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SUBJECT: DETAILED EMISSION POTENTIAL CALCULATIONS OF HIGH USE PESTICIDE PRODUCTS USING A CONFIDENTIAL STATEMENT OF FORMULA BASED METHOD

ABSTRACT

This memorandum details the emission potential (EP) calculation of 11 high use pesticide products utilizing the California Department of Pesticide Regulation's (DPR's) recently suggested Confidential Statement of Formula (CSF)-based speciation EP method (Oros 2009). Although, the CSF-based method does not replace the more established thermogravimetric analysis (TGA) EP determination, it does provide a quick, easy and efficient alternative method that has been shown to provide TGA comparable EP estimates (Oros and Spurlock 2011). Therefore, CSF-based EP determinations can be used, on a case-by-case basis, until TGA data has been reported by registrants and verified by DPR. Of the 11 pesticide products selected, 6 were found to have an EP value of 0%. Roundup PowerMax®, Glystar Plus®, Mirage®, Rely®, and Ignite 280 SL® EPs were calculated to be 35.28%, 31.27%, 23.80%, 10%, and 7.34%, respectively. For some of the pesticide product formulation ingredients where the specific identity or vapor pressures (VPs) were not available, unless otherwise noted, the ingredients were assumed to contribute to the volatile fraction of the product, and thus, were included in the EP calculation. Therefore, it is noteworthy to point out that some of the calculated EPs might be higher than EP values determined via TGA.

INTRODUCTION

DPR requires newly registered liquid products to submit or refer to TGA data already on file to determine the product's EP. TGA has been shown to provide highly accurate EP calculations and the procedure has been fully explained elsewhere (DPR 1995). Briefly, the pesticide liquid sample is heated to a starting temperature of 35°C and weighed. The sample is then heated from 35°C to 115°C at a rate of 5°C per minute and held isothermally until the rate of sample mass loss drops below a defined threshold. The TGA method uses a final holding temperature of 115°C to facilitate volatilization and loss of water contained in the formulation. The mean of three replicate measurements is used to estimate a product's EP.

Although TGA has been shown to provide accurate and precise EP estimates, TGA is a rather laborious and time intensive EP estimation method. Additionally, the TGA method cannot be used for certain products that break down under experimental TGA conditions or for products that are too volatile to handle (e.g., some fumigants). Therefore, when TGA data is not available, due to time required by registrants to respond with TGA data call-ins or to a product's sensitivity for TGA analysis, DPR, on a case-by-case basis, can implement CSF-based EP values while TGA data is pending receipt and approval. This CSF-based EP method calculation is quick, relatively simple, and has been proven to offer EP estimates comparable to those determined via the more intense TGA-based EP measurements (Oros and Spurlock 2011).

In this memorandum, I detailed the CSF-based EP determination of 11 high use pesticide products. (Note: Due to the confidential nature of pesticide product CSFs, the actual product ingredients will not be disclosed in this memorandum).

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), and percentage by weight of the chemical in the formulated product.

B. Vapor Pressure for Determining Volatility

For the purpose of this memorandum, VPs at 25°C (VP25°C) were used to determine a chemical's ability to volatilize. The specific vapor pressure cutoff utilized to determine a chemical's volatility was set at 5.0 x 10-2 Pascal (Pa), as determined in a previous DPR study (Oros and Spurlock 2011). Chemicals with a VP25°C approximate to 5.0 x 10-2 Pa or greater were showed to be able to volatilize under TGA conditions and thus were included in CSF-based EP calculations.

C. Sample Steps in Confidential Statement of Formula-based Emission Potential Calculation

The first step in determining the EP of each pesticide product is to identify the percentage by weight of each chemical in the formulated product using the submitted CSF. Due to the confidential nature of the pesticide product formulations, once obtained from DPR's Pesticide Registration Branch, CSFs were kept at all times in locked drawers except for when they were actually being utilized. Table 1 gives an example of a submitted CSF for a liquid pesticide product.

The second step is to determine each component's VP25°C. For this paper, VP25°C data were collected from each chemical component's Material Safety Data Sheets, when available, and from the Syracuse Research Corporation's Interactive Physical Properties Database (<http://www.syrres.com/what-we-do/databaseforms.aspx?id=386>).

The last step is to sum the weight percent of all chemicals whose VP25°C ≥ 5.0 x 10-2 Pa. For example, in Table 1, chemical ingredients B and C have a VP25°C ≥ 5.0 x 10-2 Pa, therefore the product's CSF-based calculated EP would be 40%, which is the weight percent sum of ingredients B and C.

Table 1. Example CSF for a pesticide product with the addition of VP25°C.

