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M E M O R A N D U M

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DATE: August 17, 2009

SUBJECT: PILOT PROJECT PROPOSAL: ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND EMISSION SPECIATION AND REACTIVITY BASED ON PRODUCT COMPOSITION

SUMMARY

This memorandum proposes a pilot project to estimate speciation and ozone reactivity of pesticide products containing high levels of volatile organic compounds (VOCs). Speciation refers to the actual composition of VOCs emitted from individual products, while ozone reactivity refers to the tropospheric ozone formation potential of VOC emissions from individual products. The goal of this pilot study is to evaluate the scientific issues, uncertainties, and resources needed to account for reactivity in the Department of Pesticide Regulation's (DPR's) emission inventory, and identify potential approaches to resolving these scientific and practical issues. In the longer term, this scientific investigation aims to improve the scientific basis for the DPR's VOC regulation program, and provide additional scientific data in support of more efficient and defensible VOC regulatory approaches.

The general approach will be to develop a procedure for using product composition data as reported in each product's Confidential Statement of Formula (CSF), thermogravimetric (TGA) emission potential (EP) data, component vapor pressure data and reactivity data as the basis to estimate product speciation and reactivity. This initial study will focus on the top 80 VOC-emitting products in each of two years: the 1990 base year and the most recent 2007 inventory year. These top 80 products account for 90 percent and 85 percent of adjusted San Joaquin Valley pesticide ozone season emissions in 1990 and 2007, respectively.

This proposal has been submitted to external stakeholders for comment. The summarized comments along with DPR's responses are provided as an appendix to this proposal. 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.

OBJECTIVE

- Estimate speciation of VOC emissions for individual pesticide products from product CSFs and TGA-measured EP data.

- Estimate relative ozone formation potential using a reactivity metric such as the maximum incremental reactivity (MIR) scale, where MIR = [g Ozone produced] / [g VOC].

BACKGROUND

Since inception, the VOC regulatory program has focused on the VOC content of pesticides. For instance, DPR recently initiated a reevaluation of "certain liquid agricultural and commercial structural pesticide products," requiring registrants to reformulate high-VOC pesticide products to low-VOC formulations. The purpose of the reevaluation was to reduce the mass of pesticidal VOC emissions in ozone nonattainment areas. However, it is well documented that different chemicals, such as volatile solvents, exhibit different ozone formation reactivities in the atmosphere and in chamber experiments (e.g., Figure 1) (Carter 1990; Carter 1994; Carter et al., 1995; Russell et al., 1995; Bergin et al., 1998; Carter et al., 2005; Carter 2007; Carter and Malkina 2007). Consequently, reformulation of pesticide products may not necessarily result in lower ozone formation if the reformulated mixture includes more atmospherically "reactive" chemicals. A more direct and efficient method for decreasing ozone formation is to identify product constituents with the greatest potential to form ozone (by scientific evaluation), and reduce their presence by reformulation.

Similarly, the standard TGA adopted by DPR to estimate product emissions does not address chemical reactivity. As a result, TGA-based product emission estimates do not reflect the relative ozone formation potential of different products. This means that DPR's current approach is inefficient in the sense that low ozone-contributing products are given the same regulatory attention as products with high ozone formation potential.

PROPOSED METHODS

Speciation

For fumigant products that are essentially 100 percent volatile (such as pure chloropicrin), the product MIR will be equal to the MIR for the pure active ingredient (i.e., chloropicrin). However, liquid products such as emulsifiable concentrates are typically mixtures of several components, some of which are essentially nonvolatile. Therefore, the initial step for those products will be to estimate speciation of mass emissions. This may be done using individual pesticide product TGA data and product composition data as reported in CSFs. Different approaches to this problem will be investigated. An initial speciation approach will be to attempt

