Control of Ozone Formation from Household and Commercial Product Use

Development of an Effective Regulatory Approach

American Chemistry Council

Solvents Industry Group

Solvent Industry Group

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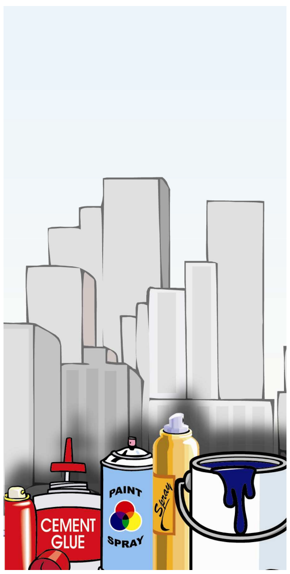
The paints, cleaners, and personal care products we use to beautify and sanitize our homes, offices, and belongings contain a wide range of volatile chemicals that may be contributors to urban air pollution. These chemicals, known commonly as VOCs, are essential to the overall performance of these products. A common definition of a VOC refers to any chemical that is capable of entering the atmosphere and participating in a chemical reaction that leads to ozone formation. This broad definition encompasses many types of chemicals in addition to the VOCs used as solvents in household and commercial products. Although the use of solvent VOCs has been curtailed over the last 40 years, more ozone reductions are necessary to achieve our goals of a safe and healthy atmosphere. The complete removal of solvent VOCs from the marketplace is not a practical optional, however, since the performance properties of many items depends on the use of some solvent as an aid to formulation and application.



Enormous effort has been made in reformulating products to eliminate the nonessential use of solvent VOCs while retaining their properties in a range of applications. For the most part, these gains have been achieved through the nonselective removal of VOCs, regardless of their relative ability to react and form ozone, the main component of urban smog. This "shotgun" approach to VOC control, which treats all VOCs as equal contributors to ozone formation is no longer a viable method for reducing emissions. Aggressive control of VOC use in the twenty-first century demands the replacement of current management practices in favor of controls that rely on the principles of photochemical reactivity.

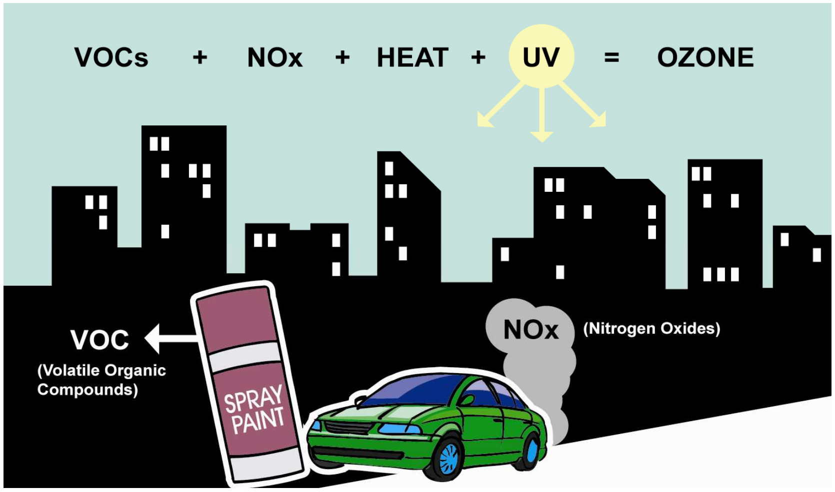
…… targeting those solvent VOCs with the highest reactivity is more effective than the nonselective removal of all VOCs

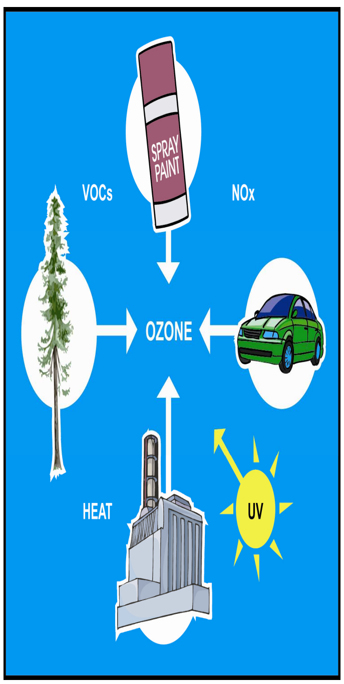
This new approach recognizes that some solvent VOCs are far more reactive in the atmosphere than others, and that targeting the most reactive will achieve a far greater benefit at a lower cost. Although some VOC control plans utilize reactivity principles, more needs to be done to accelerate the conversion to a new control policy and reduce the ozone threat in a technically correct and environmentally sound manner.

