

Scientific Critique of South Coast Air Quality Management District Paper

“Non-Volatile, Semi-Volatile, or Volatile:

Redefining Volatile for Volatile Organic Compounds”

October 2012

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**ABSTRACT**

A draft paper entitled “Non-Volatile, Semi-Volatile, or Volatile: Redefining Volatile for Volatile Organic Compounds” authored by Uyên- Uyên T. Võ and Michael P. Morris is subjected to a scientific critique. The paper presents ambient evaporation data for organic compounds of varying volatility that is portrayed as drawing into question the regulatory criteria and test methods used to determine what low-vapor-pressure compounds are exempted from the regulatory definition of “Volatile Organic Compound” (VOC) for various uses. The paper fails to grasp the crucial differences between the technical term “volatile” and the regulatory term “VOC”, which relates to the ability to contribute significantly to formation of ozone in tropospheric ambient air through vapor-phase photochemistry. In this critique, the scientific concepts and studies are noted that limit the ability of low-volatility organic compounds to contribute significantly to tropospheric ozone formation and refute the arguments in the draft paper.

**SCIENTIFIC CRITIQUE**

“Non-Volatile, Semi-Volatile, or Volatile: Redefining Volatile for Volatile Organic Compounds” authored by Uyên- Uyên T. Võ and Michael P. Morris was obtained from the authors in the form of a draft paper dated August 31, 2012, as well as a presentation dated June 21, 2012, that was presented at an Air & Waste Management Association meeting. This scientific critique was conducted by a number of chemists and environmental scientists in the consumer products industry.<sup>1</sup>

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<sup>1</sup> Scientists involved in developing this critique included representatives from the Consumer Specialty Products Association, Personal Care Products Council, American Chemistry Council, American Cleaning Institute, American Coatings Association, Automotive Specialty Products Alliance, National Aerosol Association, International Sanitary Supply Association, and International Fragrance Association North America.

The abstract of the paper begins with the erroneous statement that, "The term volatile organic compound (VOC) is poorly defined because volatility is subjective." (Page 1) Volatility is not in any way subjective, but rather is a basic, measurable physiochemical property that is well defined. It is measured as the pressure exerted by molecules of a substance's vapor (i.e., gas phase) in thermodynamic equilibrium with its condensed phase(s) (i.e., liquid and/or solid) in a closed system at a given temperature.<sup>2</sup> Vapor pressure is often measured at 20°C or 25°C in units of either mm Hg or pascals.<sup>3</sup> As vapor pressure increases with temperature, it is closely related to boiling point, which is the temperature at which the vapor pressure is equal to the pressure exerted by ambient air. Numerous physical laws have been established relating to vapor pressure and boiling point, including the Clausius-Clapeyron relation of vapor pressure with temperature, Raoult's Law for calculating vapor pressures of mixtures, and many others. All liquids (and solids) have vapor pressures, but they are often too low to be measured accurately.

As to the contention that the term "VOC" is "poorly defined," this appears to be caused by the apparent confusion between the technical scientific term and the regulatory term. The technical scientific term "VOC" is a relative term for which there are no set criteria for the relative volatility needed for a material to be considered "volatile" under conditions of interest. However, the regulatory definition of VOC is quite different (and indeed much more restrictive) than the scientific use of the term. The current U.S. Environmental Protection Agency's regulatory definition of VOC for the purpose of regulatory enforcement of the Clean Air Act is as follows:

"Volatile organic compounds (VOC)" means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.<sup>4</sup>

Atmospheric photochemical reactions occur in the vapor phase in the troposphere. Consequently, the final phrase in this definition excludes compounds that are either too low in photochemical reactivity (which EPA has defined as lower in ozone formation potential than ethane) or too low in volatility (or having other physiochemical characteristics) to have significant participation in atmospheric photochemistry. EPA specifically evaluates and lists individual chemicals having negligible photochemical reactivity as exemptions to the definition

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<sup>2</sup>For example, Chang, Chemistry, 9<sup>th</sup> Ed., McGraw-Hill, pg 518. The U.S. EPA defines volatility as being indicated by a substance's vapor pressure. It is a tendency of a substance to vaporize or the speed at which it vaporizes. Substances with higher vapor pressure will vaporize more readily at a given temperature than substances with lower vapor pressure. <http://www.epa.gov/iaq/voc2.html#4> accessed 9/26/2012)

<sup>3</sup> Conversion factors: 1 pascal = 0.0075 mm Hg; 1 mm Hg = 133.3 pascals. High vapor pressures are often expressed in kilopascals (kPa). 1 kPa = 1000 pascals.

