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MEMORANDUM

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SUBJECT: METHODOLOGY FOR DETERMINING VOC EMISSION POTENTIALS OF
PESTICIDE PRODUCTS

OVERVIEW

The purpose of this memorandum is to document changes made to the Department of Pesticide Regulation's (DPR's) procedures for estimating emission potentials (EP) of pesticide products. DPR uses EPs to calculate potential volatile organic compound (VOC) emissions from pesticides.

BACKGROUND

The potential VOC emission of reactive organic gases (ROG) from a given application of a pesticide product is proportional to the product specific EP:

$$\text{potential VOC emission (pounds ROG)} = (\text{pounds product applied}) \times \text{EP}$$

The EP is that fraction of a product that is assumed to contribute to atmospheric VOCs. Consequently, the accuracy of DPR's annual estimated potential VOC emission inventory depends directly on the accuracy of EP values. The current "gold-standard" for determining EPs is thermogravimetric analysis (TGA; DPR, 1994). However, only about 30-40 percent of the total mass of applied pesticides that are included in DPR's annual VOC inventory consists of products for which TGA EPs have been obtained. Other methods for estimating EPs have been devised for non-TGA products. These methods have included water and/or inorganic subtraction, where the entire product is assumed volatile except for the water and inorganic portion. The portion of nonvolatile components are determined using the product's confidential statement of formula. Finally, EPs for many other products are assigned based on default EP values.

Default EPs are defined based on formulation category (e.g., emulsifiable concentrate, flowable concentrate, dusts and powders) and have previously been arbitrarily defined in the past as the highest approved TGA EP in a formulation category. One rationale for setting the default EP to the high default value was to encourage pesticide registrants to voluntarily provide TGA data for their products. However, DPR receives TGA data for only a few products out of the many annually registered. The assignment of the arbitrary high default EP values is, therefore, ineffective for encouraging submission of TGA data. Further, the use of high default EP values



has been a significant source of error in previous VOC inventories because the high default EPs are inaccurate estimates of EP for those products that are assigned defaults.

A second significant source of error in past inventories is from high-use products that have inaccurate or unrealistic EPs. One example is sodium chlorate cotton defoliant products. In 2000, 11.3 million pounds of sodium chlorate were reported in the PUR. There are only a few sodium chlorate products with TGA data; EPs for these are zero or close to zero. However, historical estimated EPs for other sodium chlorate products based on water subtraction or water/inorganic subtraction methods range up to 82 per cent. As demonstrated later in this memorandum, sodium chlorate defoliant products do not contain VOCs, so that their EPs should actually be zero. Consequently, previous emission estimates for sodium chlorate products have been high by several million pounds. Other high-use product classes for which EP re-evaluations are discussed in this memorandum include sulfur, petroleum oils, and metam sodium.

Significant and variable sources of error in estimated VOC emissions prevent accurate evaluation of long-term emission trends, even though trend analysis is a stated goal of the VOC program (DPR, 1996). The purpose of this memorandum is to document recent changes in (1) the methodology for determining default EPs, and (2) EPs assigned to certain high-use product classes. The goal is to improve the accuracy and consistency of DPR's VOC inventory estimates.

DEFAULT EPs

The median is a common measure of central tendency in non-normal populations. VOC emission estimates using default EPs equal to the median TGA EP in a formulation class are more realistic than estimates based on the current extreme-value TGA EP defaults. Figure 1 illustrates the distribution of TGA EPs for ten formulation classes. Using these data, default EPs for the formulation classes in Table 1 are now defined as the median TGA-based EP in each formulation category. One exception to this approach is pressurized products; there are no TGA data for pressurized products due to obvious technical difficulties in conducting TGA for pressurized products. Consequently, default EPs for all pressurized products are defined as 100.