Role of VOCs in Ozone Formation

VOCs may contribute to the formation of ozone in a complex series of reactions that requires the presence of heat, sunlight, and nitrogen oxides or NOx, whose primary source is automobile exhaust.

Many nonattainment areas are located in major urban hubs, such as Houston, Los Angeles, and Philadelphia, that are natural targets for VOC control.





To reduce ozone levels in the atmosphere, both VOC and NOx emissions can be controlled; but, depending on their relative amounts, one component or the other will be the most effective target. For instance, in a NOx rich urban environment, the rate of ozone formation is directly related to the amount of VOC available. The opposite may be true in rural environments where VOCs are in excess and the removal of NOx translates into an ozone decline.

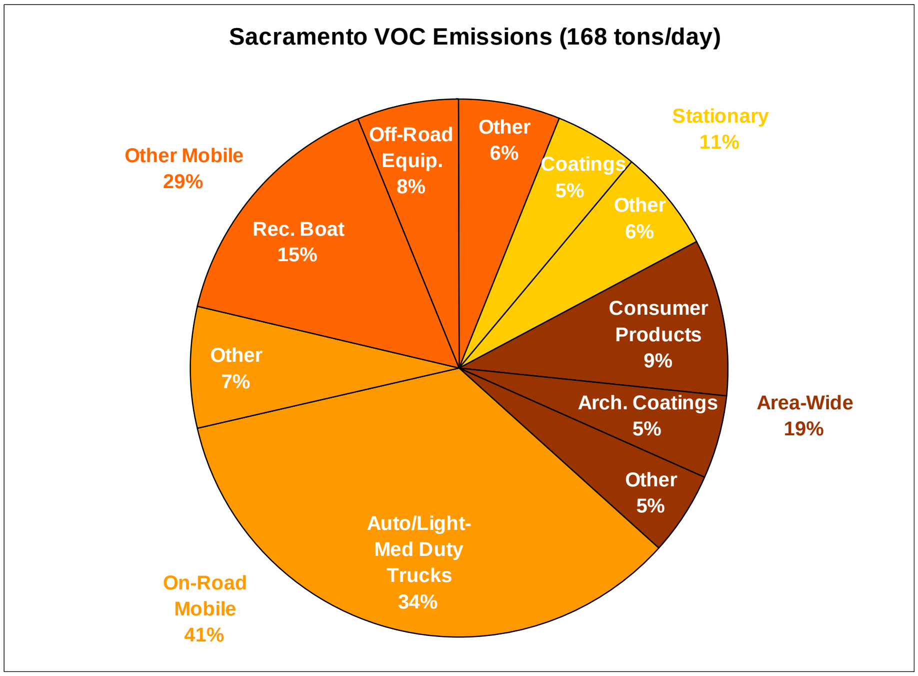
The VOCs emitted into an urban environment come from the following four sources:

- **Vegetation** – biogenic sources are generally important in rural environments, but some cities in the Southeast have major emissions from trees and plants.
- **Mobile** – mobile emissions come from the transportation sector and are the result of evaporative and exhaust emissions from the use of on-road and off-road vehicles; including trains, planes, watercraft, construction equipment.
- **Stationary** – these emissions are from fixed locations and include the fugitive releases of VOCs from industrial and non-industrial locations that use or manufacture volatile chemicals.

- **Area** – area sources of VOCs emissions include the widely dispersive releases associated with the use of consumer and commercial products.

Cities like Atlanta where biogenic emissions dominate, need to extract a larger percentage of their VOCs reductions from the remaining source categories.

