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SUBJECT: REVISIONS TO PROCEDURES FOR ESTIMATING VOLATILE ORGANIC COMPOUND EMISSIONS FROM PESTICIDES

The Department of Pesticide Regulation's (DPR's) volatile organic compound (VOC) emission calculation procedures were modified in February 2005. These modifications were implemented in the February 2005 revision of DPR's 1990–2003 annual VOC inventories. The modifications improved the accuracy of the VOC inventory and corrected inconsistencies between the inventory and the pesticide use report (PUR.) These modifications included: (1) modifying default emission potentials (EP) for certain methyl isothiocyanate (MITC)-generating fumigant products, (2) including VOC contributions for additional agricultural-use products that had been excluded in previous VOC inventories, and (3) changing procedures in the VOC calculation program for determining probable outliers in the PUR input data.

The revised procedures resulted in small increases in the VOC inventory; the average increase in May to October emissions in all non-attainment areas (NAA) across all years was 1.01% (Figure 1 attached.) However, the increases in certain NAAs were either larger or smaller than the statewide average. The largest change was in NAA 3, the Southeast Desert, where the average increase across all years was 2.74%, followed by NAA 1 with a 2.60% increase, NAA 2 with 1.48% increase, NAA 5 with a 0.96 % increase, and NAA 4 with a 0.06% increase. The calculation changes are summarized below.

1. <u>Potassium N-methyl dithiocarbamate (metam-potassium) products</u>

These products are soil fumigants. The reported agricultural use of metam-potassium products has steadily increased from 14,800 pounds of metam-potassium products in 1999 to 2,396,900 pounds in 2002. Similar to sodium N-methyl dithiocarbamate (metam-sodium), metam-potassium products rapidly degrade in moist soil, releasing the fumigant MITC. Metam-sodium product EPs are calculated on a "MITC-equivalent" basis (Spurlock, 2002) and metam-potassium product EPs are now calculated similarly:

> Assuming quantitative stoichiometric conversion of methyl-potassium to MITC following application, 1 gram of metam-potassium applied yields 0.503 grams MITC. The "MITC-equivalent" EP for a metam-potassium product containing **X** massfraction of active ingredient is then given as: ***product EP = 0.503 * X***

2. Products in formulation categories T0 (other, liquid) and U0 (other, dry) with reported agricultural uses

DPR's VOC inventory excludes pesticide products that are consumer products because emissions from these products are regulated by the Air Resources Board. Such products have historically been assumed to be products in formulation categories D0 (gel, paste, cream), F0 (impregnated material), I0 (paint/coatings), T0 (other, liquid), and U0 (other, dry.) Formulation categories T0 and U0 contain relatively few total products. However, certain products in those categories are registered for agricultural use and contain commonly used active ingredients, such as carbaryl, imazethapyr, glyphosate and others. Consequently, products in formulation categories T0 (other, liquid) and U0 (other, dry) with reported applications to agricultural sites are now included in DPR's VOC inventories.

There are no thermogravimetric analysis (TGA)-based EPs for any products in these formulation categories. As a result, default EPs for these products cannot be assigned in the standard manner of calculating the median TGA-based EP for their respective formulation category (Spurlock, 2002.) The method that is used to estimate default EPs for formulation class T0 (other, liquid) is to equate the default EP to the median of all TGA-based EPs in all liquid formulation categories: O0 (solution/liquid, read-to-use), Q0 (liquid suspension), S0 (liquid concentrate), and C0 (flowable concentrate) (Figure 2, attached.) The default EP calculated for formulation category T0 (other, liquid) is 6.91. Similarly, the default EP for formulation category U0 (other, dry) is now defined as the median of all TGA-based EPs in the dry formulation categories R0 (dry flowable), P0 (wettable powder), N0 (soluble powder), E0 (granular/flake), and A0 (dust/powder) (Figure 3, attached.) This default EP for formulation category U0 (other, dry) is 2.05.

3. Changes to determining probable errors in PUR data prior to calculating the inventory

California's annual PUR serves as the basis for calculating the VOC inventory. Approximately 2.5 million pesticide applications are reported annually in the PUR where, roughly speaking, each application represents a record in the PUR. A small number of these records contain errors. Methods to identify probable errors in the PUR have been devised (Wilhoit, 1998.) Several of the methods are based on comparison of a product's use rate as calculated from the reported data for each PUR record (=amount of product applied/unit treated) to certain criteria. In the VOC inventory, each record's computed use rate has been previously compared to (a) absolute numerical rates of 200 lbs/acre (nonfumigants) or 1000 lbs/acre (fumigants) which are used to distinguish probable outliers from accurate data (criterion 1a, Wilhoit, 1998), (b) a maximum use rate for a particular product/application site/unit treated combination of 50 times the median rate for all such product/application site/unit treated records (criterion 2b, Wilhoit, 1998), and (c) absolute numerical rate criteria derived from a neural network procedure (criterion 4d, Wilhoit, 1998.) Records whose use rates exceed one or more criteria are then assumed to be probable outliers, and have historically been excluded from the inventory. Outlier identification procedures for the VOC inventory have now been modified as discussed below.