TABLE 1. New default EPs for various formulation classes (December, 2001)

Formulation Code	Formulation	New median TGA default EP
A0	DUST/POWDER	1.53
B0	EMULSIFIABLE CONCENTRATE	39.15
C0	FLOWABLE CONCENTRATE	4.80
E0	GRANULAR/FLAKE	3.70
H0	OIL	3.47
J0	PELLET/TABLET/CAKE/BRIQUET	5.18
K0	PRESSURIZED DUST	100 [†]
L0	PRESSURIZED GAS	100 [†]
M0	PRESSURIZED LIQUID/SPRAYS/FOGGERS	100 [†]
N0	SOLUBLE POWDER	1.15
O0	SOLUTION/LIQUID (READY-TO-USE)	7.30
P0	WETTABLE POWDER	1.85
R0	DRY FLOWABLE	1.02
Q0 & S0	SUSPENSION & LIQUID CONCENTRATE	5.71 [‡]

[†] default EP of all pressurized products defined as 100

[‡] Q0 and S0 formulation classes are combined due to (a) low number of Q0 products (n=6) and (b) no significant difference in median TGA for these formulation classes (Wilcoxon rank sum test, p = 0.8).

RE-EVALUATIONS OF HIGH-USE PRODUCT CLASSES.

A. Sodium chlorate products

Sodium chlorate defoliant products range from about 18 to greater than 50 percent (w/w) sodium chlorate. Sodium chlorate is an extremely strong oxidizing agent, and so is a fire hazard when in contact with organic chemicals (Eka Chemical, 2001; Merck Index, 1989). Sodium chlorate products are usually liquid formulations - no solid products have been reported used in the PUR since 1990. Confidential statements-of-formula (CSF) for sodium chlorate defoliant products show only water, aluminosilicates (clay), inorganic salts, and/or urea fire retardant (e.g., Drexel Chemical Co., 2001). Of these, urea is the only organic compound. Urea is highly polar, nonvolatile, hydrophilic, and has a very low Henry's law constant (4.4×10^{-8} atm m³ mol, UNEP\IRPTC, 2001). Urea, therefore, partitions into water or moist soil as opposed to the atmosphere. In addition, urea degrades rapidly to ammonia and carbon dioxide. Consequently, it is inappropriate to classify urea as a volatile organic compound. Therefore, all sodium chlorate defoliant formulations (active ingredient $\geq 18\%$) are now assigned an EP of zero in the absence of other information to the contrary.

B. Metam sodium products

Metam sodium is a nonvolatile organic salt that is the active ingredient in numerous fumigant products. All metam sodium products are formulated and sold as concentrated aqueous solutions containing only metam sodium and water. However, when metam sodium is applied, the actual volatile fumigation agent is methyl isothiocyanate (MITC). MITC is a degradation product of metam sodium that is rapidly formed post-application.

There are 3 metam sodium products for which TGA data have been reported. A previous strict interpretation of the TGA data for these products yields EP=0 because concentrated aqueous solutions of metam sodium are essentially nonvolatile under the experimental conditions of the TGA test. Obviously, the standard assumptions of the TGA test are invalid for metam sodium fumigant products.

TGA data for ALL metam products will, henceforth, be disregarded, and metam sodium EPs will now be calculated on an "MITC-equivalent" basis based on product composition as follows:

Assuming quantitative stoichiometric conversion of metam sodium to MITC following application, 1 gram of metam sodium yields 0.566 grams MITC. The "MITC-equivalent" EP for a metam sodium product containing **X** mass fraction metam sodium is then given as:

$$\text{product EP} = 0.566 * X$$

C. Sulfur products [≥ 50 percent sulfur and no other active ingredients]

Sulfur products typically account for more than 20 percent of the total mass of applied pesticide products in DPR's annual pesticide use report (PUR); more than 69 million pounds of sulfur products were reported applied in the 2000 PUR. One consequence is that even small inaccuracies in high-use sulfur product EPs will lead to significant errors in estimated VOC emissions.

Agricultural sulfur products are available in both solid (dust, wettable powder) and liquid (flowable, liquid concentrates) formulations. The solid formulations often contain nonvolatile diluents in addition to sulfur dust. These can include various clays, talc, or gypsum powders. In addition, wetting agents such as surfactants and/or detergents are added to dry wettable powder formulations to aid their mixing in solution. Such materials are typically high molecular weight and amphoteric, possessing very low or no volatility. The liquid formulations also contain similar components, but may also contain small amounts of high molecular weight thickeners such as xanthan gum.