Although each of these sources contribute to the atmospheric burden of VOCs, some sources are more amenable to control than others, especially in an urban environment. Vegetative sources, for example, cannot be reasonably controlled; and cities like Atlanta where biogenic emissions dominate the landscape, need to extract a larger percentage of their VOC reductions from the remaining source categories.



Constructing an emissions inventory from a survey of VOCs in the 4 major source categories is a crucial first step in the identification of potential control options.

Although the relative contribution of the three major VOC sources can vary according to location, the pie chart for the Sacramento nonattainment region is reasonably representative of the distribution observed in many urban environments. As shown, mobile emissions are the dominant source of VOCs in most situations. Solvent VOC emissions from the three area sources categories are by comparison far lower, comprising about 19% of the overall total. The solvent VOCs emitted from individual area sources each contribute to less than 10% of the total emission inventory. Though the solvent VOCs from these product areas are not major contributors, they are a potentially controllable sources that are often addressed in any ozone attainment plan.

The USEPA recently released figures to show that VOC emissions from non-biogenic sources in the US have declined by 52% in the 16 year period ranging from 1980 to 2006. A closer examination of this information reveals, however, that the majority of these gains were made in the early years of the program. The chart below shows that the reduction of VOC emissions has tailed off in recent years and that more moderate mass reductions can be expected in the future.

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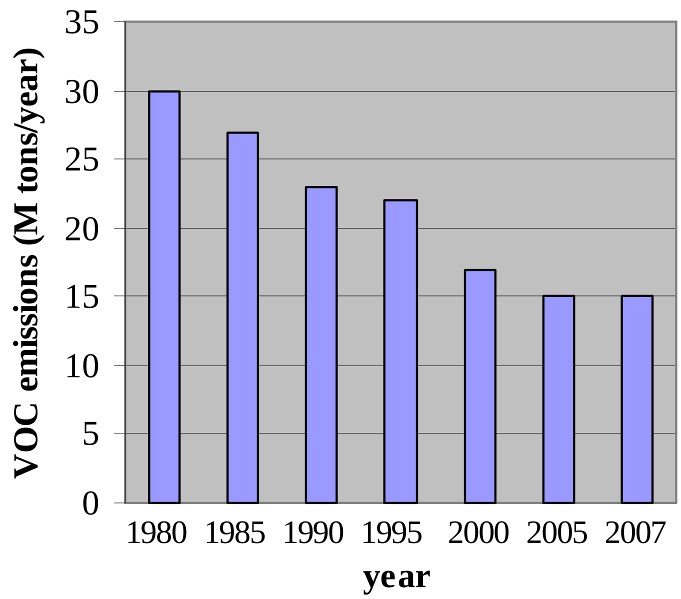


This shrinking pool of VOCs available for ozone control has important implications for the development of control options. Many ozone nonattainment areas in the East and Southwest have projected large shortfalls in their VOC reduction goals. This has necessitated far stricter emission limits on solvent VOCs to compensate for increases associated with population growth. These new restrictions highlight the need for innovative ways of thinking about the relationship between VOC use and ozone formation. Despite these problems, there has not been any attempt to systematically entertain new options for solvent VOC control.

The California Air Resources Board was the first to pass an Aerosol Coatings regulation in 2001 that incorporated the principles of photo-chemical reactivity.

Ozone control in the US : a selective history

Limiting the creation of urban ozone through VOC control has been a regulatory priority for over 40 years. The first rules can be traced back to Los Angeles District's Rule 66, which targeted the release of many VOC species in an attempt to limit the formation of urban ozone. Rule

66 was a pass/fail regulation that only considered those reactive VOCs considered to have appreciable ozone-formation potential.

For nearly two decades, ozone control in the United States focused entirely on limiting VOC emissions. It was only after the passage of the Clean Air Act Amendments of 1990 that NOx became a target for future action. NOx regulations provided an important new tool in the fight against ozone pollution, since their implementation in many parts of the country brought far greater benefit than the control of VOCs alone. But because NOx controls are not as effective in urban environments, where the rate of ozone formation is directly related to VOC emissions, both ozone precursors must be subjected to control.