<sup>4</sup> 40 CFR § 51.100(s)

of VOC.<sup>5</sup> For low vapor pressure (LVP) compounds that do not participate due to low volatility, EPA relies on a variety of test methods designed for specific commercial products or operations, or in the case of consumer products, a definition of LVP based on the vapor pressure criterion of less than 0.1 mm Hg at 20° C (which is equal to 13.3 pascals).

The authors are correct in noting that the various test methods currently used to measure the amount of “VOC content” in a material differ markedly. (Page 1) However, they do not make a compelling case in their contention that, “These differences lead to varying VOC content results which may conflict with one another, resulting in regulations that can limit the environmental benefits anticipated or unnecessarily exclude potential alternative formulations.” (Page 1) Indeed, contrary to the author’s apparent contention, all of the current methodologies used for the determination of VOCs probably overestimate to varying degrees what materials in commercial products and operations actually participate significantly in atmospheric photochemistry.<sup>6</sup>

The authors are correct in noting that, “The EPA exempts solvents in consumer products with a vapor pressure of 0.1 mm Hg or less at 20°C, concluding that those compounds have little or no volatility and that an exemption will not result in significant VOC emissions and contribute to ozone formation.” (Page 2) They are less correct in observing that, “However, the measurement for vapor pressure becomes difficult at values below 7.5 mm Hg and most vapor pressure endpoints are ten to a hundred times lower.” (Page 2) While this has been historically true, the vapor pressure methodologies incorporated by CARB into Method 310<sup>7</sup> are fully capable of accurate and precise measurements needed for assuring compliance with the 0.1 mm Hg criterion. In addition, the carbon-number and boiling point criteria were not added by CARB in the 1990s due to inaccuracy or imprecision of the vapor pressure measurements, but to simply minimize (in the case of carbon-number) needless testing of known nonvolatile materials, and (in the case of boiling point) to easily accommodate complex hydrocarbon mixtures that may contain both LVP and more volatile constituents. In addition, the criterion is not “12 or more carbons” but rather “more than 12 carbons.” (Page 3)<sup>8</sup>

The European and Canadian 250°C boiling point criterion (Page 3) is only found in their current paint regulations, and is not relevant to other consumer products, which have yet to be

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<sup>5</sup> Ibid, 51.100(s)(1)

<sup>6</sup> For example, Mania, Daniel J., Bruck, Michele L, Fezzey, Sarah, Floyd, F. Louis —PRA Laboratories, Inc., "Sources of Error in VOC Determination via EPA Method 24", Journal of Coatings Technology, 73, (919), August 2001, [http://www.eaglabs.com/cmss\\_files/attachmentlibrary/Source-of-Error-in-VOC-Determination-via-EPA-Method-24.pdf](http://www.eaglabs.com/cmss_files/attachmentlibrary/Source-of-Error-in-VOC-Determination-via-EPA-Method-24.pdf), accessed 10/1/2012.

<sup>7</sup> Method 310 incorporates an improved version of ASTM D 2879-97 (Isoteniscope) and ASTM E 1719-97 (ebulliometry).