to develop a model relating TGA-based product emission potentials to the explanatory variables of individual constituent vapor pressures and their composition percentages in the individual products. One potential difficulty is that (volatile solvent) components in CSFs are usually reported in terms of commercial product names of solvent mixtures. These products are, in many cases, distillation cuts that contain many components. Data such as in Table 1 may be compiled to characterize composition and volatility of those commercial solvent mixtures. The former problem can be addressed by use of material safety data sheets for specific products, literature information on composition of typical solvent mixtures or blends used in pesticide formulations, or Air Resources Board (ARB) data on solvent mixture properties. Available at: <http://www.arb.ca.gov/db/solvents/solvent_pages/Hydrocarbon-HTML/Aromatic_150.htm>. Many other product components can likely be excluded based on very low vapor pressures. These probably include many surfactants and emulsifiers. A second potential problem is nonideal chemical volatilization behavior, wherein the volatility of a mixture may not be simply related to the weighted sum of the individual components' vapor pressures. In previous discussion with registrant formulation chemists, they have suggested that TGA-based emission potentials can be accurately estimated based on solvent content. This implies that nonideality may not be a severe problem. Ultimately the potential impact of nonideal volatilization behavior will need to be evaluated after product compositions are classified by chemical class and compared to TGA data.

Finally, an alternate approach to estimating product volatility may be to use multivariate statistical techniques to relate the composition of a large number of products to their measured TGA data. Such methods may include principal components analysis, factor analysis, or multiple regression of TGA EP on chemical class composition using data for multiple products.

Reactivity

VOC/NOx ratios in rural agricultural areas may be quite different than in urban areas. Consequently, the suitability of different available metrics for describing relative reactivity in rural airsheds will be investigated. One metric that will be considered is MIR. The ARB has used MIR values for a number of scientific and regulatory applications. The MIRs values were originally derived from the SAPRC-99 chemical mechanism, and ARB plans to update the values based on the newly updated SAPRC-07 mechanism in 2009. The SAPRC-07 mechanism is the current state of knowledge, and was developed by Dr. William Carter, UC Riverside (Carter 2007). The MIR scale is based on measured ozone formation data of VOCs with hydroxyl radical,, NO, and μv light obtained under standard ambient conditions in environmental chamber experiments. MIR values for ~1100 individual VOCs (including certain pesticides) or mixtures and various classes of hydrocarbon solvents have been developed. The SAPRC-07 chemical mechanism and MIR database is periodically updated to include new chemicals as they are identified and submitted for MIR determination. MIR values for selected pesticides have been reported (Table 2) (Carter et al., 1997; Carter and Malkina 2007).

In using the MIR (or other reactivity scale), the overall relative product VOC reactivity can be estimated from a product's speciation profile. Table 3 provides an illustrative example for a theoretical product showing how speciation data and component MIRs can be used to calculate a product's effective MIR using Equation 1:

[1] $$MIR_{product} = \sum_i f_i \times MIR_i$$

where, f_i = speciation fraction = mass fraction of the ith VOC component in the product, and MIR_i is the maximum incremental reactivity of the ith component ([g Ozone produced] / [g VOC]) . The ozone formation *potential* for an application of a product may then be calculated as:

[2] $$OFP = lbs\,applied \times EP \times AMAF \times MIR_{product}$$

where, OFP = ozone formation potential (lbs ozone), EP = product emission potential, and AMAF = application method adjustment factor (Barry et al., 2007; typically assumed 1 for nonfumigants).

COORDINATION

DPR staff will coordinate this effort with the Research Division of the ARB. Preliminary contacts with ARB staff have indicated a high level of interest in this pilot project. ARB has adopted reactivity-based VOC regulations. Available at: <http://www.arb.ca.gov/research/reactivity/reactivity.htm> for fuels (as part of the clean fuels/low emission vehicle program) and for aerosol coatings, and is currently evaluating other VOC sources (such as consumer products and architectural coatings) for reactivity-based regulation. The U.S. Environmental Protection Agency has adopted a reactivity-based regulation for aerosol paints, similar to the ARB's aerosol coatings regulation. DPR staff will work closely with ARB personnel who are responsible for MIR data development.

CONFIDENTIALITY

Because the use and protection of a registrant's CSF is necessary, DPR will identify "best practices" for handling confidential CSF information and coordinate with ARB where needed to meet our special needs. Current security efforts include limiting information access to selected personnel and using password protected computers and files. Because there are a limited number of inert ingredients used in formulating pesticide products, MIRs empirically derived for a single chemical (e.g., single active or inert ingredient) or mixture (e.g., aromatic 100, aromatic 150 and aromatic 200) can be used for determining the product MIR of many formulations that include that chemical or mixture. In addition, ARB has developed a system of 24 "bins" of hydrocarbons

that provides MIR values for mixtures based on their volatility and the chemical classes that they contain (e.g., aromatics or cyclo-alkanes).

