Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

MEMORANDUM

Edmund G. Brown Jr.
Governor

TO: Randy Segawa
Environmental Program Manager I
Environmental Monitoring Branch

Original signed by Frank Spurlock for

FROM: Daniel R. Oros, Ph.D.
Environmental Scientist
Environmental Monitoring Branch

Frank C. Spurlock, Ph.D.
Research Scientist III
Environmental Monitoring Branch
916-324-4124

Original signed by

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SUBJECT: ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND OZONE REACTIVITY. PART 1: SPECIATING TGA -BASED VOLATILE ORGANIC COMPUND EMISSIONS USING CONFIDENTIAL STATEMENTS OF FORMULA

ABSTRACT

This memo describes a Confidential Statement of Formula (CSF)-based speciation/emission potential (EP) estimation procedure. EP refers the volatile fraction of a pesticide product under the conditions of the Department Pesticide Regulation's (DPR's) thermogravimetric analysis (TGA) method (Marty et al., 2010). EP is assumed to represent product volatilization under actual use conditions. Speciation refers to identification of the actual chemical species comprising the volatile fraction of a pesticide product. In this paper we document the EP estimation procedure and assess its accuracy by comparing product CSF estimated-EPs to measured-EPs. The volatile components of 134 nonfumigant products reported as used in the 1990 and/or 2007 San Joaquin Valley (SJV) ozone season pesticide volatile organic chemical (VOC) inventory were identified using product CSFs and an empirical vapor pressure (VP) cutoff. The total percentage of estimated volatiles in each product was then compared to TGA-measured EPs. The VP_{25C} cutoff (vapor pressure at 25C) that yielded the best agreement between estimated and measured EPs was approximately 0.05 Pa. Components with $VP_{25C} > 0.05$ Pa were classified as volatile, while those with $VP_{25C} < 0.05$ were classified as nonvolatile. A paired t-test demonstrated a small but significant bias in estimated EPs relative to measured values. The mean difference between measured and estimated EPs (TGA-measured EP CSF-estimated EP) was +1.4% (p=0.003), the measured TGA EPs being greater. This difference was attributable to inadequate or inaccurate product composition information in most cases. For some products, composition data for the concentrated manufacturing use products (MUP) used to formulate end use products (EUP) was not available. The net effect was a low bias in CSF-estimated EPs because unidentified volatile components in the MUP

(e.g. solvents) were not accounted for in the EUP CSF. However, the CSF-estimation procedure also identified products where TGA-measured EPs were substantially in error. This occurred when water was present in the liquid MUP used to formulate the EUP, but was not accounted for in the EUP TGA data submission. When this happens, the water volatilized during TGA analysis is incorrectly assumed to be a VOC and the TGA-measured EP is too high. An additional source of TGA error was due to the absorption of water by clays or other hygroscopic materials in certain dry EUPs, again causing an upward bias in the TGA-measured EPs. In spite of the deviations between TGA-measured and CSF-estimated EPs, overall the agreement between the two was good. Regression of estimated EPs on measured EP yielded a slope not significantly different than one (slope = 1.02; 0.99, 1.05; 95%CI) with an R^2 of 0.985. Recommendations include CSF analysis of additional products with the goal of refining the 0.05 Pa VP_{25C} cutoff, and more consistent use of CSFs in evaluating TGA data and correcting questionable data. Finally, the CSF analysis provides a method to estimate the composition of pesticide product volatile components, thereby supporting eventual incorporation of reactivity into the VOC inventory.

1. INTRODUCTION

The current pesticide volatile organic compound (VOC) inventory is a mass-based inventory that tracks pounds of VOCs emitted from agricultural and commercial structural pesticide applications. The inventory does not account for differences among VOCs in their ability to participate in ozone forming reactions, i.e. their "ozone reactivity." DPR recently proposed a pilot study to examine how ozone reactivity could be incorporated into the pesticide inventory (Oros, 2009). The objective of the study is to quantify the relative ozone reactivity of individual pesticide products. In estimating relative ozone reactivity, the first step is identify the composition of a product's volatile emissions (speciation). The second step is then to determine the product's relative ozone formation potential using individual component reactivity data. These reactivity data may include Maximum Incremental Reactivity or Equal Benefit Incremental Reactivity data, among others (Carter, 1994). This memorandum

- describes a method for speciating emissions using pesticide product CSFs,
- compares CSF-estimated and TGA-measured-EPs for several high VOC contributing products, and
- documents potential problems that arose when estimating VOC speciation using CSF data.

2. METHODS

A. Compilation of Confidential Statement of Formulas

The CSFs for pesticide products typically contain the following information: chemical name, source product name, Chemical Abstracts Service registry number, purpose in formulation

(e.g., inert or active ingredients[A.I.s]), and percentage by weight of the chemical in the formulated product. Individual chemicals listed in CSFs are primarily classified as either A.I.s or inert ingredients. The Code of Federal Regulations, 40 Code of Federal Regulations Part 180 (sections 180.910 – 180.960) outlines inert ingredients that the U.S. Environmental Protection Agency (U.S. EPA) has approved for use in pesticide products (<http://www.epa.gov/opprd001/inerts/lists.html>), and these "inerts" are used in pesticide products in California. DPR lists over 981 A.I.s and 13,417 pesticide products for use here in California (<http://www.cdpr.ca.gov/docs/label/actai.htm>, data accessed on December 24, 2009).

For this pilot study, registrant-submitted CSFs were compiled for the top nonfumigant VOC-emitting EUPs in the SJV in each of 2 years: the 1990 base year and 2007. When available, CSFs were also obtained for the MUPs used to formulate the EUPs. In total, CSFs were compiled for a total of 84 distinct California-registered products. The products (including their subregistrations and label revisions, as explained later) corresponded to 58% and 60% of SJV adjusted nonfumigant ozone season emissions in 1990 and 2007, respectively.