The Clean Air Act Amendments also marked the beginning of an aggressive attempt to control solvent VOCs by identifying areas that were not in compliance with the national ambient ozone standard. Those States with ozone nonattainment areas were required to submit a more detailed State Implementation Plan or SIP for tackling their air pollution problems. A necessary ingredient to these plans was the requirement for a 15 percent reduction of VOC release over a 6 year period in those areas in moderate violation of the standard.

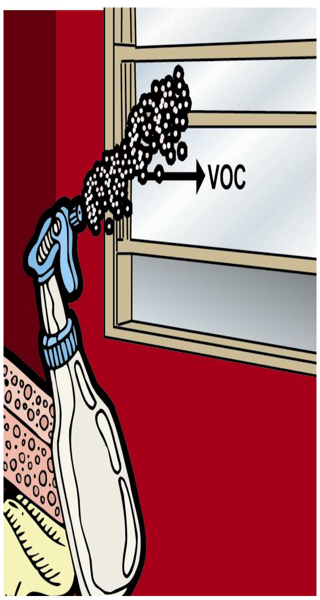
To assist the States in carrying out these goals, the CAA Amendments required the USEPA to regulate consumer and commercial product categories that accounted for at least 80 percent of the solvent VOC emissions in nonattainment areas. Although this list of potential control categories was created after first considering the ozone-forming potential, or reactivity, of individual VOCs in each product category, there was no stipulation that photochemical reactivity be used as the basis for controlling VOC release from these sources.

Using the list of product categories, the USEPA created two types of control measures that the States could utilize to limit the use and release of solvent VOCs. The first type of control measures were called Control Technique Guidelines or CTGs, which are not regulations but recommendations that target facilities using large amounts of VOC-containing products whose composition can be controlled through arrangements with the supplier. Since 2006, CTGs have been issued for 12 VOC categories. Some CTGs specify solvent VOC content limits

The rules for consumer products and architectural coatings were created in 1997 and are in the process of being updated.

for products, but most identify emission limits for the application of a particular type of coating. The second type of control measures are rules, which are aimed at the manufacturers of consumer and commercial products. These EPA rules are applied to products that are in use by the general public rather than industrial facilities. Once implemented, they apply nationwide and can affect those living in both attainment and nonattainment areas. Rules have been issued for 5 product categories.

- *Consumer products*
- *Architectural coatings*
- *Automobile refinish coatings*
- *Portable fuel containers*
- *Aerosol spray paints*



Although ozone contribution to air pollution is indisputable, the methods used to control VOC release from consumer products have been the subject of considerable debate for many years. Two alternatives are available to State and Federal regulators:

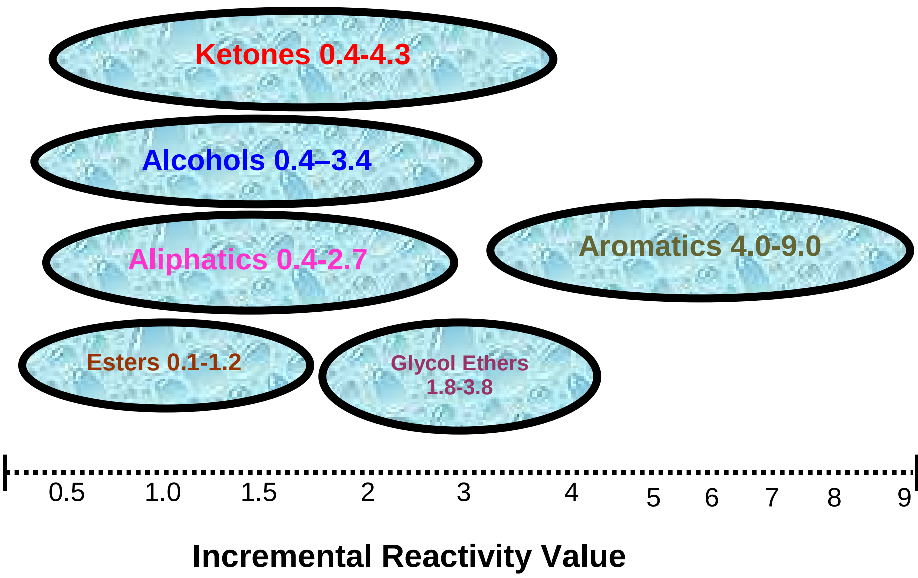
i) treat all reactive VOCs as equal contributors to urban smog without any consideration of relative impact (mass-based approach); or

ii) Encourage industry to reformulate to the VOC species which have the least potential for ozone formation (reactivity-based approach).