BENEFITS

Reactivity-based VOC control regulations will be more scientifically defensible and more cost-effective than traditional mass-based methods for estimating and regulating emissions. A reactivity-based inventory more accurately reflects actual potential ozone impacts of pesticide products than our current mass based inventory. An additional benefit is that DPR will not have to regulate numerous chemicals that do not contribute to ozone formation, but rather will be able to focus on those that substantively contribute to ozone formation. Through reactivity determinations utilizing the SAPRC-07 chemical mechanism, reactive and nonreactive chemicals can be identified. Finally, the use of the MIR values will provide more flexibility and cost savings to the registrants when formulating new and reformulating existing products. However, increased costs may be incurred in laboratory analytical work for enforcement purposes. This is because enforcement may require speciation, rather than just TGA to determine VOC content.

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Table 1. General composition and approximate component vapor pressures (VP) of aromatic 100, 150, and 200 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 Rohde, 1989; Vapor pressure data: Syracuse Research Corporation Environmental Fate Database, <http://www.syrres.com/eSc/efdb.htm>; U.S. Environmental Protection Agency SPARC. Available at: <http://www.epa.gov/Athens/learn2model/part-two/onsite/sparcproperties.htm>.
B. N = Number of chemicals in class; full chemical list and VP data given in appendix 1.
C. Tetrahydronaphthalenes

Table 2. Summary of pesticide compounds and calculated ozone impacts in the MIR scale. Source: Carter and Malkina (2007).

Compound (MIR)

Methyl bromide (0.03)
Methyl isothiocyanate, MITC (0.35)
1,3-Dichloropropenes (4.64)
Chloropicrin (2.18)
Aromatic 200 solvent (6.88 [bin 24])
Xylene range solvent (7.59 [bin 21])
Molinate (1.68)
Kerosene (1.71)
Methylisobutyl ketone (4.28)
Acrolein (7.55)
Glycerine (3.26)
Propylene glycol (2.74)
Thiobencarb (0.72)
N-Methyl pyrrolidinone (2.55)
S-Ethyl-N,N-dipropylthiocarbamate (EPTC) (1.82)
Oxyfluorfen (0.0003)
Pebulate (1.84)
Carbon disulfide (0.28)
Base ROG Mixture (3.71)
Ethane (0.31)
Methane (0.014)

Table 3. Illustrative calculation of effective product MIR using speciation data and component reactivities for theoretical product. Component reactivities from Carter (2007) and Carter and Malkina (2007).

Contents	Weight Fraction in Product	Weight Fraction in Speciation Profile	Component MIR	Weighted Reactivity
N-Methyl pyrrolidinone	0.05	0.06	2.55	0.15
Aromatic 100	0.50	0.59	7.42	4.38
Active Ingredient	0.30	0.35	1.84	0.64
Nonvolatile surfactants and emulsifiers	0.15	0.0	---	---