B. Classification of Product Components

Many pesticide products use the same chemical ingredients. These can function as an A.I., anti-caking agent, anti-foaming agent, dye, emulsifying agent, odorant, solvent, surfactant, or thickener. Except for solvents, most of these ingredients have low volatility. Many, such as surfactants, have high molecular weight and very low VPs. Such components are not espected to contribute significantly to tropospheric VOCs.

Active Ingredients: An A.I. is any substance or group of substances that prevents, destroys, repels or mitigates any pest, or that functions as a plant regulator, desiccant, defoliant, or nitrogen stabilizer. End use nonfumigant pesticide products are often formulated from MUPs. MUPs usually contain a high percentage of A.I., and may consist of the technical grade of A.I. only, or may contain inert ingredients, such as solvents or stabilizers, etc. that serve different functions in the product formulation. Most A.I.s are not sufficiently volatile to contribute to tropospheric VOCs due to their high molecular weight and low VPs.

Antifreezes: Antifreezes are used to prevent freezing of a pesticide product. Common antifreeze agents used in pesticide products are ethylene glycol and propylene glycol.

Emulsifying/Dispersing Agents: Emulsifiers have a hydrophobic and a hydrophilic end, which act by surrounding an immiscible molecule, including oils, and forming a protective layer keeping the molecules from clumping together. Dispersing agents are used to keep an emulsion

well dispersed. Emulsifier and dispersing agent compositions can include very large polymers of high molecular weight and low VP.

Odorants: Odorants are used as volatile indicators due to their distinctive odor and volatility. An odorant commonly used in pesticide products is methyl salicylate also known as wintergreen. The VP_{25} of methyl salicylate is comparable to some solvents.

Oils: Oils such as mineral oil and soybean oil generally function as solvents. Mineral oil is composed mainly of alkanes (typically 15 to 40 carbons) and cyclic paraffins, while soybean oil is composed mainly of unsaturated fatty acids including oleic acid ($C_{18:1}$), linoleic acid ($C_{18:2}$), linolenic acid ($C_{18:3}$). Oils are composed of a range of high molecular weight components that generally have low VPs.

Solvents: Organic solvents are liquids that are used to dissolve active ingredients. Examples of several solvents approved by U.S. EPA for use in pesticide products include: methyl isobutyl ketone, cyclohexanone and N-methyl-pyrrolidinone. Most solvents are volatile enough to contribute to tropospheric VOCs based on their low molecular weight and high VPs.

Solvent Mixtures: Solvent mixtures (e.g. aromatic 100, aromatic 150, aromatic 200) are also used in pesticide products. Aromatic solvent mixtures are generally distillation cuts with a range of volatile components and VPs. The major difference between the aromatic solvent mixtures is carbon number. which increases with distillation range. For instance, aromatic 100 is largely composed of $C_{9\text{-}10}$ dialkyl and trialkylbenzenes, aromatic 150 is composed largely of $C_{10\text{-}11}$ alkylbenzenes and aromatic 200 includes $C_{10\text{-}14}$ alkylnaphthalenes (Table 1).

Surfactants: Surfactants aid in suspending the A.I. when the product is mixed with a solvent. When applied in the field, surfactants may also allow easier spreading of a product by lowering the surface tension of the liquid. Surfactants are typically high molecular weight, amphoteric and possess very low or no volatility.

Other Agents: Carriers (e.g., clays, fruit pulp, crushed corn cobs, etc.), thickeners, anti-caking agents, anti-foaming agents, preservatives, and dyes are also used in non-fumigant products. Most are used in low amounts in pesticide products and generally have high molecular weight and low VPs.

Table 1. General composition and approximate component vapor pressures (VPs) of aromatic product solvent mixtures[A]

	aromatic 100	aromatic 150	aromatic 200	mean VP of chemical class
Total Aromatics (%)	>99.5%	>99.5%	>99.5%	Pascals/(N)[B]
CHEMICAL CLASS				
alkylbenzenes				
C8	~5-10%	<5%	<5%	924/(4)
C9	80%	<5%	<5%	328/(8)
C10	10%	58%	<5%	118/(17)
C11	<5%	12%	<5%	46/(4)
indanes/THN[C]	<5%	14%	6%	26/(4)
alkylnaphthalenes				
C10	<5%	11%	<5%	24/(1)
C11	<5%	<5%	52%	5.8/(2)
C12	<5%	<5%	20%	2.4/(4)
C13	<5%	<5%	8%	0.9/(2)

[A] Composition data: Krenek and Rhode, 1988; Vapor pressure data: Syracuse Research Corporation Environmental Fate Database, <http://www.syrres.com/eSc/efdb.htm>; U.S. EPA SPARC <http://www.epa.gov/Athens/learn2model/part-two/onsite/sparcproperties.htm> (SPARC references - Hilal et al., 2003a, 2003b)
[B] N = Number of chemicals in class used to calculate mean
[C] Tetrahydronaphthalenes

C. Analysis of Vapor Pressure for Determining Volatility

Vapor pressure at 25C (VP_{25C}) was used to discriminate between chemicals that did or did not volatilize under the experimental TGA conditions.

Vapor pressure: The pressure of a vapor in equilibrium with a condensed phase (liquid or solid). While VPs vary with temperature, we used each chemical's VP at 25°C as a relative measure of a chemical's tendency to vaporize at the TGA temperature of 115C.

VP_{25C} data were collected from various databases accessible via the worldwide web including the European Union's Footprint Pesticide Properties Database (<http://sitem.herts.ac.uk/aeru/iupac/index.htm>), California Air Resources Control Board's Consumer Product Solvent Database (<http://www.arb.ca.gov/db/solvents/all_cmpds.htm>), and Syracuse Research Corporation's Interactive Physical Properties Database (<http://www.syrres.com/what-we-do/databaseforms.aspx?id=386>). Because vapor pressure are

sometime variable, we compared database values with published literature data where necessary to identify an accurate VP_{25} for each chemical.

The VP_{25C} of common chemicals included in high use pesticide products from 1990 and 2007 years are shown in Table 2. From the data it is obvious that solvents generally have much higher VP_{25C} than most A.I.s. In a few cases the VP_{25C} of some nonfumigant A.I.s are comparable to those of low volatility solvents.

