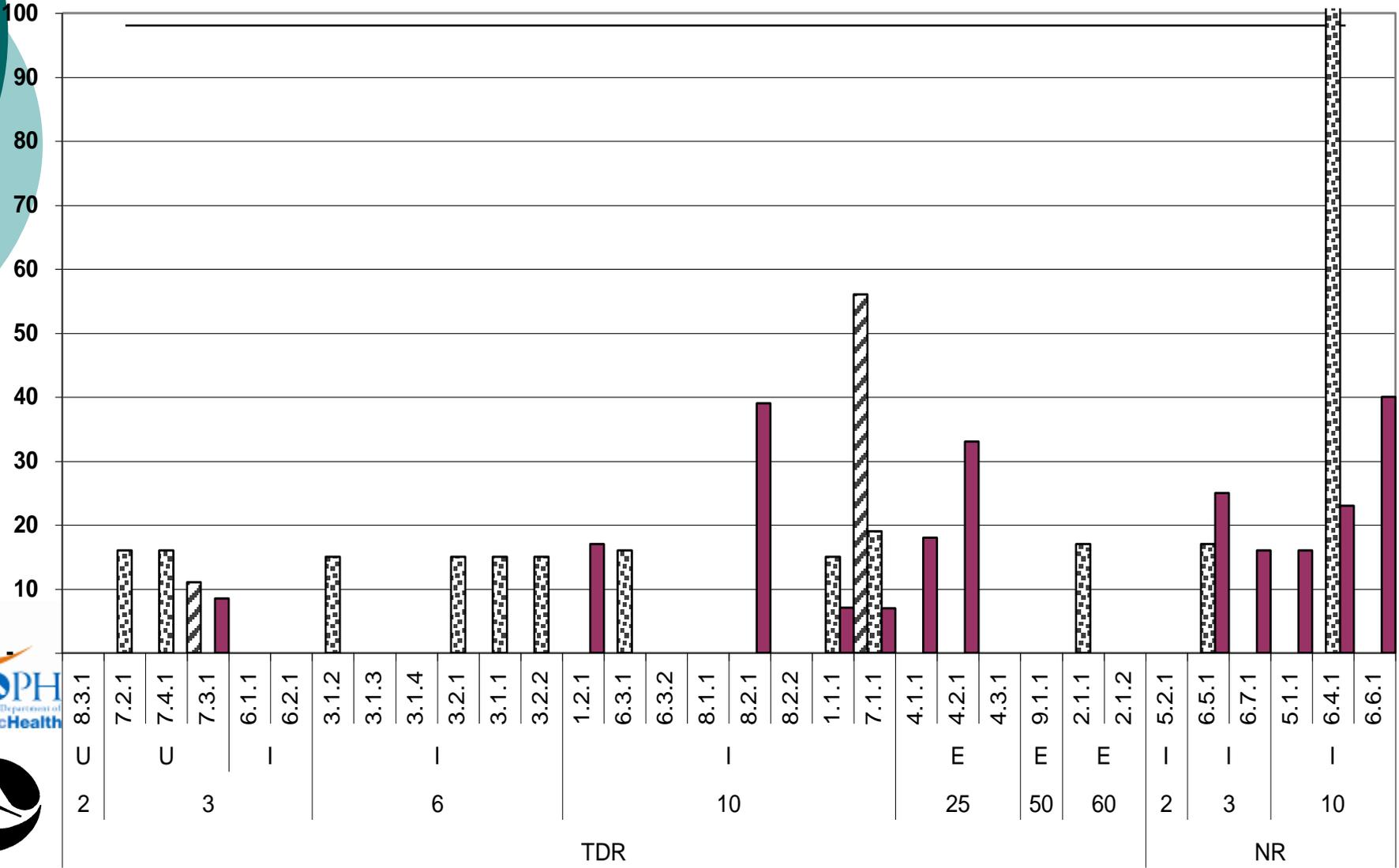
*Source: CIWMB, 2004*

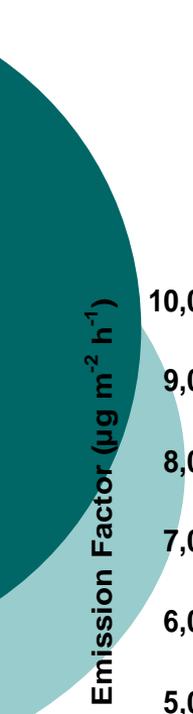
Benzothiazole
  Cyclohexanone
  Methyl Isobutyl Ketone