Overall, sulfur products are expected to display very low volatility, as demonstrated by the available TGA data (figure 2a). It should also be noted that the TGA protocol for solids does not include a sample-drying step and does not account for the presence of absorbed water in the product (DPR, 1994). Because many of the sulfur products contain significant amounts of clay (capable of significant water absorption), it is expected that TGA values for such products are probably high biased in some cases. This bias may be as much as several percent depending on clay properties, percent composition, and ambient humidity.

Based on the foregoing information, sulfur products for which (1) there are no TGA data, and (2) contain at least 50% sulfur, and (3) do not contain any other active ingredients are now assigned a default EP of 0.6, equal to the current sulfur TGA median.

D. Petroleum oil (unclassified) and Mineral Oils [≥ 80 percent active ingredient]

Petroleum and mineral oils are similar to sulfur in that they represent very high pesticide use, nearly 25 million pounds in the 2000 PUR. In addition, many of the above types of oil products are classified as formulation category O0 (solution/liquid ready-to-use) or B0 (emulsifiable concentrate) instead of H0 (oils). This typically happens because registrants choose the formulation category when filling out the registration application and DPR does not have any requirements or strict guidelines for formulation category. The principal difficulty for VOC estimates is that default EPs for the three categories vary widely: 7.13, 39.15, 3.47 for formulation classes O0, B0, and H0, respectively. The use of defaults based on formulation codes results in a 10-fold range of variation in EPs. This decreases the accuracy of the VOC inventory and causes excessive year-to-year variability in the inventory when there are shifts in oil product use between formulation categories.

The measured TGA EPs for petroleum oil (unclassified) and mineral oil are all quite low, with a median of 1.53 and a maximum of 6.03 (n=12, figure 2b). Consequently, petroleum oil (unclassified) or mineral oil products for which (1) there are no TGA data, and (2) contain at least 80% petroleum oil (unclassified) or mineral oil, and (3) do not contain any other active ingredients will now be assigned a default EP (= 1.53), equal to the oil median in Figure 2.

SUMMARY

Several modifications to past procedures for assigning EPs to products without TGA data are detailed here; these changes will provide a more realistic estimate of pesticidal VOC emissions than in the past. The changes in EP estimation methods will commence with the VOC inventory conducted in December 2001. Additional EP re-evaluations will occur in the future as other refinements are developed.

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Figure 1. TGA EP distributions for various formulation classes