Table 2. Vapor pressures of common chemicals included in high use pesticide products from 1990 and 2007.

Chemical Name	CAS	VP at 25°C (Pa) unless noted	VP Reference
Active Ingredients			
Phorate	98-02-2	385	SRC
Pebulate	1114-71-2	12	SRC
EPTC	759-94-4	3	SRC
Butylate	2008-41-5	2	SRC
Molinate	2212-67-1	0.7	SRC
Naled	300-76-5	0.03	SRC
Diazinon	333-41-5	0.012	SRC
Trifluralin	1582-09-8	6.1E-03	SRC
Methamidophos	10265-92-6	4.7E-03	SRC
Metolachlor	51218-45-2	4.2E-03	SRC
Oxydemeton-methyl	301-12-2	3.8E-03	SRC
Alachlor	15972-60-8	2.9E-03	SRC
Chlorpyrifos	2921-88-2	2.7E-03	SRC
Dimethoate	60-51-5	2.5E-03	SRC
Thiram	137-26-8	2.3E-03	SRC
Metalaxyl	57837-19-1	7.5E-04	SRC
Fenpropathrin	39515-41-8	7.3E-04	SRC
Tribufos	78-48-8	7.1E-04	SRC
Ethofumesate	26225-79-6	6.5E-04	SRC
Methidathion	950-37-8	4.5E-04	SRC
Azinphos-methyl	86-50-0	2.1E-04	IUPAC
Carbaryl	63-25-2	1.8E-04	SRC
Prometryne	7287-19-6	1.7E-04	SRC
Fenamiphos	22224-92-6	1.3E-04	SRC
Dicofol	115-32-2	5.3E-05	SRC
Oxamyl	23135-22-0	5.1E-05	IUPAC
Propargite	2312-35-8	4.0E-05	SRC
Fluazifop-p-butyl	79241-46-6	3.3E-05	SRC

(Cont.)

Table 2. Continued

Chemical Name	CAS	VP at 25°C (Pa)	VP
Oxyfluorfen	42874-03-3	2.7E-05	SRC
Endosulfan	115-29-7	2.3E-05	SRC
Napropamide	15299-99-7	2.3E-05	SRC
Sethoxydim	74051-80-2	2.1E-05	SRC
Carboxin	5234-68-4	2.0E-05	SRC
2,4-D	94-75-7	1.9E-05	IUPAC
Cyanazine	21725-46-2	1.8E-05	SRC
Ethephon	16672-87-0	1.3E-05	SRC
Permethrin	52645-53-1	2.9E-06	SRC
Thiabendazole	148-79-8	5.3E-07	SRC
Cypermethrin	52315-07-8	4.1E-07	SRC
Clethodim	99129-21-2	3.5E-07	SRC
Esfenvalerate	66230-04-4	2.0E-07	SRC
Endothal	145-73-3	2.1E-08	SRC
Gibberellic Acid	77-06-5	1.7E-11	SRC
Solvents			
Methanol	67-56-1	16,932	SRC
Ethanol	64-17-5	7,906	SRC
Isopropyl alcohol	67-63-0	6,053	SRC
Toluene	108-88-3	3,786	SRC
Water	7732-18-5	3,173	SRC
Methyl isobutyl ketone	108-10-1	2,653	SRC
1-Methoxypropanol	107-98-2	1,667	SRC
Aromatic 100	64742-95-6	269	ExxonMobil
Monochlorobenzene	108-90-7	1,600	SRC
Ethylbenzene	100-41-4	1,280	SRC
p-Xylene	106-42-3	1,179	SRC
Cyclohexanone	108-94-1	577	SRC
Aromatic 150	64742-94-5	74	ExxonMobil
Kerosene	8008-20-6	387 (20°C)	CARB
1,2,4-Trimethylbenzene	95-63-6	280	SRC
d-Limonene	5989-27-5	264	SRC
Stoddard solvent	8052-41-3	133	CARB
Hexanol	111-27-3	124	SRC
2-Butoxyethanol	111-76-2	117	SRC
Cyclohexanol	108-93-0	107	SRC
Butyrolactone	96-48-0	60	SRC
Propylene glycol	57-55-6	17	SRC
Naphthalene	91-20-3	11	SRC

(Cont.)

Table 2. Continued

Chemical Name	CAS	VP at 25°C (Pa) unless noted	VP Reference
Aromatic 200	68477-31-6	5 (20°C)	ExxonMobil
Triacetin	102-76-1	0.3	SRC
Methyl oleate	112-62-9	0.0008	SRC
Other Ingredients			
Ethylene glycol	107-21-1	12	SRC
Methyl salicylate	119-36-8	5	SRC
Butylated hydroxytoluene	128-37-0	1	SRC
Glycerol	56-81-5	0.02	SRC

CARB. California Air Resource Board, Consumer Product Solvent

Database. Web site- http://www.arb.ca.gov/db/solvents/all_cmpds.htm
ExxonMobil Chemical. Website-
http://www.msds.exxonmobil.com/psims/psims.aspx
IUPAC. Pesticide Properties Database accessed via IUPAC Portal.
Website- http://sitem.herts.ac.uk/aeru/iupac/index.htm
SRC PhysProp Database. Syracuse Research Corporation. Website-
http://www.syrres.com/what-we-do/databaseforms.aspx?id=386

D. Speciation and Estimation of Emission Potential

Speciation: Speciation refers to identification of the actual composition of the VOCs emitted from a pesticide product. The purpose of this study was to create a robust method for speciating VOCs from a pesticide product by using the product's CSF. Table 3 illustrates a simplified CSF, including percent composition (%) of chemical ingredients (active and inerts) and their purpose in the formulation.

