California Department of Pesticide Regulation

Frequently Asked Questions: The Pesticide VOC Emission Inventory

September 2008

Definitions

- **Volatile organic compounds (VOCs)** contribute to the formation of smog
- An **emission inventory** is a systematic listing of the sources of air pollutants, including an estimate of how much pollutant each source emits.

Federal law requires California to reduce emissions of chemicals that contribute to air pollution. As part of that effort, we must find ways to reduce smog-producing emissions from pesticides in areas that do not meet air quality standards. Reliable and consistent data is critical to developing practical measures to manage emissions of smog-producing volatile organic compounds (VOCs).

As required by the federal Clean Air Act, the Department of Pesticide Regulation (DPR) estimates and tracks pesticide VOC emissions, using pesticide use reports and data on the VOC content of pesticide products. DPR relies on this information to develop strategies to reduce emissions as required under legal mandates.

DPR scientists established the nation's first emission inventory to estimate pesticide VOCs. The goal was to reduce pesticide VOC emissions with an approach that was California-specific, an effective alternative to the federal government imposing its own controls.

WHAT'S INSIDE:

Federal rules likely would not have taken into account California's unique agricultural environment, how emissions from different pesticides might vary, or the impact of indiscriminate restrictions on the California economy.

The Basics: Terminology and Concepts

What are VOCs? Why are they important?

VOC stands for "volatile organic compound." VOCs are gases that can combine with other substances in the air to form ground-level ozone ("smog"). Ozone can damage lung tissue, cause respiratory illness, and harm farm crops. In California, the primary source of VOCs is vehicle exhaust. Industrial operations also emit VOCs, as do thousands of products, including pesticides.

For a map of California's pesticide VOC nonattainment areas, go to www.cdpr.ca.gov, click on "A-Z Index," then "Nonattainment area maps."

Under the federal Clean Air Act, each state must meet national standards for airborne pollutants. States must specify how they plan to do that in a federally approved "State Implementation Plan" (SIP). If a state fails to do so, the U.S. Environmental Protection Agency (U.S. EPA) must develop its own plan and can impose restrictions to attain the national standards.

Many regions in California do not meet these standards and are therefore designated "nonattainment areas" (NAAs). To structure solutions keyed to California, the Air Resources Board (ARB) developed a State Implementation Plan (SIP) outlining how the state would reduce VOCs from all sources, including pesticides. The pesticide part of the plan was presented to the U.S. EPA in 1994 and approved in 1997. Under this plan, DPR must track and control VOC emissions from pesticide products used in agriculture and by commercial structural applicators in five NAAs that exceeded federal ozone standards: Sacramento Metro, San Joaquin Valley, Southeast Desert, South Coast, and Ventura. (The California Air Resources Board, ARB, is responsible for VOC emissions from pesticides in consumer products.)

Under the SIP, California is expected to reduce pesticide VOCs by up to 20 percent (depending on the NAA) compared to 1990 levels. The base year is 1990 because that is the year federal Clean Air Act amendments were enacted requiring states to track and reduce pollutant emissions.

What is a nonattainment area?

A nonattainment area (NAA) is a geographic region designated by the U.S. EPA as failing to meet federal air quality standards for one or more "criteria" air pollutants, such as ozone and particulate matter. Criteria pollutants are those known to be hazardous to human health. The five nonattainment areas tracked in the emission inventory are Sacramento Metro, San Joaquin Valley, South Coast, Southeast Desert, and Ventura.

About DPR's VOC Emission Inventory

What is an emission inventory? What is it used for?

An emission inventory is a systematic listing of the sources of air pollutants, including an estimate of how much pollutant each source or category emits over a given time period. Emissions and releases to the environment are the starting point for many environmental pollution problems. Information about emissions is necessary for understanding environmental problems, for developing strategies to solve those problems, and to monitor trends.

It is neither feasible nor possible to measure emissions continuously from every individual source of pollution, and from all source types, particularly the thousands of small sources throughout a region. In practice, regulators routinely estimate atmospheric emissions using various scientific methods and approaches. Then they compile emission estimates into "inventories" or databases and report or publish the results periodically.

ARB prepares emission inventories for more than two dozen air pollutants, including particulate matter, volatile organic compounds (VOCs), and carbon monoxide.

Scientific researchers compile emission inventories as essential research tools. Government agencies see emission inventories as essential building blocks for effective pollution control policies. For DPR, ARB and other regulatory agencies, the goal is to identify problem areas and find ways to reduce emissions of pollutants, making the air healthier to breathe.

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The Pesticide VOC Inventory: What and Why

Why did DPR develop an emission inventory focused on pesticides?

The pesticide portion of California's SIP committed the state to track pesticide VOCs and reduce them by a certain percentage, compared to 1990 levels. The inventory is necessary to do this.

What information is in DPR's emission inventory?