<sup>8</sup> 40 CFR § 59.203(f)(2) and 17 CCR § 94508(98)(B)

regulated in those jurisdictions; when Canada does adopt a consumer product VOC regulation, they are currently planning consistency with USA regulations by CARB, OTC and EPA. The authors are also not accurate about consumer products in stating that, “Green Seal exempts solvents with a boiling point of 280°C.” (Page 3) That criterion is also only relevant to the Paints and Coatings standard; in all of the Green Seal consumer product standards, they use the same LVP criteria as CARB (and all other consumer product regulations) and rely on Method 310.<sup>9</sup>

Much of the information and vapor pressure data on compounds in the “Evaporation Rate” study shown in Table 1 (Page 4) appears generally accurate, and largely consistent with results obtained in many laboratories for most of these materials, but it is important to note that those reported as “<0.01” to “<0.001” are probably not quantitatively reliable. (It is important to note that the vapor pressures provided are expressed in mm Hg at 25°C instead of 20°C, which makes comparison to values measured via Method 310 difficult.) In addition, the MIR (maximum incremental reactivity) data for the low volatility species cannot be considered reliable. Dr. William Carter included estimates for many of these materials in his lists of MIR values despite an inability for these materials to remain in the vapor phase long enough to participate in chamber photochemistry where reactivity is measured and photochemical mechanisms determined.<sup>10</sup> With materials like alkyl alkanolamine, methyl palmitate, soy oil, and glycerol, Dr. Carter clearly indicates in footnotes that these data are highly uncertain.<sup>11</sup> It is indeed likely that some of these materials exhibiting vapor phase photochemistry were the result of thermal degradation from the high temperatures at which they had to be injected into the chamber.<sup>12</sup>

This problem of thermal degradation may indeed be a problem with most if not all of the current test methods used to determine VOC content in various non-consumer products. (Even Method 310 begins with a high-temperature—100°C—gravimetric determination of total volatiles that will quite often result in thermal degradation of some ingredients, and therefore give inaccurate determination of total volatiles; Method 310, however, includes sufficient other methodology to allow CARB’s laboratory to correct this error.)

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<sup>9</sup> See various Green Seal standards for consumer products at <http://www.greenseal.org/GreenBusiness/Standards.aspx?vid=StandardCategory&cid=3>.

<sup>10</sup> Carter, William P. L. Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales, Report to the California Air Resources Board, Contracts No. 03-318, 06-408, and 07-730, Revised January 27, 2010, <http://www.cert.ucr.edu/~carter/SAPRC/saprc07.pdf>, accessed 9/28/2012.

<sup>11</sup> Updated Maximum Incremental Reactivity Scale And Hydrocarbon Bin Reactivities For Regulatory Applications, Prepared for California Air Resources Board Contract 07-339 by William P. L. Carter, College of Engineering Center for Environmental Research and Technology, University of California, Riverside, CA 92521, Revised January 28, 2010.

<sup>12</sup> Carter, William P. L. , Luo, Dongmin, Malkina, Irina L., Investigation Of Atmospheric Ozone Formation Potentials Of C12-C16 n-Alkanes, Report to The Aluminum Association, Contract AA1345, October 28, 1996, <http://www.cert.ucr.edu/~carter/pubs/alkrept.pdf>, access 9/27/2012

A more thorough analysis of the results shown in Table 1 (Page 4) reveals that the work actually support the LVP exemption for consumer products. The ambient evaporation results labeled as “Time to 100% evaporation” in Table 1 correlate very well with their reported vapor pressures at 25 °C with the single exception being C9-C16 Hydrotreated Light Distillate.<sup>13</sup>

The evaporation results also can be shown to properly predict the regulatory classification (LVP versus VOC) when a cutoff value of *ten days* (rather than the 180 days reflected by the authors) is used in the column labeled “Time to 100% evaporation” as shown in Table 1. Three of the four compounds with “Time to 100% evaporation” values less than ten days are classified as VOCs; the single exception is Light Distillate which is classified as LVP.<sup>14</sup> The other 17 compounds with “Time to 100% evaporation” values greater than ten days are classified as LVPs.

Thus, these results show that compounds that evaporate fast are VOCs and compounds that evaporate slowly (if at all) are LVPs; VOCs therefore indeed can be classified by their vapor pressure. Correspondingly an LVP that is unlikely to enter the vapor phase will have a lower potential for ozone formation (discussed in more detail below). All this is consistent with the current LVP exemption for consumer products.