3a. Determining probable outliers among all PUR use records in the VOC inventory

In 2000, the loader procedures for entering raw data from counties into DPR's PUR were modified (Wilhoit, 2002.) Incoming raw data from counties are now screened for unusually high use rates, and those records that are classified as probable errors based on high rates of use are returned to the counties from which they originated to be checked and corrected if in error. The determination of whether a record is a probable error is based only on criteria 1a and 2b above (Wilhoit, 2002.) Records, which exceed the neural network procedure, criterion 4d above, are classified as possible errors; that is, they are considered to have rates that are "unusual in some way, but not clearly known to be in error" (Wilhoit, 2002.) To improve consistency between PUR error-handling procedures and VOC error identification procedures, criterion 4d is no longer used to identify probable outliers in the VOC inventory. Identification of probable outliers in the VOC inventory is now based on the same criteria as the PUR, criteria 1a and 2b discussed above.

3b. Determining outliers for metam-potassium and dazomet applications

Outlier criterion 1a is based on absolute use rates: records with use rates greater than 200 lbs/acre (nonfumigants) or greater than 1000 lbs/acre (fumigants) are identified as probable outliers. Due to an oversight, this PUR-error check has historically misclassified metam-potassium and dazomet as nonfumigants, although they are soil fumigants and their use rates are comparable to other products containing the fumigants methyl bromide, chloropicrin, or metam-sodium. Instead, the PUR error-checking program has screened metam-potassium and dazomet products based on the lower nonfumigant error threshold of criterion 1a (i.e. 200 lbs/acre.) Consequently, outlier screening based on PUR screen criterion 1a is inappropriate for metam-potassium and dazomet, and they are now exempted from outlier screening by criterion 1a.

Conclusion

Several changes were made to VOC inventory calculation procedures in 2005. All years of the inventory were recalculated using the modified procedures. The effect of all changes was a small increase in estimated VOC emissions in all years as demonstrated by a comparison of old and new calculated ozone season emissions in California's five non-attainment areas (Figure 1.)

Attachments

cc: Randy Segawa, Senior Environmental Research Scientist (w/Attachments)

bcc: Spurlock Surname File (w/Attachments)

References

Spurlock, F. 2002a. Methodology for Determining VOC Emission Potentials of Pesticide Products, memorandum to J. Sanders, January 7, 2002. Available on-line at <http://www.cdpr.ca.gov/docs/pur/vocproj/intro.pdf>.

Wilhoit, L. 1998. A Computer Program to Identify Outliers in the Pesticide Use Report Database. Pest Management Analysis and Planning Program, Department of Pesticide Regulation. Published PM 98-01.

Wilhoit, L. 2002. Pesticide Use Report Loading and Error-Handling Processes. Pest Management Analysis and Planning Program, Department of Pesticide Regulation. Published PM 02-01.

Figure 1. Ozone season emissions calculated from historical vs. revised VOC calculation procedures by NAA