Product effective MIR = 5.17 g ozone / g VOC emitted by product

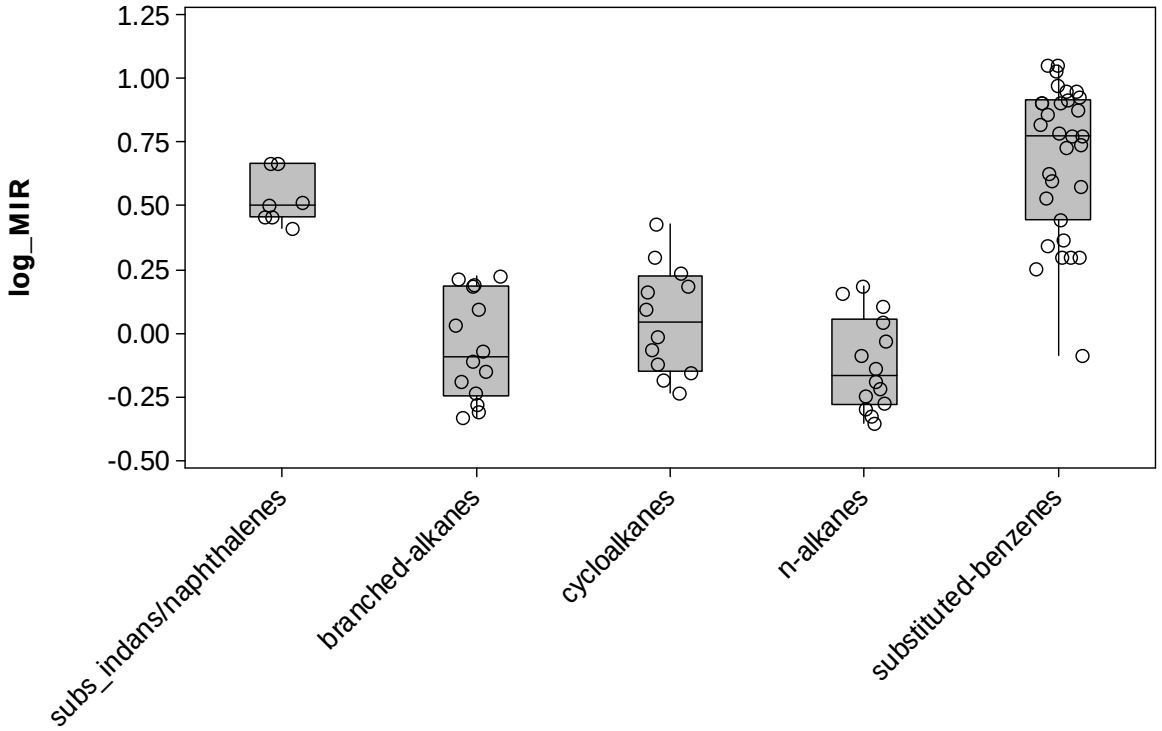

Figure 1. Comparison of log (MIR) by chemical class. Data compiled from Carter (2007).

Appendix 1. Estimated and measured VP for various aromatics

Chemical Name	CAS_No	Source	VP(Pa)	Class
Ethylbenzene	100414	SPARC	1165.2	sub_Benz-C8
m-Xylene	108383	SPARC	902.8	sub_Benz-C8
p-Xylene	106423	SPARC	843.0	sub_Benz-C8
o-Xylene	95476	SPARC	786.3	sub_Benz-C8
1,3,5-Trimethylbenzene	108678	SPARC	298.9	sub_Benz-C9
1,2,4-Trimethylbenzene	95636	SPARC	227.0	sub_Benz-C9
1-Methyl-3-ethylbenzene	620144	SPARC	343.5	sub_Benz-C9
1-Methyl-4-ethylbenzene	622968	SPARC	306.0	sub_Benz-C9
1-Methyl-2-ethylbenzene	611143	SPARC	313.1	sub_Benz-C9
Naphthalene	91203	SPARC	23.7	sub_Napth-C10
2-Methylnaphthalene	91576	SPARC	5.8	sub_Napth-C11
1-Methylnaphthalene	90120	SPARC	5.7	sub_Napth-C11
i-Propylbenzene	98828	SPARC	569.4	sub_Benz-C9
n-Propylbenzene	103651	SPARC	376.9	sub_Benz-C9
i-Butylbenzene	538932	SPARC	184.4	sub_Benz-C10
sec-Butylbenzene	135988	SPARC	176.3	sub_Benz-C10
1,2,3-Trimethylbenzene	526738	SPARC	188.5	sub_Benz-C9
1-Methyl-3-*i*-propylbenzene	535773	SPARC	168.2	sub_Benz-C10
1-Methyl-4-*i*-propylbenzene	99876	SPARC	150.0	sub_Benz-C10
1-Methyl-2-*i*-propylbenzene	527844	SPARC	164.1	sub_Benz-C10
1,3-Diethylbenzene	141935	SPARC	133.7	sub_Benz-C10
1-Methyl-3-*n*-propylbenzene	1074437	SPARC	113.5	sub_Benz-C10
1,4-Diethylbenzene	105055	SPARC	116.5	sub_Benz-C10
n-Butylbenzene	104518	SPARC	113.5	sub_Benz-C10
1,3-Dimethyl-5-ethylbenzene	934747	SPARC	106.4	sub_Benz-C10
1,2-Diethylbenzene	135013	SPARC	124.6	sub_Benz-C10
1-Methyl-2-*n*-propylbenzene	1074175	SPARC	106.4	sub_Benz-C10
1,4,Dimethyl-2-ethylbenzene	1758889	SPARC	84.3	sub_Benz-C10
1,2-Dimethyl-4-ethylbenzene	934805	SPARC	76.9	sub_Benz-C10
1-Methyl-4-*t*-butylbenzene		SPARC	65.5	sub_Benz-C11
1,2-Dimethyl-3-ethylbenzene	933982	SPARC	71.7	sub_Benz-C10
1,2,4,5-Tetramethylbenzene	95932	SPARC	56.9	sub_Benz-C10
1,2,3,5-Tetramethylbenzene	527537	SPARC	52.0	sub_Benz-C10
1-*t*-Butyl-2-methylbenzene	1074926	SPARC	54.4	sub_Benz-C11
n-Pentylbenzene	538681	SPARC	35.2	sub_Benz-C11
1-Methyl-2-*n*-butylbenzene		SPARC	30.6	sub_Benz-C11
1,2,3,4-Tetrahydronaphthalene	119642	SPARC	20.3	Indane/THN
5-Methylindane	874351	SPARC	20.7	Indane/THN
4-Methylindane	824226	SPARC	19.8	Indane/THN
2-Methylindane	824635	SPARC	42.3	Indane/THN
1,6-Dimethylnaphthalene		SRC	1.9	sub_Napth-C12