The “Overall Ambient Evaporation Results” in Figure 1 (Page 6) also appear generally accurate, and largely consistent with results obtained in many laboratories for most of these materials. However, the assignments of “Volatile,” “Semi-Volatile” and “Non-Volatile” are purely subjective, and not directly relevant to determination of which materials should be classified as VOCs by the regulatory definition. More specifically, the ability for a compound to temporarily enter the vapor phase does not demonstrate the ability to persist in the vapor phase sufficiently to make it available to significantly contribute to ambient atmospheric

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<sup>13</sup> The chemical identity of light distillate referred to by the authors and corresponding data appears to be in question. The C9-C16 carbon number range appears to come from the description of CAS# 64742-47-8 which also includes a boiling range of 150-290°C, while the authors cite a boiling range of 216-278°C. It does not appear to match any ASTM D86 boiling ranges for products on the Calumet website. Additionally a C9-C16 carbon number designation is inconsistent with a boiling range of 216-278°C. Using the boiling points of normal paraffins to define carbon number bins, as is customary for hydrocarbons, the carbon number range for 216-278°C should be C13-C16. Boiling points above 216°C indicate that this particular material should be LVP-VOC. It is possible to have VOCs and LVP-VOCs within the CAS# 64742-47-8 definition of light distillate, and determinations of VOC or LVP-VOC should be by the actual boiling range of each product, which is why the US EPA provides a range of vapor pressures for light distillates. CAS# 64742-47-8 is associated with three separate ingredients used in consumer products in the CSPA Consumer Product Ingredients Dictionary (First Update, Second Edition, October 2012), and is therefore not useful in specifying a specific hydrocarbon mixture.

<sup>14</sup> USEPA reports Light distillate vapor pressure ranges from 0.03 to 5.4 mm Hg at 25°C, so it may be a LVP depending on the particular mixture tested. SCREENING-LEVEL HAZARD CHARACTERIZATION Kerosene/Jet Fuel Category, March 2011, pg. 9, [http://www.epa.gov/chemrtk/hpvis/hazchar/Category\\_Kerosene-Jet%20Fuel\\_March\\_2011.pdf](http://www.epa.gov/chemrtk/hpvis/hazchar/Category_Kerosene-Jet%20Fuel_March_2011.pdf).

photochemistry, nor is it indicative that a compound has a predominately atmospheric environmental fate.<sup>15</sup>

The authors consider only pure solvents evaporating from open dishes or other methods designed to aggressively evaporate solvents; that may not represent actual product formulation and use which have very different conditions. In most cases these solvents are combined with other ingredients, such as surfactants, polymers and other lower vapor pressure analogues that inhibit evaporation or the solvent may also react with other ingredients and remain locked in the product. During product use, the ingredients may be contained in such a way that opportunities for evaporation are reduced or eliminated. There may be retention of the spent material in an applicator that is subsequently discarded and removed to a landfill or rinsed down a drain. Emissions from landfills and sewage treatment facilities are independently calculated and these materials may be completely retained or degraded. During use and disposal these types of consumer products are not usually discharged directly into the air, therefore a fugacity model must be used to demonstrate what component of the solvent might escape to air when discharged to another medium. Even for consumer products whose use results in emission to air, fugacity modeling is needed to determine whether the LVP or VOC compound remains in the air in the vapor phase and has the potential to engage in atmospheric photochemistry, or partitions out into other environmental media where it will be biodegraded.

The following table shows the results of subjecting some of the compounds and materials from “Overall Ambient Evaporation Results” in Figure 1 (Page 6) to evaluation using a Level III multi-media fugacity model (LEV3EPI) within the U.S. EPA EPI Suite v4.1.<sup>16</sup> The environmental distribution predicted in this model show that the materials considered LVPs in consumer product regulations often have environmental fates predominantly in water and soil rather than air, and therefore have limited availability to participate in atmospheric photochemistry and thereby fail to significantly promote tropospheric ozone formation. These data clearly show that most LVPs, and many VOCs as well, do not contribute significantly to ambient air photochemistry or formation of tropospheric ozone.