Table 3. Example CSF for a nonfumigant pesticide product

Chemical	Purpose	Percent by Weight (%)
A	Active Ingredient	10
B	Solvent	45
C	Emulsifier	2
D	Antifreeze	2
E	Water	40
F	Dye	1

Emission Potential: EP refers to the fraction of a product that is assumed to contribute to atmospheric VOCs. In this study, product EPs were estimated by summing the weight percent of all VOCs. For example, in Table 3 if ingredient B, a solvent, is identified as the only VOC in the product then the product EP is 45%, which is the weight percent (%) of ingredient B in the product. As a second example, if ingredients A and B are both identified as VOCs, then the product EP is 55%, the sum of weight percents (%) of ingredient A (10%) and ingredient B (45%). Thus, the problem of estimating product EPs from CSF data reduces to determining which chemicals are volatile and which are not. This issue is addressed in the next section.

E. Thermogravimetric Analysis

The potential for solid or liquid-based pesticide products to emit VOCs is estimated by TGA (DPR, 1994). DPR generally requires registrants to provide TGA analysis for newly registered liquid products. During TGA, pesticide products are heated in an environmentally controlled chamber and held isothermally until the rate of sample mass loss drops below a defined threshold. The mean of three replicate measurements is used to estimate a product EP. The TGA method uses a final holding temperature of 115°C (239°F) to facilitate volatilization and loss of water contained in a pesticide formulation.

The 115°C temperature has been criticized because ambient temperatures in agricultural areas where pesticides are applied are much lower. However, volatilization of chemicals depends on *both* temperature and time. In TGA, a relatively high temperature is used in conjunction with a very short testing interval. The 115°C TGA test regimen has a maximum duration of only 80 minutes. In contrast, actual volatilization of nonfumigant pesticides in the field occurs over characteristic time periods of weeks to month(s) (Ross et al., 1989; Seiber and McChesney, 1988; Seiber et al., 1991; Yates, 2006a; Yates, 2006b; Taylor and Glotfelty, 1989 and numerous references there-in). The high temperature used in the TGA test offsets the short test duration. Longer laboratory test periods would be experimentally difficult, if not impossible. The 115°C/80 minute maximum test TGA test regimen was determined based on a response surface analysis of different temperature/time combinations across a series of pesticide products. Details on the development of the TGA method for pesticides, method validation and inter-laboratory comparisons are described in Marty et al. (2010).

Carter and Malkina (2007) reported that ozone reactivities of chemicals with VP down to approximately 0.01 Pa may be effectively studied under laboratory conditions, and further suggest that such chemicals are likely to participate in gas phase reactions in the environment. As shown later, a comparison of product CSFs and TGA-measured EPs supports 0.05 Pa as a VP cutoff for distinguishing volatile product components *under experimental TGA conditions*. However, few products examined here had components with 0.01 Pa < VP < 0.1 Pa. Consequently, 0.05 Pa is an approximate cutoff, and additional product analyses is desirable to refine that cutoff value.

DPR currently assumes that volatilization under the short duration - high temperature TGA regimen approximates actual volatilization over the longer time intervals in the field. However, there is some evidence that a lower VP cutoff may be applicable for defining actual volatility in the environment. A recent paper prepared on behalf of the European Crop Protection Association evaluated 24 hr volatilization data from 190 experiments carried out with 80 crop protection chemicals (Guth et al., 2004). These studies were carried out to meet pesticide registration regulatory requirements. Based on those data, Guth et al. (2004) identified approximate lower VP limits of 0.001 Pa for volatilization from soil, and 0.0001 Pa for volatilization from crops. Below these limits they concluded “no noticeable volatility” is expected. Thus, the 0.05 Pa cutoff for identifying volatile components under TGA conditions may yield a low-biased estimate of actual post-application volatilization as it occurs in the field.

3. COMPARISON OF CSF-ESTIMATED EMISSION POTENTIALS AND THERMOGRAVIMETRIC ANALYSIS-MEASURED EMISSION POTENTIALS

In the absence of data demonstrating otherwise, DPR’s presumption is that the composition of all products that share the same primary EPA registration number are substantively the same. Consequently DPR assigns EPs determined for one product to all of it’s related sub-registrations and label revisions. In this study CSFs were estimated for a total of 84 distinct California-registered products with TGA measured EP data from the 1990 and 2007 SJV VOC inventories. Some products were used in both years, and a few of the 84 products were related label revisions or subregistrations. Consequently the 84 products represented 79 distinct EPA primary registration numbers (“Primary Registrant Firm Number-Label Number”). Most of the primary registration numbers represented at least two label revision or subregistered products that had been or were currently registered in California. Consequently the total number of (active and inactive) California products represented by the 79 distinct EPA primary registration numbers was 215. Of these, a total of 148 products were in one or both of the 1990 and 2007 inventories. The 148 products account for 58% and 60% of SJV adjusted nonfumigant ozone season emissions in 1990 and 2007, respectively. To estimate the EP from CSF data, the VP_{25C} of individual product components in each CSF were compiled. Components

with VP_{25C} >0.05 Pa were classified as volatile and their weight percent in the product summed to yield the CSF-estimated product EP.

In our initial comparisons, there were large differences (>10%) between CSF-estimated EPs and TGA-measured EPs in some cases. Most of these were attributable to unknown components in the EUP. A principal source of the unknowns was the MUPs used to formulate the EUPs. We were able to obtain MUP CSFs from the original product chemistry registration data submissions for approximately half of the cases and use these to identify the unknown components. Several of the unknowns were volatile solvents in the MUP that were subsequently added to the EUP during the manufacturing process. For these the CSF-estimated EPs were modified accordingly. In a few other cases, the unknown components turned out to be water. Because this water was not reported on the EUP CSF, the measured TGA was not properly corrected for the presence of this water in the original data submission. Consequently the TGA determination was inaccurate (high-biased). For the sake of comparisons here, water was treated as a VOC in the EP estimation procedure for these products. However, product EPs for all subregistered and label revision products of these primary registrations will be corrected in future inventory calculations and in subsequent reactivity calculations (Oros and Spurlock, 2010).