2-Ethylnaphthalene		SPARC	3.8	sub_Napth-C12
1-Ethylnaphthalene		SPARC	3.4	sub_Napth-C12
2,3-Dimethylnaphthalene		SPARC	0.5	sub_Napth-C12
1-Ethyl-2-methylnaphthalene		SRC	0.7	sub_Napth-C13
2-*i*-Propylnaphthalene		SPARC	1.1	sub_Napth-C13

SPARC CALCULATOR
<http://www.epa.gov/Athens/learn2model/part-two/onsite/sparcproperties.htm>

SRC - Syracuse Research Corporation Environmental Fate Database
<http://www.syrres.com/esc/efdb.htm>

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M E M O R A N D U M

TO: Randy Segawa
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Daniel Oros, Ph.D. *Original signed by*
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DATE: August 14, 2009

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

INTRODUCTION

The Department of Pesticide Regulation (DPR) recently invited stakeholder comment on a draft proposal to investigate speciation and reactivity of volatile organic compound (VOC) emissions from pesticides (Oros, 2009). Comments were received from the Western Plant Health Association (WPHA), Dow Agrosciences (DAS), Exxon Mobil Chemical Company (EMCO), the California Integrated Waste Management Board (CIWMB) and the California Department of Food and Agriculture (CDFA). The CDFA comments were supportive of the reactivity proposal. This memorandum summarizes the comments from WPHA, DAS, EMCO, and CIWMB and provides DPR's response to those comments.

1. Two commenters expressed reservations about promulgating volatile organic compound reactivity-based regulations at this time due to scientific uncertainty.

Western Plant Health Association:
"We consider the current level of scientific understanding on the complex interactions of VOC with nitrogen oxides (NOx) in rural airsheds insufficient for possible consideration in promulgating meaningful pesticide VOC reduction regulations at this time."

"WPHA does not recommend the addition of reactivity factors into the rural airshed VOC EP *(emission potential)* inventory data simply because the scientific basis and understanding to support this concept presently has not advanced to the level needed to support it."

Dow Agrosciences:
"The Oros (2009) proposal to integrate reactivity factors into the mass-based inventory system lacks the fundamental scientific basis to support effective regulatory policies."