DPR uses data on VOC content and pesticide use to prepare an annual estimate of VOC emissions from agricultural and commercial structural pesticide applications in the five NAAs. There is an emission inventory for each year since the 1990 base year. The inventory includes only applications from May 1 through October 31, the peak ozone season in California.

DPR updates the database each year when annual pesticide use report data from the previous year becomes available.

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How DPR calculates VOC emissions

Estimated VOC emissions = (Emission potential of the product) X (Pounds of pesticide product applied)

How does DPR calculate how much VOC is emitted from an application?

To estimate the VOC contribution of individual agricultural and structural use pesticides, DPR multiples:

The fraction of a pesticide product estimated to be VOCs (its "emission potential")
by
The amount of that product applied.

Because DPR has monitoring data from field applications of fumigants such as methyl bromide, this calculation is adjusted for fumigants to account for how emissions vary depending on fumigation method.

DPR does not have this kind of field data on nonfumigants.

For example:

Farmer Joe applies 100 pounds of Lorsban 4E to his orchard. The emission potential of Lorsban 4E is 51.32%. It is not a fumigant, so the calculation would be:

- 100 pounds x 0.5132 = 51.32 pounds estimated VOC emissions

Farmer Jane applies Tri-Clor-EC — a fumigant — to her unplanted field, using drip irrigation. In this example, the calculation would include an adjustment since DPR has data to show how different application methods affect emissions.

Tri-Clor-EC's VOC content is 94%. With drip irrigation, 12% of the applied VOCs are emitted, so the calculation would be:

- 1000 pounds x 0.94 x 0.12 = 113 pounds estimated VOC emissions

How is the VOC content of each product determined?

The pesticide plan adopted by DPR and ARB in 1994 committed California to developing a way to estimate VOC emissions from each of the thousands of pesticide products used in the state. After workshops and consultations with laboratories, pesticide makers and ARB, DPR adapted a laboratory method called thermogravimetric analysis (TGA) to estimate a product's VOC content (its emission potential).

DPR chose the TGA method because it provided a simple, inexpensive, and consistent method of estimating relative volatility for most pesticide products.

How does the TGA method work?

The TGA method is similar to methods used by U.S. EPA and ARB (methods 24 and 310, respectively) to estimate VOC content.

The TGA method involves placing the sample in an environmental chamber containing a heater and a scale on which the weight of the sample before testing is recorded.

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How DPR calculates VOC emissions (continued)

The sample is heated to 115° C. (239° F.) and as volatile chemicals turn into vapor, the weight of the product decreases. When this loss stabilizes, the remaining product is the nonvolatile portion. Its weight and the weight of any water and other inorganic compounds in the product are subtracted from the weight of the sample before testing to arrive at the VOC content. (The amount of water and other inorganic ingredients is included in the product's confidential statement of formula, on file with DPR.)

What if DPR does not have laboratory data on a pesticide product's potential emissions?

The TGA method cannot be used for certain products. These include products that break down under experimental TGA conditions or that cannot be easily analyzed by the method because they are too volatile to handle (such as some fumigants). This laboratory data is also not available for products which were no longer being made DPR when adopted the TGA method.

DPR usually considers TGA to be the most desirable method for estimating the emission potential of a pesticide product and uses that data when it is available. When it is not available, DPR uses other approaches to decide emission potentials:

- Using the VOC emission potential already measured in TGA analysis of an identical or nearly identical pesticide product.
- Using the confidential statement of formula on file with DPR to find out the percentage of water and other inorganic chemicals in the product. This is subtracted and the remainder is assumed to produce emissions that must be included in the inventory.
- Assigning an estimated value based on an evaluation of a product's unique chemistry and composition. DPR takes this approach for high-use products with well-known chemical properties.
- Assigning a default (representative) emission potential.

When are default emission values used?

Many products in the early 1990s were assigned default emission values because TGA was not available. By the late 1990s, many of these products were no longer being made, so they could not be tested.

DPR assigned default values to some products without TGA data because their product chemistries make it clear they contribute little VOC emissions. Other products do not contain inorganic chemicals or water (meaning the subtraction method cannot be used), so default emission potentials are used for these products.

How are default values calculated?

DPR typically sets default emission values at a representative level, based on measured data that reflect the behavior of similar products. DPR assigns most default emission potentials based on the product's formulation category. Different formulation types have different VOC contents. For example, liquids have more VOCs than solids. Formulation categories include emulsifiable concentrate, flowable concentrate, dust, powder, and compressed gas.

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How DPR calculates VOC emissions (continued)

Before 2002, defaults were set at the highest TGA value DPR had on file for the formulation. In 2002, to get a more representative estimate of emissions, DPR began assigning defaults at the median value. The default emission potential for an emulsifiable concentrate, for example, would be set at the median for that category: 39.15 percent. This means that, for emulsifiable concentrate products for which TGA data is available, half have VOC content below 39.15 percent of amount applied and half have VOC content above that level.