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<sup>15</sup>Final Proceedings Workshop on Combining Environmental Fate and Air Quality Modeling Organized by the Reactivity Research Working Group's Atmospheric Availability and Environmental Fate Subgroup, June 27-29, 2000, Research Triangle Park, NC, [http://narsto.org/sites/narsto-dev.ornl.gov/files/Appendix\\_F\\_Vol%26Fate.pdf](http://narsto.org/sites/narsto-dev.ornl.gov/files/Appendix_F_Vol%26Fate.pdf), Accessed 9/25/2012

<sup>16</sup><http://www.epa.gov/oppt/exposure/pubs/episuite.htm>, accessed 9/26/2012

## Attachment D - CSPA Comments on ARB Agenda Item # 13-2-2

**Table 1: Vö and Morris (2012) selected organic compounds sorted by “Time to 100% Evaporation” with added environmental distribution results from the LEV3EPI™ model. \*Non-volatile (NV), semi-volatile (SV), and volatile (V)<sup>17</sup>**

Compound name	Classification based on Evaporation at 6 months*	Regulatory Classification in Consumer Product Regulations	Time to 100% Evaporation (days)	Vapor Pressure (mm Hg @ 25°C)	Predicted Partitioning			
					Air (%)	Water (%)	Soil (%)	Sediment (%)
Isopropyl Alcohol (IPA)	V	VOC	0.9	33	4.58	45.2	50.1	0.0856
Ethyl Lactate	V	VOC	1.9	1.2	3.61	43.7	52.6	0.0818
C9-C16 Hydrotreated Light Distillate (Light Distillate)	V	Partial VOC/ Partial LVP	1.9	<0.01 to 0.3	22.4	69	2.51	6.15
N-Methyl pyrrolidinone (NMP)	V	VOC	9.2	0.5	0.066	32.5	67.3	0.0697
Benzyl Alcohol	V	LVP	14	0.14	1.03	34	64.8	0.0929
Dodecane (C12)	V	VOC	16	0.3	22.4	69	2.51	6.15
Propylene Glycol	V	LVP	63	0.13	0.397	34.5	65	0.061
Ethylene Glycol	V	LVP	126	0.09	1.44	36.1	62.4	0.0638
2,2,4-Trimethylpentane diol Diisobutyrate	V	LVP	147	0.004	0.85	18.6	80	0.503
2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	V	LVP	154	0.01	0.883	29.6	69.4	0.0906
Pentadecane (C15)	SV	LVP	>180	0.01	11.1	72.4	5.61	10.9
Dipropylene Glycol	SV	LVP	>180	<0.01	0.0771	38.4	61.5	0.0718
2-Methyl Hexadecane	SV	LVP	>180	<0.01	7.46	80.2	3.5	8.82
Hexadecane (C16)	SV	LVP	>180	0.005	3.46	37.5	55	4.08
Naphthenic Oil (Hynap N60HT)	SV	LVP	>180	<0.001	unknown	unknown	unknown	unknown
Heptadecane (C17)	SV	LVP	>180	<0.001	10.4	78.4	5.72	5.44
Naphthenic Based Metal Working Fluid (MWF)	SV	LVP	>180	unknown	unknown	unknown	unknown	unknown
Alkyl Alkanolamine	NV	LVP	>180	<0.01	0.000728	37.8	62.2	0.071
Methyl Palmitate	NV	LVP	>180	<0.001	1.96	20.5	73.5	3.97
Soy Oil	NV	LVP	>180	<0.001	0.0103	17.8	82.2	4.97E-09
Glycerol	NV	LVP	>180	<0.001	0.484	35.3	64.2	0.0624

<sup>17</sup> The modeling study that provided the above partitioning data examined the environmental distribution of the selected VOCs using a Level III multi-media fugacity model (LEV3EPI™) within the USEPA EPI Suite™ (2012) software package which is based on the work of Mackay et al (1996). The model predicts the partitioning of compounds among air, soil, water, and sediment under steady state conditions for a default model environment. The model default input values were used in this analysis; environmental emission rates were 1000 kg/hr to air, 1000 kg/hr to water, 1000 kg/hr to soil, and zero emissions to sediment.