Department of Pesticide Regulation's response:
DPR does not propose to promulgate regulations or otherwise implement reactivity concepts into the VOC inventory at this time. DPR also agrees that there are unanswered scientific questions about how reactivity might be eventually incorporated into the current mass-based VOC inventory. The purpose of the proposed study is to identify the scientific uncertainties and questions, and to then investigate potential solutions. As stated on DPR's Web site posting for solicitation of comments on the reactivity proposal:

"DPR proposes to evaluate selected pesticide products, and estimate the reactivity of various active and inert ingredients. DPR will evaluate the scientific issues, uncertainties, and resources needed to account for reactivity in its emission inventory and regulatory restrictions."

Change to proposal:
Text added in the introduction to further emphasize that this is a scientific investigation, and not a regulatory proposal.

2. Three commentors expressed concern over the use of the Maximum Incremental Reactivity (MIR) scale to describe ozone formation potential.

Western Plant Health Association:
"WPHA asks DPR to recognize that MIR's that have been established for urban airsheds have very limited significance to the SJV NAA and other rural airsheds. These rural agricultural airsheds are more likely to be NOx-limited. Lack of this necessary reactant would significantly limit further formation of tropospheric ozone from VOC emissions. "

Dow Agrosciences:
"The proposed MIR scale has questionable significance for rural NOx-limited air-sheds"; "(there is)... some basis to consider that the SJV may be a NOx-limited air shed, and thus that the proposed MIR reactivity metric would over-estimate OFP (*ozone formation potential*)"; "More study is needed to understand whether the proposed MIR's have application for air sheds such as the rural SJV NAA prior to building these into the current mass-based VOC inventory system."

Exxon Mobil Chemical Company:
"CDPR Should Evaluate the Appropriateness of the Application of Reactivity Values in Agricultural Areas and Identify the Most Appropriate Reactivity Metric For the Agricultural Scenario. What is the Appropriate Metric for Assessing Ozone Formation Potential in the San Joaquin Valley and Other Predominantly Agricultural Areas?"

Department of Pesticide Regulation's response:
DPR agrees that the MIR may not be the best metric for modeling actual ozone formation under NOx-limited conditions. However, DPR does not model or estimate actual ozone formation. The 1994 State Implementation Plan requires DPR to achieve VOC emission reductions relative to the 1990 base year (where the VOC emissions may be adjusted for reactivity if such information exists). Consequently the relative reactivity ranking of different chemicals is most important.

DPR does intend to evaluate different metrics for their suitability to describe the relative ozone formation potential of different chemicals. This scientific evaluation might include a comparison of different reactivity metrics for various NOx levels, and/or investigation of ambient NOx monitoring data for the SJV to more fully characterize NOx levels.

Change to proposal
Text will be added stating that the suitability of different available metrics for describing relative reactivity in rural airsheds will be investigated.

3. Minor edit

The California Integrated Waste Management Board pointed out that the proposal states "These top 80 products account for 90 percent and 85 percent of adjusted San Joaquin Valley ozone season emissions in 1990 and 2007, respectively. " This is incorrect. That statement has been revised to say "These top 80 products account for 90 percent and 85 percent of adjusted San Joaquin Valley pesticide ozone season emissions in 1990 and 2007, respectively. "

4. Continue to refine and improve the mass-based inventory by using an alternate method to measure emission potentials and employ a low vapor pressure exemption.

Western Plant Health Association:
"WPHA suggests that a better approach would be to continue to refine and improve the accuracy of the current and baseline mass-based pesticide VOC inventory system. This approach would be transparent and provide a defensible foundation for possible future regulatory initiatives targeted to limit tropospheric ozone formation."

"These accuracy improvements would include: incorporating soil sorption effects (as per the work of Alan Viets, Ph.D. of Bayer CropScience)."

"WPHA had recommended to DPR that agricultural pesticides with LVP (*low vapor pressure*) or non-reactive species be granted an exemption to further regulatory hurdles. However, DPR had determined not to provide for such an exemption despite ARB's decision to grant a LVP exemption for consumer pesticide products of similar formulation. "

Dow Agrosciences:
"..... worst case TGA results might be further refined to reflect additional factors. These refinements would include incorporating soil sorption effects (as per the work of Alan Viets, Ph.D. of Bayer Cropscience), considering the atmospheric availability of low vapor pressure (LVP) VOC's based on the unique application practices for agricultural products."

Department of Pesticide Regulation's Response:
These comments are outside the scope of the proposed project. In addition, DPR has previously responded to these comments in letters to WPHA dated October 20, 2008, and May 2, 2007.