For seven other primary registration numbers where unknown components were > 4% of the EUP, the MUP CSFs could not be located. While some of these yielded relatively good agreement between CSF-estimated and TGA-measured EPs, others showed marked deviations-likely due to unidentified solvents in the MUPs used to formulate the EUPs. All seven were excluded from subsequent analysis to reduce the uncertainty in CSF-estimated EPs and to provide a consistent basis dataset for comparison of the two EP methods. Thus, the final basis data set consisted of 72 primary registration numbers representing 200 total products, of which 134 were in one or both of the 1990 and 2007 inventories. These 72 primary registration numbers represented 45% and 54% of SJV adjusted nonfumigant ozone season emissions in 1990 and 2007, respectively.

Based on a t-test of paired differences between measured and estimated EPs (difference = TGA measured EP-CSF estimated EP), there was a small but significant difference between estimated EPs and the measured values (paired t-test, $p=0.003$). The mean difference between measured and estimated EPs was 1.4%, the TGA EPs being greater. There were two causes for these differences: error in the CSF-estimation procedure and error in the experimental TGA determinations. In the CSF estimation procedure there were numerous products with small amounts of unknown components, even after censoring those products with > 4% unknowns. In the case where these are volatile, the resultant CSF-estimated EPs were low-biased. However, when water is present as an unknown in the MUP, either due to introduction in the MUP or absorption by hygroscopic materials such as clays, the TGA value will be high-biased. We have observed several products in this study and elsewhere that contain bentonite, kaolin or other finely-divided high surface area materials, and that also yield nonzero EPs even though they

contain no volatile organic chemicals. For example, a recent FTIR analysis analysis of TGA emissions from six sulfur products concluded that the observed mass loss was attributable to water (McConnell et al., 2008). The result of this artifact is a high-bias in TGA-measured EPs.

Finally, there is evidence that DPR's basic assumption, that "the composition of all products that share the same primary EPA registration number are substantively the same" may not always be true. For example, one primary EPA registration number had two CSFs submitted at different times that differed substantially in percentage of volatile solvent and other components. Composition differences between products that share the same primary EPA registration number will be especially problematic in situations where the CSF of one is compared to the TGA data for another.

Overall the agreement between estimated and measured EPs was quite good, with the 5th - 95th percentile range of (TGA measured EP - CSF estimated EP) of -3% to 7% (Figure 1). A regression of CSF-estimated EPs on TGA-measured EPs yields a slope that is not significantly different than one (0.99, 1.05; 95%CI; Figure 2). We conclude that pesticide emissions under TGA conditions can be accurately speciated using CSF analysis. It's also apparent that TGA and CSF analysis are complementary, and both should used to derive product EPs.

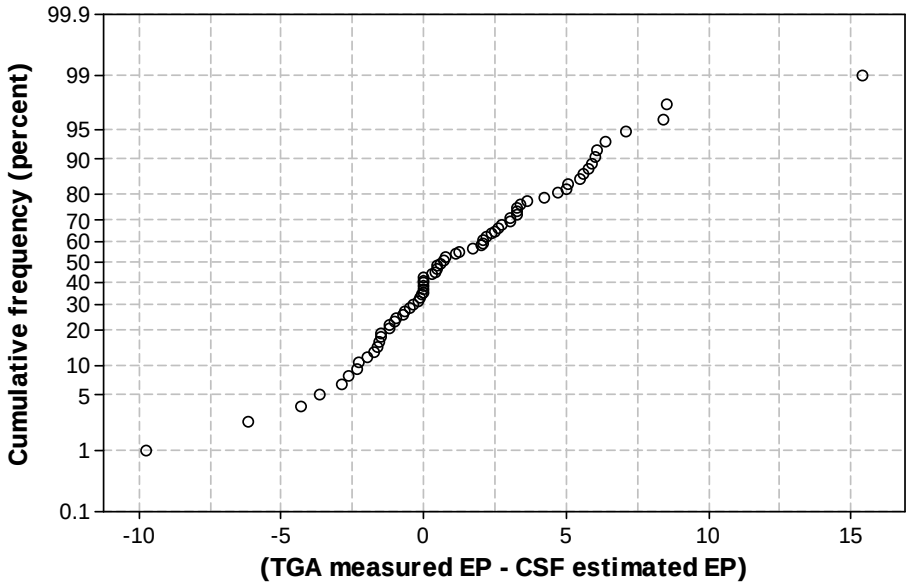

Figure 1. Cumulative frequency of (TGA measured EP-CSF estimated EP) for data compiled for 72 primary registration numbers.

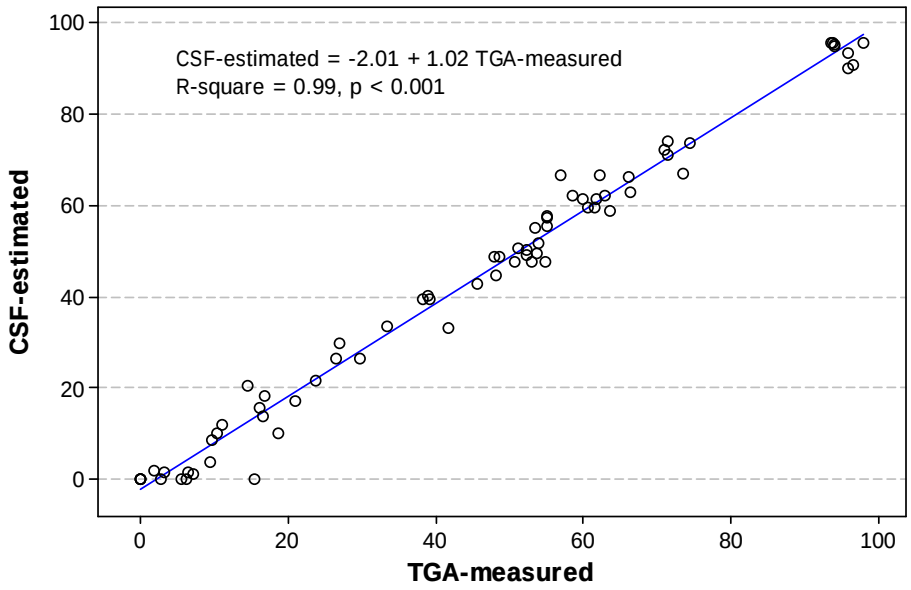

Figure 2. Regression of CSF-estimated EPs on TGA-measured EPs based on data compiled for 72 primary registration numbers.