Although about 45 percent of products in the inventory have default emission potentials, many are relatively nonvolatile solids with only a small contribution to total emissions.

When does DPR develop an estimated value rather than assign a default value?

When a product has high use or its composition and chemistry point to unusually high or very low emissions, DPR attempts to develop a more realistic estimated value rather than use default emission potential.

Starting in 2002, DPR analyzed various pesticide products in several high-use product classes with well-defined compositions and chemistries.

These products included certain sulfur-containing dusts and powders, sodium chlorate, certain petroleum oil and mineral oil products, and various inorganic pesticides such as nitrogen, sodium hypochlorite, chlorine, sulfur dioxide and sulfuryl fluoride.

The purpose was to identify products for which emission potentials could be better estimated based on composition data rather than assignment of default values.

In addition, DPR developed emission potentials based on product chemistry for several fumigants so their volatilities could be expressed in terms of the VOC content of the chemical released after the parent compound breaks down in the field. These included sodium tetrathiocarbonate (volatile chemical, carbon disulfide) and two related active ingredients, metam-potassium and metam-sodium (volatile chemical, methyl isothiocyanate, or MITC).

Does DPR account for how emissions might vary with different application methods, under field conditions?

Intensive research on field fumigant emissions has been conducted for the last 15 years, to develop restrictions to protect public health. As a result, DPR has fumigant emission data measured from several dozen field studies spanning a range of fumigants and application methods. Using this data, DPR can take into account varying fumigant emissions under field conditions.

Previously, when calculating the VOC inventory, DPR had assumed 100 percent volatility for fumigant chemicals. However, field measurements show that emissions vary with application method and fumigant being used. Actual emissions range from 9 to 100 percent of the amount applied, but most have emission rates less than 100 percent. Fumigations with tarps, water treatments, or through drip irrigation generally have lower emissions.

In 2007, DPR analyzed the available fumigant emission data to develop fumigant

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How DPR calculates VOC emissions (continued)

application method adjustment factors. Applying these "emission ratings" produces better estimates of VOC emissions under field conditions by accounting for how the application method and fumigant can affect emissions.

DPR is open to making similar adjustments for nonfumigant pesticide products, but alternative methodologies have not been submitted to DPR that can be incorporated into the inventory. Developing this data for the thousands of nonfumigant products will be a scientific challenge, as the studies must include measurements of VOC emissions of both active and other ingredients, and emissions of major VOC breakdown products. In addition, since it is known that some pesticide products emit VOCs for days to months, emissions data for relatively long periods may need to be developed.

DPR will need to evaluate any methodology to determine how to apply it to the inventory from the 1990 base year to the present. This is made more difficult because there are many products that are no longer made and for which little product information is available.

How does DPR determine how much of a pesticide product is used?

DPR uses two factors to estimate VOC emissions: a product's emission potential and how much was used. California is fortunate to have a reporting system for pesticide use that allows for a consistent, annual estimate of pesticidal VOC emissions.

State regulations require reporting of all agricultural applications and structural applications by commercial pest control businesses. The pesticide use reports include information on the pesticide product applied, how much was applied, date and location.

DPR's inventory includes all reported agricultural pest control, and structural pest control by commercial applicators. What uses does this include?

California law defines agricultural pesticide use broadly. It includes not only pesticides used on agricultural commodities, but also those used in forests, waterways, landscaped areas, and rights-of-way.

Agricultural use accounts for most pesticide VOC emissions in the five areas of the State that are of regulatory concern.

The major categories of pest control that are not considered agricultural use are home-and-garden, industrial, institutional and structural.

Structural use (which is included in the VOC emission inventory) refers to applications by a licensed structural pest control operator to manage household pests (such as rodents or insects), wood-destroying pests (like termites), or other pests that may invade buildings.

Most post-harvest commodity fumigations are considered industrial pest control and are not included in DPR's agricultural and structural emission inventory. (However, they are included in ARB's VOC inventory.)

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How is the pesticide VOC inventory used?

California must reduce every source of VOCs to solve its air pollution problems. Pesticides account for about two percent of VOCs statewide, but in several regions, they are among the top ten sources.

DPR's commitment under California's SIP is to reduce pesticide VOC emissions by up to 20 percent, compared to 1990 levels, in the five nonattainment areas. Pesticide VOCs have already been reduced 20 percent in the South Coast and the Sacramento Metro NAAs.

California must reduce every source of VOCs to solve its air pollution problems. Pesticides account for about two percent of VOCs statewide, but in several regions, they are among the top ten sources.

DPR uses the VOC inventory to identify the various pesticidal sources of VOCs, track changes in pesticide VOC emissions over time, suggest and evaluate potential VOC emission reduction strategies, and track progress in meeting pesticide VOC reduction goals.