Chemical Name	Weight Percent (%)	Purpose in formulation	VP25°C (Pa)
A	60	Active Ingredient	2.10×10^{-6}
B	32	Solvent	1.67×10^{3}
C	8	Surfactant	3.20×10^{-1}

D. Emission Potential Calculations of 11 High-Use Pesticide Products

Due to the repetitive nature of the EP calculations via the CSF-based method, for this memorandum, I am only including two detailed EP calculations as various pesticide products contain similar or identical chemical ingredients or are a repackaged product from a previously used pesticide product with a different brand name. For this memorandum, I have chosen to detail the complete EP calculation of the pesticide products Mad Dog® and Ignite 280 SL® as one was found to contain an EP value of 0% and the other contains 7.34%.

Mad Dog®

Note: Due to the sensitive and confidential nature of the pesticide formulation information, I have changed each ingredient's name in the formation in Table 2. Furthermore, I have also altered the weight percent of the ingredients in the table without affecting the overall EP calculation.

Table 2. Summary of Mad Dog® CSF and component's VP25°C.

Components in Formulation	Purpose in formulation	Weight Percent (%)	VP25°C (Pa)
50% Technical Solution Glyphosate salt	Active Ingredient	30.00%	10^{-6}
50% Water in Technical Solution	Solvent	30.00%	10^{3}
Diluent	Diluent	35.00%	10^{3}
Emulsifier A	Emulsifier	2.50%	NA
Emulsifier B	Emulsifier	2.50%	NA

EP = Σ (WP of ingredients with a VP25°C ≥ 5.0 x 10^{-2} Pa) – (WP of diluent)
EP = (35.00% + 30.00%) - (35.00% + 30.00%)
EP = 0%

Ignite 280 SL®

Note: Due to the sensitive and confidential nature of the pesticide formulation information, I have changed each ingredient's name in the formation in Table 3. Furthermore, I have also altered the weight percent of the ingredients in the table without affecting the overall EP calculation.

Table 3. Summary of Ignite 280 SL® CSF and component's VP25°C.

Components in Formulation	Purpose in formulation	Weight Percent (%)	VP at 25°C (Pa)
90% Glyphosate acid in solution	Acid Equivalent	31.00%	10^{-5}
10% solvent in glyphosate acid solution	Solvent	1.30%	Unknown*
pH adjustor (80%)	Base	12.00%	10^{4}
20% solvent in pH adjustor solution	Solvent	3.00%	Unknown*
Solvent blend	Solvent	7.50%	Unknown*
Antifoam Agent	Antifoam	0.20%	NA
Diluent	Diluent	45.00%	10^{3}

EP = Σ (WP of ingredients with a VP25°C ≥ 5.0 x 10^{-2} Pa) – (WP of diluent)
EP = (12.00% + 3.00% + 7.50% + 1.3% + 45.00%) - 45.00%
EP = 23.80%

If VPs were unknown, product was assumed to be volatile unless proven otherwise.

For a complete list of CSF-based calculated EP values, see Table 4 below.

Table 4. Summary of Calculated EPs.

Product Name	EPA Registration Number	Calculated EP (%)
Alecto 41S®	9468-33-AA	0.00
Buccaneer Glyphosate Herbicide®	55467-10-AA	0.00
Buccaneer Plus Glyphosate Herbicide®	55467-09-AA	0.00
Glystar Plus®	42750-61-AA	31.27
Honcho Plus Herbicide®	524-454-ZB	0.00
Ignite 280 SL®	264-829-AA	7.34
Mad Dog®	34704-889-ZA	0.00
Mirage®	34704-889-AA	23.80
NuFarm Credit Systemic Herbicide®	71368-20-AA	0.00
RELY Herbicide®	264-652-ZA	10.00
Roundup PowerMax®	524-549-AA	35.28

CONCLUSION

Due to the time and effort required to perform TGA-based EP calculations, in 2009 DPR suggested CSF implementation as a temporary EP calculation alternative while TGA data is pending submission by registrant and approval by DPR. In this memorandum, I detailed the EP calculation of 11 pesticide products using the suggested CSF-based EP determination method.

The 11 pesticide products selected in this memorandum were chosen due to their high use or to the fact that no EP value had been previously reviewed and approved. Of the 11 pesticide products selected, 6 were found to have an EP value of 0%. Roundup PowerMax®, Glystar Plus®, Mirage®, Rely®, and Ignite 280 SL® were determined to have EP values of 35.28%, 31.27%, 23.80%, 10%, and 7.34% respectively.

Although EP values calculated via the CSF-based method were previously shown to be comparable to those found via TGA (Oros and Spurlock 2011), it is noteworthy to point out that the technique does not make TGA obsolete. Due to the nature of TGA measurements, EP values determined from TGA more accurately depict the volatile emissions that actually occur in the field. Additionally, the fact that the CSF-based method depends on the arbitrarily established vapor pressure of 5.0 x 10-2 Pa as a product's volatility determinant, provides the method with a possible bias which may or may not truly depict correct EP determinations in all cases.

REFERENCES

DPR (1995). "Estimation of Volatile Emission Potential of Liquid Pesticides by Thermogravimetry." Environmental Monitoring Branch, Department of Pesticide Regulation. Sacramento, California. Available at: <http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/tga_method.pdf>.

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