4. CONCLUSION

In summary, a simple vapor pressure cutoff was used to distinguish "volatile" and "nonvolatile" product components under TGA conditions using product CSFs. While a few issues arose in compiling and analyzing the data, we anticipate these will be easily resolved as CSF analysis becomes routine. The problems included:

- difficulty obtaining complete composition data for some EUPs. One principal cause was difficulty in locating CSFs for MUPs used to formulate EUPs. In some cases this resulted in our inability to identify all volatile components in a product.

- difficulty locating product CSFs for older products where the primary registrant had sold the product or if the company re-organized.

- lack of composition data for proprietary mixtures such as certain surfactants and emulsifiers; these sometimes contain unidentified VOC components. While the total VOC contribution from such mixtures is relatively low in comparison to other pesticide product components (i.e. generally <<5%), they are a potential source of error when using CSFs to estimate EUP EPs.

The accuracy of the CSF-based EP estimation/speciation procedure was demonstrated using data compiled for 72 EPA registration numbers representing 134 products reported as used in the 1990 and/or 2007 SJV pesticide VOC inventories. Regression of CSF-estimated EPs on TGA-measured values yielded a slope not significantly different than one with a correlation coefficient $r > 0.99$ ($p<0.001$). A small bias was observed, with the mean of (TGA-measured EP-CSF-estimated EP) of +1.4% (*paired t-test*, $p=0.003$). This bias was attributable to incomplete product composition information for some products. However, the bias is comparable to the error in TGA analysis of some products. For example, formulations containing finely-divided hygroscopic materials such as clays may absorb water, leading to errors in TGA measured EPs.

DPR plans to retain TGA as the primary method for estimating product emission potentials. However, in spite of the small bias, the data support the use of CSF analysis in both review of TGA data and for speciating TGA emissions. Detailed CSF analysis should be viewed as complementary to the TGA EP determination method. There were a number of cases where problems or errors in the TGA determination became evident after review of product CSFs. Use of both TGA and CSF data to determine EPs will improve the accuracy of the inventory.

In most cases, CSF analysis allowed clear and unambiguous speciation of volatile components in pesticide products under TGA conditions. We recommend conducting further paired comparisons of CSFs and TGA data to refine our current 0.05 Pa vapor pressure cutoff used to classify components as to “volatile” or “not volatile” under TGA conditions.

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Mary-Ann Warmerdam
Director

Department of Pesticide Regulation

Edmund G. Brown Jr.
Governor

M E M O R A N D U M

TO: Randy Segawa
Environmental Program Manager I
Environmental Monitoring Branch

FROM: Frank C. Spurlock, Ph.D. *Original signed by*
Research Scientist III
Environmental Monitoring Branch
916-324-4124

DATE: January 28, 2011

SUBJECT: RESPONSE TO STAKEHOLDER COMMENTS ON PROJECT REPORTS: ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND EMISSION SPECIATION AND REACTIVITY BASED ON PRODUCT COMPOSITION

INTRODUCTION

The Department of Pesticide Regulation (DPR) invited stakeholder comment on two documents:

ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND OZONE REACTIVITY. Part 1: Speciating VOC Emissions using Confidential Statements of Formula, September 15, 2010 DRAFT, D. Oros and F. Spurlock

ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND REACTIVITY. Part 2: Reactivity-weighted emissions, September 15, 2010 DRAFT, D. Oros and F. Spurlock

These two reports summarize the results of a pilot DPR research project to evaluate scientific issues, uncertainties, and potential approaches for incorporating ozone reactivity into DPR's inventory of volatile organic compound (VOC) emissions. The initial project proposal (Oros, 2009) stated "DPR emphasizes that this is a proposal for an investigation to identify scientific questions and answers, as opposed to a proposal to implement new regulations at this time." In previous responses to stakeholders (Spurlock and Oros, 2009), DPR stated that "DPR does not propose to promulgate regulations or otherwise implement reactivity concepts into the VOC inventory at this time." In inviting comments on part 1. and part 2 memorandum above, DPR asked stakeholders:

- to focus their comments on the scientific/technical aspects of the documents, and
- that comments on policy issues or impacts on the state implementation plan (SIP) were not relevant.

Comments were submitted by the U.S. Environmental Protection Agency, (U.S. EPA), Region IX , Dow Agrosciences (DAS), the Western Plant Health Association (WPHA) and Exxon Mobil

Chemical Company (EMCO). This memorandum summarizes DPR's responses to submitted comments.

A. Department of Pesticide Regulation general response to all stakeholders

A1. Relevance. Several people provided comments that were not relevant to the scientific and technical evaluation of the two reactivity pilot project documents listed above. These included, among others, extensive discussion of the suitability of the currently accepted thermogravimetric analysis (TGA) method for determining pesticide product emission potential (EP), applicability of TGA to field conditions, the concept of "atmospheric availability," the putative need for NOx controls in conjunction with VOC controls to reduce ozone in certain geographic areas, and the need for development of nonfumigant emission adjustment factors to account for environmental fate processes that may mitigate nonfumigant VOC emissions. DPR has previously responded to these comments in letters to the WPHA dated October 20, 2008, and May 2, 2007, and in a 2009 memorandum (Spurlock and Oros, 2009). In this document, DPR does not respond to any comments that are not directly relevant to the scientific/technical content of the two reactivity pilot project documents listed above.

B. U.S. Environmental Protection Agency comments

B1. General Issue - Handling Confidential Business Information
"The Clean Air Act (CAA) contains specific requirements which give the public access to any records, reports or information obtained by EPA except in cases where trade secrets are involved." The comment goes on to describe potential conflict between confidential product composition information and CAA/SIP requirements that emissions data are public information.