ARB also incorporates information from DPR's inventory into its statewide estimate of VOC emissions from all sources.

Does DPR update its methodology to reflect the most current scientific research?

Since 2002, DPR has made many changes to improve the inventory. For example, DPR revised default emissions potential values to make them more representative, by using a median rather than the highest emission potential for the generic group. In addition, DPR set up a procedure to develop special, product chemistry-based emission potentials for high-use products with well-understood properties.

In 2005, DPR required pesticide makers to provide laboratory data on the VOC content of nearly 800 nonfumigant products, chiefly emulsifiable concentrates. These liquid products are high VOC contributors because of solvents in the formulations; they account for about half of the pesticide VOCs in the San Joaquin Valley. In 2006, DPR moved to cancel nearly 100 products whose registrants failed to provide the data. Most manufacturers responded by sending the information, while others withdrew their products from the market.

DPR is open to further changes that can improve the inventory or values that go into the inventory calculations. However, there are limitations to the kinds of changes that DPR scientists can make. Since the purpose of the inventory is to determine whether emission reductions have occurred over time, any new methodology must be applied to products from 1990 to the present, so consistent comparisons of relative emissions can be made. Except for fumigants, no data has been submitted to DPR that provides a better description of pesticide volatility in field conditions. Also, some changes to the inventory are not possible unless data can be obtained on products used extensively in the 1990 base years but which are no longer

made. The law requires consistent methodology be used to make comparisons across all data in the inventory.

The first inventory in the early 1990s overestimated VOC emissions by 500 percent in the San Joaquin Valley and by 200 percent in Ventura. Has that been corrected?

Those estimates were published at least two years before DPR completed its first emission inventory. The initial estimates were also inaccurate. They were not based on either emission potential data or pesticide use reporting data, the two underpinnings of DPR's emission inventory.

The most important point, however, is that DPR never used those estimates for evaluation, decisionmaking, or regulation.

No emission inventory can be an exact reflection of actual emissions. Inventories are estimates based on the most reliable data available.

How reliable is the inventory?

No emission inventory can be an exact reflection of actual emissions. Inventories are estimates based on the most reliable data available, which is then compiled and analyzed using transparent, verifiable methodology.

Emission inventories are regulatory tools from which information and strategies are developed. The key is that they be scientifically based and systematic. Uncertainties in the inventory are unavoidable, but if they are understood, the database allows for valid comparison of relative emissions from year to year, rigorous evaluation, and sound decisions. For DPR's pesticide emission inventory, using a consistent approach to compare data is critical because the VOC reduction goals are expressed as a percentage relative to emissions in the 1990 base year.

DPR's inventory contains data for every year since 1990. Each year contains about 2.5 million pesticide use records and emission potential records for roughly 5,000 products. Errors or uncertainties in any record affect emission estimates. DPR scientists have intensively examined the data on which the inventory is based, and the calculations that go into the estimates. They understand the uncertainties and take every measure possible to account for them.

DPR analysis indicates that compliance with use reporting requirements is high, that 90 to 95 percent of agricultural use is reported. In addition, DPR has built more than 50 error-checks into its use reporting software. Moreover, under- or over-reporting is likely to occur consistently across all kinds of pesticide applications. This means that, even if the use reporting database contains errors, it is representative of relative use and can be relied on for analysis.

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Other potential factors that affect emission estimates include uncertainties in emission potentials. Default values are assigned for products for which DPR does not have emission potential data. However, such products account for only a small fraction of emissions because many are low-volatility solid products. For example, DPR estimates that emissions from these products make up less than 10 percent of current pesticide VOC emissions in the San Joaquin Valley.

Research indicates methyl bromide emits VOCs that do not react to form ozone. Why doesn't California take methyl bromide out of the emission inventory?

Different VOCs create different amounts of ozone, and some are essentially nonreactive, that is, they do not create ozone. The methyl bromide industry has presented research to U.S. EPA and requested that the substance be declared exempted as nonreactive. Under the federal Clean Air Act only U.S. EPA can exempt a VOC from regulation because it is nonreactive.

For more information

Go to www.cdpr.ca.gov, and click on the "Fumigant/VOC Regs," one of the red Quick Links in the center of the page. Sign up for free e-mail updates on activities in our VOC program by going to www.cdpr.ca.gov, and click "Join E-Lists" in the left column.

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About the Department of Pesticide Regulation

The California Department of Pesticide Regulation (DPR) protects human health and the environment by regulating pesticide sales and use and by fostering reduced-risk pest management. DPR's strict oversight includes product evaluation and registration, environmental monitoring, residue testing of fresh produce, and local use enforcement through the County Agricultural Commissioners. DPR is one of six boards and departments within the California Environmental Protection Agency.