These data, shown in Table 1 above, clearly support the minimal potential atmospheric impact for many lower volatility compounds, particularly those compounds with high water solubility. Even more volatile (but polar and highly water soluble) compounds such as isopropanol and ethyl lactate (both VOCs) have only a limited percent of their emissions remain in the air, with the balance partitioned out into water and soil, where it is readily biodegraded. Even the non-polar hydrocarbon LVPs<sup>18</sup> are partially partitioned into other environmental compartments rather than remaining in the ambient air. The media into which discharge occurs can have a significant impact on the partitioning. Therefore, for product uses that result in emissions solely to other media (*e.g.*, water or soil), even lower air fates can be expected for these compounds.

The modeling study data above predicts that only limited percent of the LVP masses stay partitioned in the air, as shown in Table 1, not the 100% of the mass implied by the authors. LVPs prefer to partition into the water or soil environmental compartments. Other multi-media modeling studies, such as the study by Foster, *et al* (2006) have also reported that the less volatile chemicals partition into the soil and water, thus a lower fraction of the emitted mass reacts in the atmosphere and a significantly lower fraction of the emitted mass is a potential ozone precursor.<sup>19</sup> The study by Foster clearly showed that at volatilities below 10 Pa (0.075 mm Hg), hydrocarbons begin to partition from air in the urban environment to water, soil, vegetation and urban film.<sup>20</sup> The important role of urban films in the sorption and removal of organics from the air has been recognized more fully in recent years.<sup>21</sup>

The important question is “*does the exemption of LVP solvents reduce ozone formation.*” A careful scientific evaluation shows the answer to be yes: lowering volatility can be as important as lowering reactivity in lowering VOC emissions and ozone impacts. Several steps are required to form ozone via atmospheric photochemical reactions. The first step is that a consumer product has to be used in a manner that results in a vapor phase emission, and the second step is that the VOC has to remain in the vapor phase long enough to reach the ambient atmosphere, and then remain available in the vapor phase long enough to become engaged in tropospheric photochemistry. LVPs have more time to biodegrade or to distribute into other

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<sup>18</sup> The most non-polar compounds are C9-C16 Hydrotreated Light Distillate (Light Distillate), Dodecane (C12), Pentadecane (C15), 2-Methyl Hexadecane, Hexadecane (C16), Naphthenic Oil (Hynap N60HT), Heptadecane (C17), Naphthenic Based Metal Working Fluid (MWF), Methyl Palmitate and Soy Oil.

<sup>19</sup> The Role of Multimedia Mass Balance Models for Assessing the Effects of Volatile Organic Compound Emissions on Urban Air Quality”, Karen L. Foster, *et al*, *Atmospheric Environment* 40 (2006) 2986-2994.

<sup>20</sup> *Ibid.*

<sup>21</sup> “Modeling Urban Films Using a Dynamic Multimedia Fugacity Model,” *Chemosphere* 87 (2012) 1024-1031.



environmental compartments, such as water or soil, rather than distribute into the air and help form ozone.

The authors could have performed a more relevant study, such as measuring concentration of these VOCs in the air over time. As noted by Carter in his MIR studies, many organic materials are “sticky”<sup>22</sup> and this is an indication of how likely both VOC and LVP are to become incorporated in surface films and biological materials.<sup>23</sup> The evaporation studies would have been much more realistic had they included typical formulations and typical surfaces in the chamber, and then evaluated ambient concentrations of organic materials in air samples taken periodically. This would have been a more appropriate means for determining the potential vapor emissions of organic compounds in consumer products, especially in formulations in conditions consistent with typical usage.

Many of the materials that the authors classify as “Volatile Compounds” (Page 6) because they can evaporate within six months actually would not be expected to contribute significantly to ambient air VOCs. Even isopropanol and ethyl lactate, the most volatile compounds evaluated (and both VOCs), only have limited air fates, with the balance being biodegraded in water and soil. Propylene glycol and ethylene glycol, classified as LVPs, demonstrate only very limited air fate, again with most being biodegraded in soil and water. The two isobutyates, both LVPs by vapor pressure, also contribute little to air, and both have extremely low MIRs, near that of ethane and acetone, considered negligibly photochemically reactive. Benzyl alcohol, an LVP, also contributes minimally to air emissions.