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

B2. Thermogravimetric Analysis
"The TGA method, along with precision and bias data, should be submitted for approval if it will be used to determine compliance with a SIP approved rule."

DPR's Response
This comment on SIP requirements is outside the specific scientific/technical scope of the two documents.

B3. Reactivity-based regulation
"EPA has only allowed in very limited cases, the use of low vapor pressure as a condition to exclude a compound from a VOC limit. However, under a reactivity-based regulation, all VOCs should be counted as they all contribute to ozone formation, although at different rates."

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

B4. Referring to the Part 1. document
Page 11 concludes there is evidence that DPR's basic assumption that "the composition of all products that share the same primary EPA registration number are substantially the same" may not always be true. DPR concludes this may be problematic for estimating emissions. Can DPR estimate how large or small this issue may be?

DPR's Response
We are not sure whether, or how important, this putative issue might be. We anticipate the further analyses of product CSFs, as recommended in the Part 1 and Part 2 reports, may provide more information by allowing us to compare CSFs and TGA data of more products that share a common EPA registration number.

B5. Referring to Document 2
"To estimate the ozone forming potential of the unspeciated nonfurnigant products, DPR "assumes that the overall reactivity of unspeciated mass emissions is equivalent to the mean reactivity of the speciated product emissions". It is not clear why using the "mean reactivity" of the speciated emissions, which represent 32 and 34% of the SJV nonfumigant ozone season emissions, is an appropriate and conservative assumption to scale up the unspeciated nonfumigant fraction. "

DPR's response
The Part 2 report provides an illustrative example of estimating pesticide product VOC reactivity across the entire inventory. Given the limited scope of this pilot project, only a relatively small number of product CSFs were analyzed to provide product speciation data. If DPR decides to transition to a reactivity-based inventory, DPR recognizes that a larger set of products would have to analyzed. One the other hand, there will always be at least some products for which data will not be available so that speciation would have to be estimated. This would be analogous to defining default emission potentials as is currently done for certain products.

Change to DPR documents in response to comment B5, new text added in *italics*
The conclusion of Document 2 states that the two reports "provide the outline of a scientifically defensible method to incorporate reactivity into DPR's current mass-based VOC inventory." Additional work remains, including more accurate characterization of certain component reactivities [e.g. aromatics (Carter, 2009a; selected semi-volatile active ingredients; Table 2], *additional analysis of pesticide product CSFs and TGA data to explicitly speciate a larger portion of the inventory*, and additional analysis to refine the current vapor pressure cutoff (0.05 Pa) used to discriminate between volatile and nonvolatile product components.

C. Western Plant Health Association comments

C1
WPHA expressed concern over maintaining confidentiality of product formulation data used to speciate emissions.

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

C2. WPHA states
"We also continue to urge the DPR to include application factors for nonfumigant products as they've done with fumigants. The easiest way to begin, as a first step, would be to include a factor for soil incorporated herbicides and insecticides."

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

C3. WPHA states
"WPHA is concerned with the new definition for VOCs that establishes a cutoff of 0.05 Pa. This proposed standard is inconsistent with other VOC definitions in the industry and other regulatory authorities."

DPR's response
DPR did not propose a new definition for VOCs in the two documents. The vapor pressure cutoff was determined to identify which product components volatilize under TGA conditions. The regression analysis indicates that 0.05 Pa is an *approximate* vapor pressure dividing line for discriminating between chemicals that are volatile under TGA conditions and those that are not.

C4. WPHA states
"WPHA provides several comments and extensive discussion of the current TGA emission potential determination procedure, concluding: "As a consequence of a VOC limit of 0.05 Pa, products previously dismissed (<20% EP) would be brought back into the pesticide VOC inventory."

DPR's response
See General Comment A1.

C5. WPHA states
"WPHA recommends the DPR evaluate whether current VOC regulations and reformulation requirements are working."

DPR's Response
This comment refers to policy, so is outside the specific scientific/technical scope of the two documents.

C6
"WPHA recommends the DPR keep TGA as the primary initial screen for estimating emission potential, permit use of the CSF as the alternative method to estimate emissions potential where TGA data are not available, but also include the ability for further refinements based on atmospheric availability. There is no scientific or regulatory need to set such a low VOC standard as the proposed 0.05 Pa value."

DPR's response:
See General Comment A1.

C7
"WPHA is concerned DPR would use the most conservative MIR over EBIR. Further, we question if even the EBIR is adequate, given fluctuations in NOx levels. Is there an opportunity to consider another method even better than the EBIR that would represent ambient NOx levels, such as an "ambient air incremental reactivity?"

DPR's response
DPR has not committed to using MIR, EBIR or any other particular reactivity scale at this time.

C8
"Use of reactivity factors has gained some attention in California due to successful ozone level reductions in urban areas where VOC levels are the limiting factor. However, reductions in rural areas where NOx is the limiting factor have not proven so successful. Application of incremental reactivity does not fully account for ambient atmospheric conditions in rural or agricultural areas where the available NOx level is low, or even depleted due to the underlying high VOC levels."

DPR's response
See General Comment A1.

C9
"WPHA would like to have a better understanding of how the DPR would use reactivity for estimating SOFP (Specific Ozone Formation Potential). Which method would be used, which incremental reactivity factor(s) would be applied to the San Joaquin Valley air shed (Non-Attainment Area 5), how would reactivity factors be applied, and how would this change in procedures impact the State Implementation Plan (SIP) for pesticides?" . . . "It is also unclear how new data would be included in the inventory. Would the inventory be adjusted or recalculated? Use of reactivity would significantly impact the estimated inventory baseline and

any resultant obligations to reduce baselines" . . . . . "The lack of clear direction of how reactivity would be used still does not get to the heart of the matter, which is the reaction-limiting NOx levels present in rural or agricultural air sheds. . . . "

DPR's Response:
As DPR noted to stakeholders, stakeholder comments on policy issues or impacts on the SIP were not relevant. The WPHA comment is outside the specific scientific/technical scope of the two documents.