▨ Benzene ▩ Carbon disulfide ■ Styrene

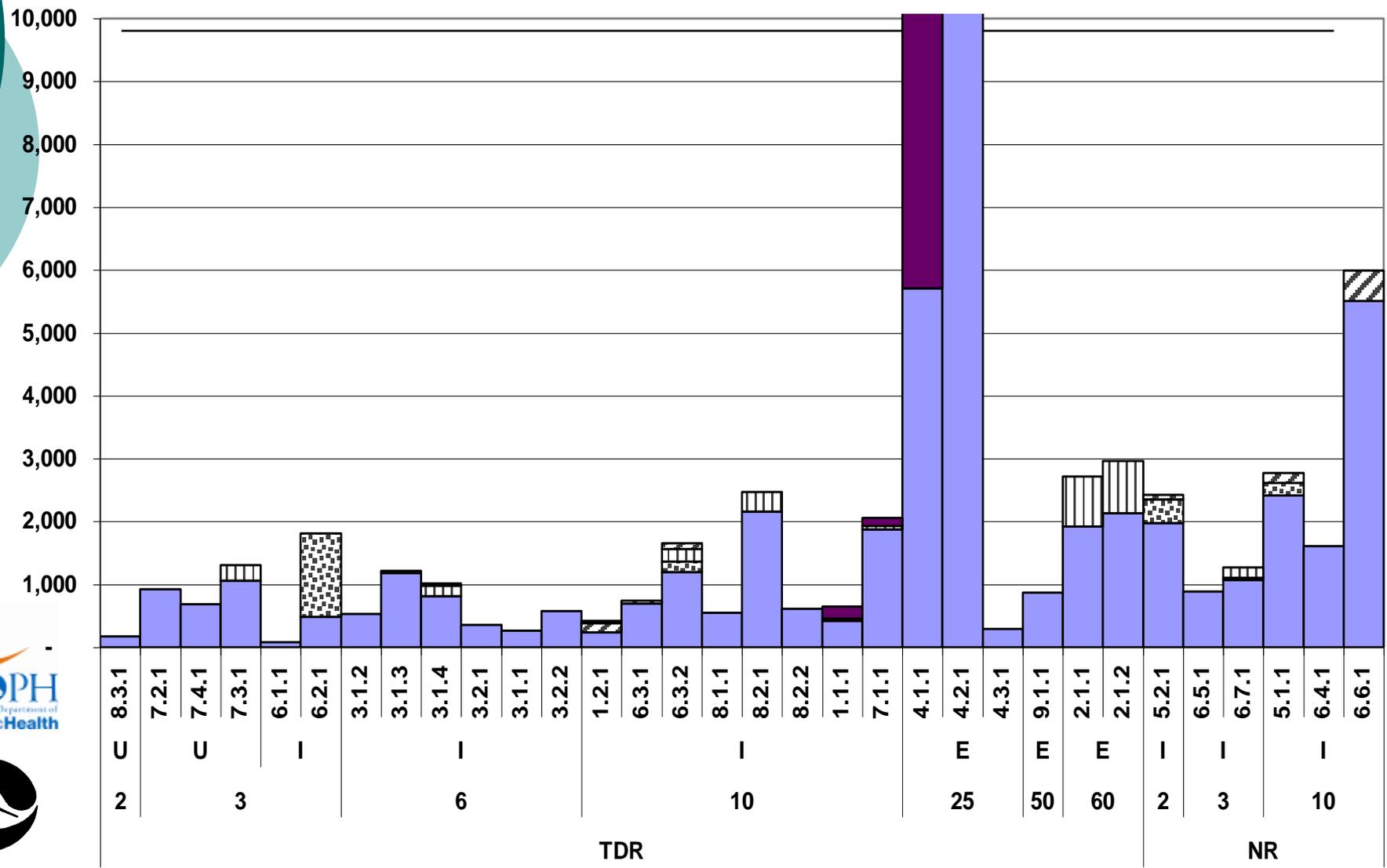
Emission Factor ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )





Identified
  Aromatic HC
  Branched HC
  Cyclic HC
  Unidentified

Emission Factor ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )



# Estimated Exposure Concentrations

$$C_m = \frac{EF * A_t}{V_R * ACH} \equiv K * EF$$

where:

$C_m$  = modeled indoor air concentration of compound [ $\mu\text{g}\cdot\text{m}^{-3}$ ]

EF = emission factor [ $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ]

$Q_C$  = chamber airflow rate [ $\text{m}^3\cdot\text{h}^{-1}$ ]

$A_t$  = exposure area of the material in the room [ $\text{m}^2$ ]

$V_R$  = room volume where material will be installed [ $\text{m}^3$ ]

ACH = air change rate [ $\text{h}^{-1}$ ]; note:  $V_R \bullet \text{ACH} = Q_R$  [ $\text{m}^3\cdot\text{h}^{-1}$ ]

K = conversion factor for a given exposure scenario



# Exposure Scenarios

Parameters	Units	Daycare or Nursery for children	Locker or Workout Room	State Office	Typical Classroom
<b>Flooring Area</b>	m <sup>2</sup>	37.2	37.2	11.1	89.2
	ft <sup>2</sup>	400	400	120	960
<b>Ceiling Height</b>	m	2.6	3.0	2.7	2.6
	ft	8.5	10	9	8.5
<b>Volume</b>	m <sup>3</sup>	96.3	113	30.6	231
	ft <sup>3</sup>	3400	4000	1080	8160
<b>Air changes per hour (ACH)</b>	h <sup>-1</sup>	0.35	0.53	0.75	0.9
<b>Conversion Factor (K)</b>	h m <sup>-1</sup>	<b>1.10</b>	<b>0.62</b>	<b>0.49</b>	<b>0.43</b>