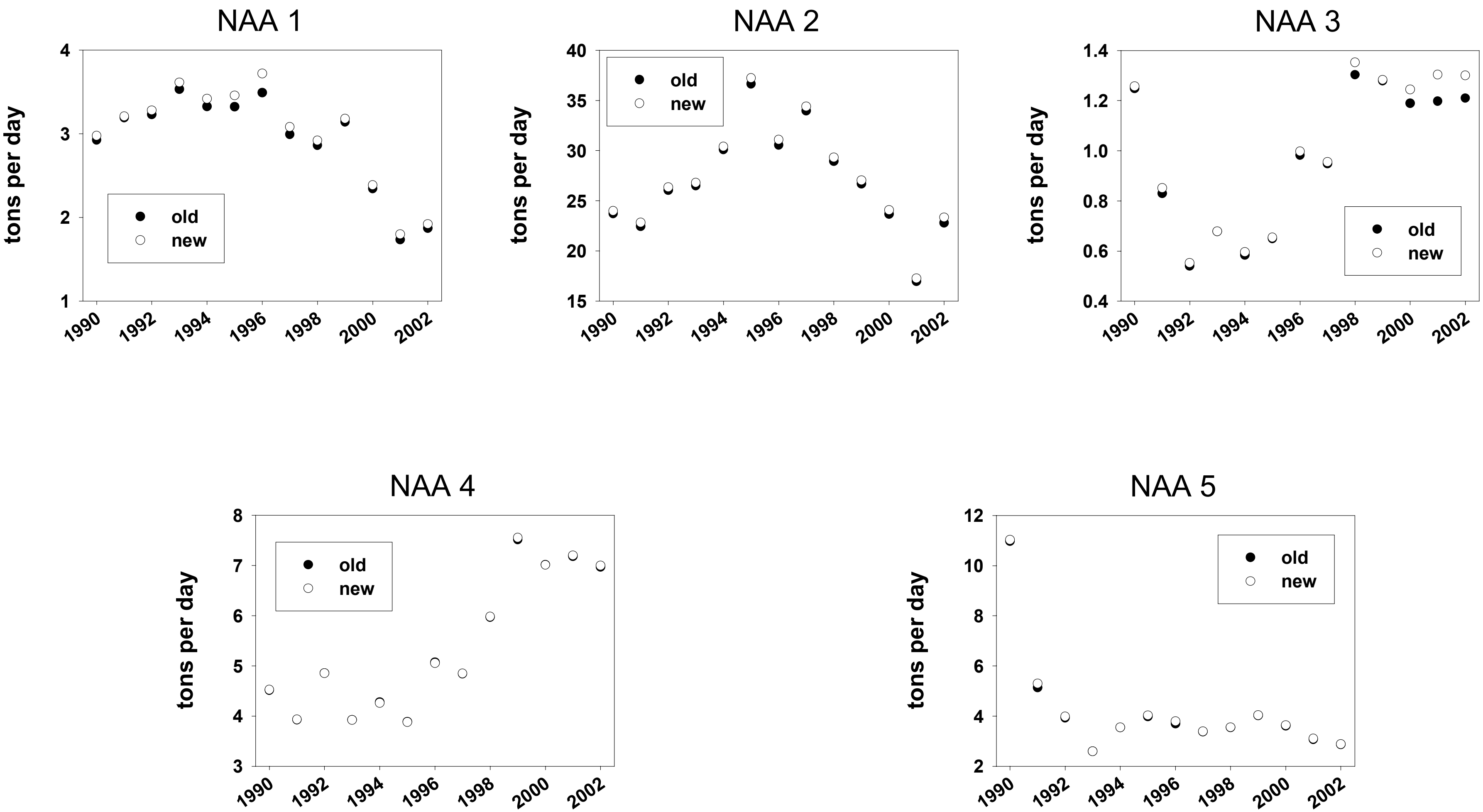

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Figure 2. cumulative frequency plot of TGA-based EPs for liquids - C0, O0, Q0, S0

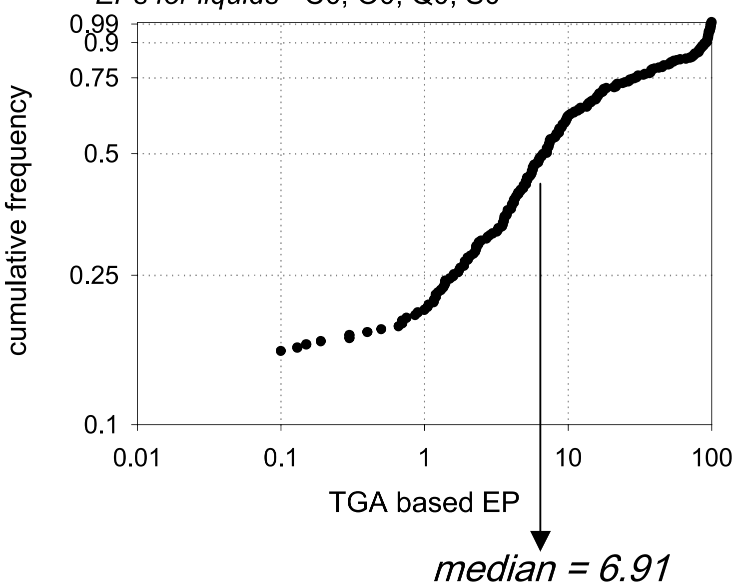

Figure 3. cumulative frequency plot of TGA-based EPs for solids - A0, E0, N0, P0, R0