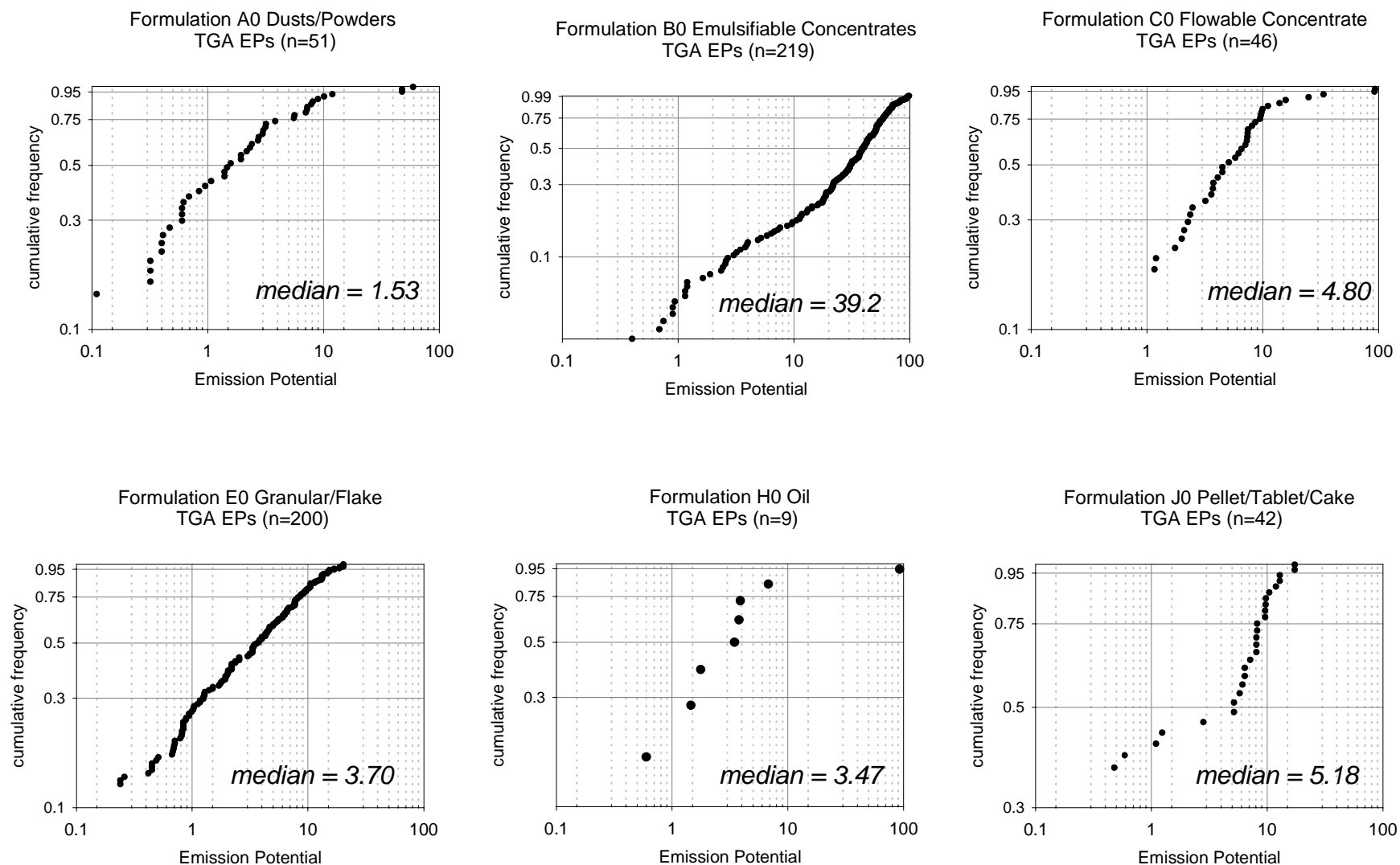


Figure 1. TGA EP distributions for various formulation classes (cont.)