The authors correctly note that some of the materials tested are “Non-Volatile Compounds,” (Page 8) but the category of materials that the authors label as “Semi-Volatile Compounds” due to their ability to evaporate as little as 5% over six months (Page 9) is overly broad. Dipropylene glycol was included by the authors, a material that can be expected to contribute only minimal emissions to the air (see data above). Even the C15, C16, and C17 hydrocarbons partially partition into soil and water, and also exhibit extremely low MIRs (0.50, 0.45 and 0.42), approaching that of ethane (0.26) and acetone (0.35), both exempted from the regulatory definition of VOC as negligibly photochemically reactive. If the MIRs for consumer product LVPs were attenuated by fugacity modeling, many LVPs could be shown to have ozone impacts smaller than ethane. (Indeed, many VOCs used in consumer products likewise would be demonstrated as negligible in their ozone impact.) In short, the exemption of LVPs in consumer

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<sup>22</sup> Carter, William P. L., Luo, Dongmin, Malkina, Irina L., Investigation Of Atmospheric Ozone Formation Potentials Of C12-C16 n-Alkanes, Report to The Aluminum Association, Contract AA1345, October 28, 1996, <http://www.cert.ucr.edu/~carter/pubs/alkrept.pdf>, access 9/27/2012

<sup>23</sup> For example, Corsi, Richard L., Won, Doyun, Rynes, Mike, "Sorptive Interactions between VOCs and Indoor Materials", *Indoor Air*, 11, 2001, 246–256.

products is consistent with the intent of the U.S. EPA in exempting compounds as negligibly photochemically reactive.

The results shown above are obtained from modeling wherein the materials are emitted into the ambient environment. If the environmental emission is solely in water or soil, with no direct air emission, the percentage of a material staying in those other environmental compartments is greatly increased. In addition, for indoor air emissions, a significant percentage of the emission of various materials might not reach ambient air due to sorption and degradation indoors.<sup>24</sup>

The studies of evaporation reported by Morris and Vö fail to account for the mass balance of materials. As noted in the fugacity models above, there are many potential fates for organic materials. Unless that fate is availability in the vapor phase for atmospheric ozone reaction, the materials should not be counted as VOCs by regulatory definition. At minimum, the evaporation studies should have been conducted in a closed space with sampling capability. Representative samples of air could then have been analyzed to demonstrate that the materials could have reacted with NO<sub>x</sub>. The difficulty reported by Dr. Carter, the principle atmospheric reactivity researcher used by both SCAQMD and CARB, in volatilizing these “sticky” compounds suggests that the materials are not likely to be available for atmospheric reactions.<sup>25</sup>

In comparing the use of various test methods to determine “VOC Content” of various materials, the authors correctly conclude that differences exist. (Pages 9-11) It is clear that these methodologies were designed for differing purposes. One commonality that should be noted in the three standard methods (GC, TGA and M24) is the use of high temperatures. Few if any consumer products are subjected to high temperatures during normal use, and tests using high temperatures might not correctly simulate actual air emissions at ambient temperatures. Many materials degrade or otherwise react at high temperatures in ways not seen at the ambient temperatures at which the products are designed to be used. This effort to redefine LVP-VOC does not acknowledge the possibility of thermal degradation for the tested materials.

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<sup>24</sup>For example, see Springs, M., J. R. Wells, Morrison, G. C.. 2011. “Reaction Rates Of Ozone And Terpenes Adsorbed To Model Indoor Surfaces.” *Indoor Air* 21 (4) (August 1): 319-327. Weschler, Charles J., Nazaroff, William W.. 2008. “Semivolatile Organic Compounds in Indoor Environments.” *Atmospheric Environment* 42 (40) (December 1): 9018-9040. Won, D, Rynes, M.. 2008. “Sorptive Interactions Between VOCs And Indoor Materials.” *Indoor Air* (January 1). Jia, C., S. Batterman, C. Godwin, S. Charles, Chin, J-Y. 2010. “Sources and Migration Of Volatile Organic Compounds In Mixed-Use Buildings.” *Indoor Air* 20 (5) (October 1): 357-369. Weschler, Charles J., Nazaroff, William W. 2010. “SVOC Partitioning Between The Gas Phase And Settled Dust Indoors.” *Atmospheric Environment* 44 (30) (September 1): 3609-3620.