C10
"The determination of unspeciated VOCs based on Equation 3, using average speciation reactivity factors, raises some concern."

DPR's response
See response to comment B.5.

C11
"Incorporating reactivity would not be consistent with how "consumer products" pesticides are evaluated."

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

C12
"WPHA believes it is premature to discuss further changes to the existing inventory method if there is no need to do so."

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

D. Dow Agrosciences comments

D1
". . . .. the proposed approaches for inserting reactivity into the current mass-based VOC emission regulations and a new more stringent definition of VOC raise some concerns" . . . ."Dow AgroSciences also reformulated other products to reduce their estimated VOC emissions potential.".....

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

D2
"Speciation to Predict Estimated VOC Emissions". . . . "we do not believe speciation should be a method initiated by DPR for existing registered products."

DPR's Response
DPR plans to retain TGA as the primary method for determining EPs. However DPR also plans to use CSF analysis on a case-by-case basis to estimate EPs when TGA data are unavailable or to troubleshoot questionable TGA-based EPs.

Change to DPR document 1, Conclusion section in response to comment, new text added in *italics*
"DPR plans to retain TGA as the primary method for estimating product emission potentials. In spite of the small bias, these data support the use of CSF analysis in both review of TGA data and for speciating TGA emissions. Detailed CSF analysis should be viewed as complementary to the TGA EP determination method . . . Use of both TGA and CSF data to determine EPs will improve the accuracy of the inventory."

D3
"III. Proposed new VOC Standard' . . . "The proposed new VOC cut-off of 0.05 Pascals appears to be a new definition for a VOC."

DPR's Response
The 0.05 Pa cutoff is not a definition for a VOC. See response to comment C3.

D4
"IV. Reactivity proposal further overestimates VOC emissions". . . "We acknowledge the Department's inclusion of Equal Benefit Incremental Reactivity (EBIR) to more closely approximate rural air sheds. However, the proposal stops short of defining when MIRs vs. EBIRs would be appropriate. This would be critical to a registrant's understanding to accomplish "real" reductions. We respectfully recommend the research proposal should clearly detail what specific circumstances it proposes to employ MIRs vs. EBIRs."

DPR's response
DPR has not committed to using MIR, EBIR, or any other particular reactivity scale at this time.

E. Exxon Mobil Chemical Company Comments

**** EMCO Comments on report #1 ****

E1
"VOC reductions, on any basis (mass or reactivity), will only be effective in reducing ozone in an area that is VOC-limited or that is transitional between VOC and NOx limited. Negligible changes to improve air quality would be expected in NOx-limited areas . . . ."

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

E2
"ExxonMobil believes that, as a first step, air quality modeling (such as the Comprehensive Qir Quality Model with Extensions, Community Multi-Scale air QualityModel) should be conducted to understand the parameters that impact air quality in California's agricultural air sheds."

DPR's Response
This comment is outside the specific scientific/technical scope of the two documents.

E3
"Environmental fate, atmospheric availability and product life cycle considerations are critical to understanding and assessing overall impacts on VOC emissions and ozone (O3) formation potential from pesticide products."

DPR's response
See General Comment A1.

E4
"The creation of a CDPR VP cut-off results in another, new definition for a VOC."

DPR's Response
The 0.05 Pa cutoff is not a definition for a VOC. See response to comment C3.

E5.
"CDPR's initial calculation of a vapor pressure (VP) cut-off is based on a limited dataset, thus it is premature determine a VP cut-off of 0.05 Pa." . . . ."ExxonMobil agrees with CDPR that more data points are needed to determine a VP cut-off, and that multiple cut-off values should be evaluated with appropriate statistical analyses before concluding on a defined VP VOC cut-off."

DPR's Response
DPR and EMCO are in agreement that the 0.05 VP cutoff is approximate and that more data are needed. No response is necessary.

E6
"CDPR should document their assumptions that the use of the short-term, high temperature TGA emissions potential (EP) data can be used to extrapolate field conditions where temperatures do not approach the 115C/80 minute maximum test TGA test regimen."

DPR's response
See General Comment A1.

E7
"Current approach proposed by CDPR assumes 100% EP for non-fumigants, whereas, certain liquid formulations may have physical-chemical characteristics that retard emission rates and are recognized to absorb/absorb to soil, further limiting potential emissions."

DPR's response
See General Comment A1.

E8
"CDPR should correct VP values presented in Table 2 and ensure that the values they are using are in their calculations are relevant for the products under evaluation."

DPR's response
The vapor pressure values in Table 2 were changed. This has no effect on the final results.

**** EMCO Comments on report #2 ****

E9
"EMCO has concerns with three assumptions: 100% of the estimated VOC is volatilized, whereas there are methodologies to estimate adsorption/absorption of VOC components," . . . "100% of the estimated VOC content reacts to form O3, thus ignoring alternate environmental fates and atmospheric availability". . . "a single application method adjustment factor of 1.0 is sufficient for all non-fumigant products."

DPR's response
See General Comment A1.

E10
"CDPR should determine and apply the most appropriate reactivity metric for the agricultural air sheds."

DPR's response: DPR has not committed to using MIR, EBIR or any other particular reactivity scale at this time.

E11
"CDPR should take into account and incorporate environmental fate and atmospheric availability concepts into the product adjustment factors."

DPR's response
See General Comment A1.

E12
"CDPR should evaluate and document the basis for their assumption that non-speciated mass emissions can be based on the average value of speciated emissions."

DPRs Response
See Response to Comment B5.

REFERENCES

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Spurlock, F. and D. Oros. 2009. Response to stakeholder comments on pilot project proposal: estimating pesticide product volatile organic compound emission speciation and reactivity based on product composition. August 14, 2009 Memorandum to R. Segawa, Environmental Monitoring Branch. Available on-line at: <http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/2159_segawa.pdf>.