Estimated Concentrations	Emission Factor @ Day 14 $\mu\text{g m}^{-2} \text{h}^{-1}$	CREL	Scenario	
			Day-care	Classroom
		----- $\mu\text{g m}^{-3}$ -----		
<b>NR Interior-use products</b>				
Benzothiazole	3900	-	4,300	1,640
<b>TDR Interior-use products</b>				
Benzothiazole	880		973	371
<b>Benzene</b>	<b>56</b>	<b>60</b>	<b>62</b>	<b>24</b>
<b>Formaldehyde</b>	<b>17</b>	<b>9</b>	<b>19</b>	<b>7</b>
<b>Naphthalene</b>	<b>10</b>	9	<b>11</b>	<b>4</b>
<b>Toluene</b>	<b>1200</b>	<b>300</b>	<b>1,330</b>	<b>505</b>
<b>TDR Exterior-use products</b>				
Benzothiazole	610		674	257
<b>Formaldehyde</b>	<b>29</b>	<b>9</b>	<b>32</b>	<b>12</b>
<b>Naphthalene</b>	<b>410</b>	<b>9</b>	<b>450</b>	<b>173</b>
<b>Toluene</b>	<b>1900</b>	<b>300</b>	<b>2,100</b>	<b>800</b>
<b>m/p-Xylene</b>	<b>2900</b>	<b>700</b>	<b>3,200</b>	<b>1,220</b>
<b>o-Xylene</b>	<b>1600</b>	<b>700</b>	<b>1,770</b>	<b>670</b>



# Longer-term Emissions

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- Many chemicals' emissions substantially reduced by ~30 days; however, several compounds remained through the 90-day conditioning period.
- Persistently high VOC levels may trigger sensory impacts.
- Ample pre/post-occupancy *flush out* (or off-site pre-conditioning) is appropriate when TDR and NR flooring products are used indoors.

# CDPH Study Summary

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- TDR and NR flooring emit higher levels of VOCs than other flooring types; nonetheless, emissions rarely exceeded *health-based guidelines*.
- Emissions somewhat different for NR and TDR (indoor). Higher emissions for thicker and *exterior-use* products.
- Subject to screening (e.g., *Section 01350*), we feel TDR and NR products are generally acceptable for indoor use; *exterior* or *exterior-interior* products should be avoided.
- Consider allowable limits for TVOC emissions for rubber flooring to be used indoors.



# Acknowledgments

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- Subcontract to **Public Health Institute (PHI)**
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  - **CDPH:** Weldon Hall, Ryan Johnson, Janet Macher, Robert Miller, Paola Taranta, Jeff Wagner & Kunning Zhu
  - **PHI:** Judith Lubina, Carol Alliger & Mike Peters.
  - **CalRecycle:** Gregory Dick, Brian Helmowski, William Orr & Dana Papke
  - **Advisory panel:** Anthony Bernheim, *AECOM Design*; Alfred Hodgson, *Berkeley Analytical Associates*; Richard Lam, *OEHHA*; Hal Levin, *Building Ecology Research Group*; Dana Papke and Linda Dickinson, *CalRecycle*



# OEHHA: Reference Exposure Levels for TDF Emissions

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- The Tire Derived Rubber Floor Emissions Study measured emissions of chemicals from tire-derived flooring (TDF) over time.
- The study also modeled air concentrations that would be generated under conditions of indoor use.
- Such air concentrations can be compared to health values to help determine the potential for human health impacts.
- Cal Recycle asked OEHHA to develop non-cancer health values (*Reference Exposure Levels*) for four chemicals that were emitted from TDF.

# OEHHA: iRELs for TDR Emissions

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- Indoor or *iREL* values are air concentrations at or below which health impacts would not be expected, even in sensitive members of the general population with repeated 8-hr exposures for a significant fraction of a lifetime.
- The iREL values are derived from useful animal and human toxicology studies on these chemicals. Their derivations are presented in the summaries.
- The iREL summaries are presented in Appendix E of the *Tire-Derived Rubber Floor Emissions Study Contractor Report*.



# OEHHA: iRELS for TDF Chemicals

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<u>Chemical</u>	<u>iREL(<math>\mu\text{g}/\text{m}^3</math>)</u>
N-Methyl-3-pyrrolidinone	2000
Naphthalene	13
1, 2, 4-Trimethylbenzene	300
Ethylene glycol mono-N-butyl ether	300

# OEHHA: iRELS vs. 8-hr RELs and chronic RELs

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- The 8-hour RELs are similar to the idea of iREL with a little bit different procedure and may also be useful to interested parties.
- The 8-hour RELs are only available for 6 chemicals at this point, with a few more in the process.
- If an 8-hr REL becomes available for any of the four iREL chemicals in the future, OEHHA would recommend the 8-hour REL, because it will be based on more recent data and procedures.
- Chronic RELs are used in the Section 1350 process.



# OEHHA Summary

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- iRELS are available for four chemicals that were found in TDF.
- These iRELS are not part of any regulatory program but can be used by interested parties.
- We would like to thank Cal Recycle for providing the funding to develop these iREL values and we hope this work will be useful.