5. Develop AMAFs by including sorption/degradation/application method effects on volatilization.

Western Plant Health Association:
"WPHA also recommends that DPR should continue to integrate further mass-based inventory corrections that consider the environmental fate of the VOC's used in pesticides. Appropriate factors should include, but not be limited to:

- Soil sorption effects
- Product specific agricultural use-practices, and
- Consideration for the entire formulation matrix for cases when co-formulants or formulations, and adjuvants rapidly degrade in the soil/water/air media

"include the impacts of demonstrated soil sorption effects that limit the "atmospheric availability" for low volatility VOC's and accounting for other degradative processes that prevent gas phase reactions with NOx to form tropospheric ozone is crucial to predict a realistic effect on ozone production."

Dow Agrosciences:
"As we have discussed previously with the Department, we feel it is more appropriate to continue to include the impacts of demonstrated soil sorption effects that limit the atmospheric availability for low volatility VOCs and accounting for other degradative processes that prevent gas phase reactions with NO, to form tropospheric ozone."

Exxon Mobil Chemical Company:
"DPR Should Consider Environmental Fate and Atmospheric Availability Concepts To Provide a More Realistic Mass-Balance of VOC Emissions in the Agricultural Field"

Department of Pesticide Regulation's Response:
These comments are outside the scope of the proposed project. In addition, DPR has previously responded to these comments in letters to WPHA dated October 20, 2008, and May 2, 2007.

6. The Department of Pesticide Regulation Should Consider A Holistic Approach, Utilizing A Life Cycle Assessment Of the Total Agricultural Scenario

Exxon Mobil Chemical Company:
"We suggest that it is most beneficial to consider ground- level OFP through a Life Cycle Assessment (LCA). In general, if the goal is to reduce ground- level ozone, the reaction chemistry and subsequent alternative uses/pesticide product re-formulations need to be combined into a single analysis. For example, it is important to first determine whether the location of interest is under VOC-limited or NOx- limited conditions and to have an understanding of how meteorological and other environmental conditions can affect the ozone formation chemistry. It is also important to compare the quantities and sources of VOC that may be involved for current use and reformulated pesticide products, as well as the application and use requirements for these substances. For example, if a product is reformulated to one that is less efficacious and requires multiple field applications (versus other effective products) what effect does increased use of field equipment have on the total VOC emissions? Could a reformulated product result in a product which is more water-soluble that would result in emissions to other environmental media, such as groundwater, thereby creating a more significant environmental issue in California. Kumar et al. (2008) found that VOC emissions from farm equipment can contribute to VOC emissions at concentrations greater than that from applied pesticide products. They also showed that VOC emission concentrations from the plants (biogenic emissions) were higher than the pesticide product VOC emissions."

Department of Pesticide Regulation's Response:
These comments are outside the scope of the proposed project. The proposed project is a research study to evaluate the technical feasibility of accounting for reactivity in DPR's VOC inventory. If the study shows this is technically feasible, several other major steps must occur before DPR could implement the reactivity adjustments, including revisions to the state implementation plan. Until these other steps occur, the current pesticide element of the state implementation plan requires DPR to reduce the mass of pesticide VOC emission by specified amounts in specified areas. DPR's primary goal is to comply with its legal obligation to reduce the mass of pesticide VOC emissions, with the important but secondary objective of reducing ground-level ozone. However, DPR does evaluate the impact of its VOC reduction measures holistically, assessing toxic exposure to the public and workers, environmental effects, and other

potential impacts. For example, DPR evaluated and found no potential ground water effects of its fumigant regulations that require additional irrigation to mitigate VOC emissions. DPR agrees that reformulating to a product that requires more frequent applications would have the disadvantages of increasing emissions from farm equipment as well as increasing toxic exposure, and is likely inadvisable. Fortunately, registrants have been successful in reformulating some products with lower VOC content, and maintaining efficacy with the same number of applications and amount of active ingredient.

Reference

Oros, D. 2009. Pilot project proposal: Estimating pesticide product volatile organic compound emission speciation and reactivity based on product composition. Memorandum to Randy Segawa, Environmental Monitoring Branch.