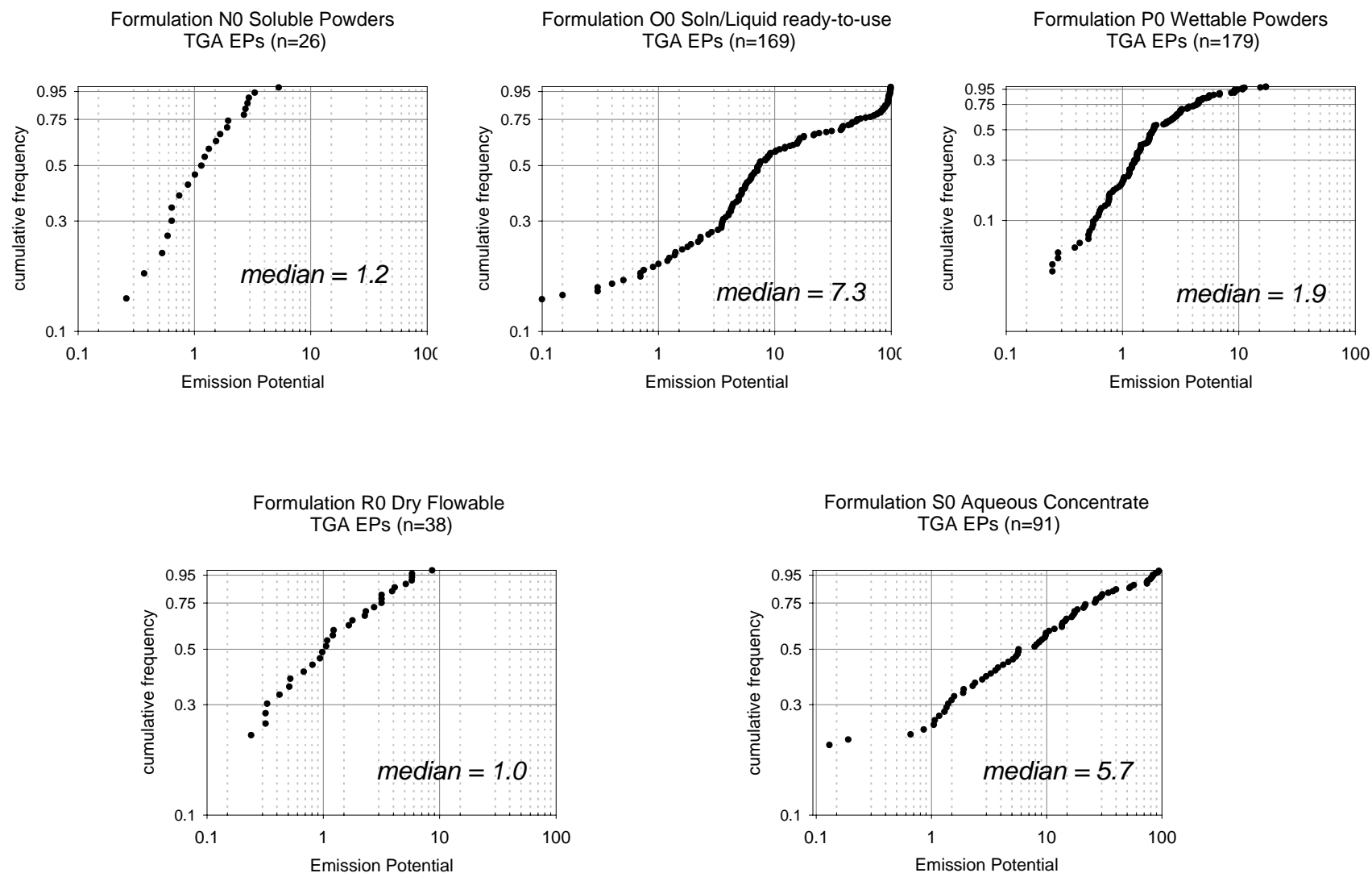


Figure 2A. Distribution of TGA EPs for sulfur products
[$\geq 50\%$ sulfur, no other organic active
ingredients, n=27]

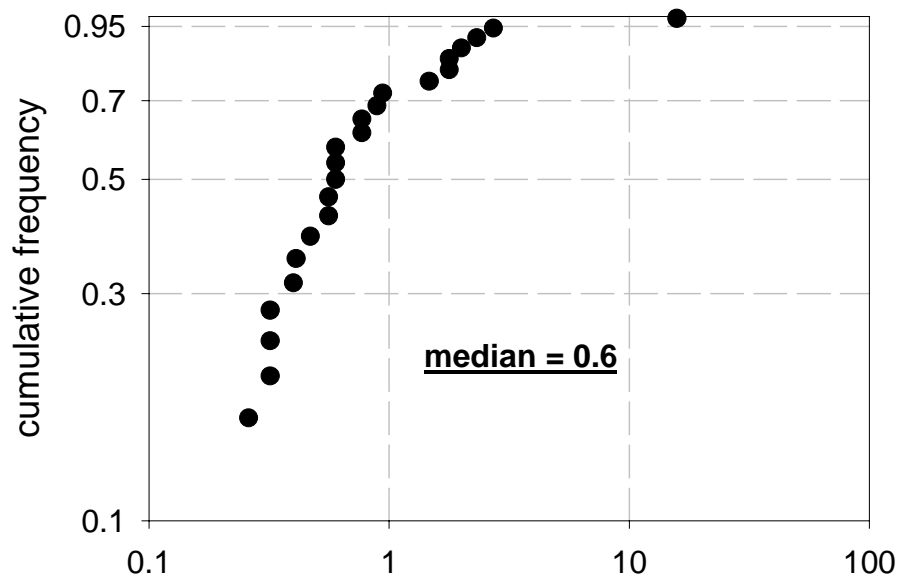


Figure 2B. Distribution of TGA EPs for petroleum oil
(unclassified) and mineral oil [$\geq 80\%$ oil, no
other organic active ingredients, n=12]