<sup>25</sup> Carter, William P. L. , Luo, Dongmin, Malkina, Irina L., Investigation Of Atmospheric Ozone Formation Potentials Of C12-C16 n-Alkanes, Report to The Aluminum Association, Contract AA1345, October 28, 1996, <http://www.cert.ucr.edu/~carter/pubs/alkrept.pdf>, access 9/27/2012

The authors' evaluation of boiling point versus "% Non-Volatile" (as found in their evaporation study) in Figure 8 (Page 12) clearly demonstrates the unreliability of their study in predicting air emissions and ozone impacts. Boiling point correlates well with vapor pressure, since they are essentially the same attribute simply measured at different temperatures. But even boiling point and vapor pressure do not represent a straight-line correlation. It is important to understand that the use of the alternative boiling point criterion in the consumer products regulations is based on normal hydrocarbons, which have the highest boiling point for a given vapor pressure of the materials at 20°C. Polar organics of a given vapor pressure tend to have lower boiling points. The same is true of the carbon-number criteria, which correlates only very roughly with volatility when materials of very different chemistries are included.<sup>26</sup> Normal hydrocarbons have the highest carbon-number (C12) that can demonstrate vapor pressure above 0.1 mm Hg at 20°C. Therefore the alternative carbon-number and boiling point criteria for LVPs simply serve to avoid unnecessary vapor pressure determinations and can be permitted only when the vapor pressure is unknown or known to have correlation with a known vapor pressure.

The data in Figure 10 (Page 14), presented as "Correlation of Vapor Pressure and Ambient Evaporation Rates" does not show a correlation between "% Non-Volatile" and "Vapor Pressure" as the authors indicate, again demonstrating the unreliability of the authors' "% Non-Volatile" criterion. (Figure 8 shows that every material had either zero "% Non-Volatile Content" and/or zero vapor pressure.) Vapor pressure is a basic physiochemical property of every organic compound, and correlates significantly with atmospheric availability. "% Non-Volatile" as defined by the authors appears to have no such correlation.

Despite the author's errors previously mentioned regarding the Green Seal, EU and Canadian VOC/LVP criteria, the summary in Table 4 (Page 16), in conjunction with the information already noted above, provide clear evidence that the three test methods evaluated may be significantly overestimating the VOC emissions and ozone impacts for the materials and operations with which they are used.

The conclusions cited by the authors (Pages 17-18) represent a failure to understand the basic physical and chemical concepts that currently provide a scientific understanding of volatility, environmental fate, and atmospheric availability that can be used to determine what materials and uses can result in significant contributions to tropospheric ozone formation. A careful review and analysis of all data would show that lowering volatility is a valuable tool in lowering ozone formation, both in terms of lowering air emissions (lower volatility materials generally result in lower amounts of materials lost to evaporation during use), and lowering atmospheric

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<sup>26</sup> Both boiling points and carbon-number usually correlate well with volatility, however, within most closely-related groups of chemicals, e.g., linear alkanes, linear alcohols, etc.

availability and increasing alternative environmental fates. A major recommendation would be for the authors to have allowed an external peer review to ensure the scientific validity, completeness of contemporary review and improve the overall quality of the paper.

## **SUMMARY AND CONCLUSIONS**

Our scientific critique of this SCAQMD paper on volatility has identified numerous flaws and a basic misunderstanding of the environmental science and the atmospheric photochemistry, as well as the regulatory definition of VOC. Our critique uses publicly available and generally accepted scientific models to demonstrate that consumer product LVPs (and indeed many consumer product VOCs) do not participate significantly in atmospheric photochemistry or tropospheric ozone formation.

Regulatory policies cannot be changed by a single study that provides no practical alternatives. The six-month evaporation study is not a practical alternative to current regulatory criteria, nor is it relevant to the goal of reducing the impact of VOC emissions or their impacts on tropospheric ozone formation.

While the science is complex, and regulations need to be readily understandable to be workable, the consumer products regulatory approach of lowering volatility through an LVP exemption using a vapor pressure criterion is a valid and effective approach, and very comparable to the way relative photochemical reactivity is generally considered through exempting organic compounds with lower reactivity (i.e., lower ozone impact) than ethane.

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