Traditionally, solvent VOCs have been regulated using mass-based controls that limit the mass percentage of VOCs in various products or formulations, such as paint. Under this approach, VOCs are either considered reactive, and therefore subject to VOC regulation, or negligibly reactive, and thus exempt from control. Negligibly reactive compounds are compounds that, based on USEPA studies, contribute minimally to ozone formation. This list of compounds (often referred to as VOC exempt compounds) was established by USEPA and can be modified by regulation.

The California Air Resources Board is currently considering the use of reactive measures in rulemaking for hairspray and nail coating products.

Mass-based limits, which are relatively easy to issue and implement have been the avenue of choice for developing new control regulations based on their long history of use. A mass-based approach treats all non-exempt VOCs alike in their ability to generate ozone. However, solvent VOCs vary significantly in their ability to impact ozone levels. Despite the fact that mass-based controls are rapidly becoming ineffective, many State regulatory authorities have adopted the position that reactivity will only be considered as a VOC control option once mass-based opportunities have been exhausted. Although both types of controls have their own advantages and disadvantages, recent events suggest that mass-based controls are becoming ineffective and going forward significant benefits are more realistically achieved with widespread adoption of reactivity-based controls.



Diminishing returns from current policies

State compliance with the Clean Air Act is no easy matter. Preparation, submission, and approval of a SIP for bringing nonattainment areas into compliance with air pollution standards can take up to 3 years to complete. State agencies are often faced with proposing dozens of control methodologies for both VOC and NOx in a single action plan. In addition, SIPs contain a reasonable further progress provision that mandates a yearly reduction of VOC and NOx in nonattainment areas. In the face of these requirements, State authorities often need to develop VOC control options that go above and beyond those proposed by the USEPA.

Mass-based controls have become increasingly expensive to implement and comply with as the reservoir of controllable VOCs is diminished.

There is an initial appeal in adopting control plans that require the least amount of up front effort. Under these circumstances, the preferred approach to VOC control in the consumer and commercial product sector has been mass-based emission or content limits. Though this approach at first appears to respond to the problem of VOC control, there are numerous pitfalls, the most important of which is that mass-based controls are not an effective means of lowering ozone levels in urban environments.

The following list cites some of the most serious problems with the use of mass-based limits in a control scheme for solvent VOCs. In particular, mass-based controls:

- *do not utilize the latest scientific knowledge and allow the continued use of inaccurate and outmoded chemical "lumping" techniques to group VOCs into a few discrete chemical groups;*
- *have become increasingly expensive to implement and comply with as the reservoir of controllable solvent VOCs is diminished;*
- *do not provide manufacturers with enough options to reformulate their products in a manner that will preserve performance under all use conditions;*
- *are arguably at variance with Section 183e of the Clean Air Act, which requires the use of the "best available control" measures to achieve attainment;*
- *stifle innovation and product improvement by needlessly restricting solvent VOC content rather than VOC hazard;*
- *promotes the use of an exempt category of VOCs that is mistakenly believed to lack any ozone forming potential;*
- *are based on the mistaken belief that they are actually reducing urban ozone levels in all circumstances when recent evidence shows the ozone-forming potential of products is increasing.*

The number of counties in nonattainment increased from 85 to 345 with the passage of the new ozone air quality standard in 2008.

A recent analysis of the results from a solvent survey conducted before and after the implementation of mass-based controls in California has confirmed what many leading authorities have long suspected, that mass-based regulations do not reliably reduce ozone forming potential and can in fact promote the use of more reactive VOC species. This may seem to be at odds with SIP requirements which stipulate that the value of all recommended control measures be substantiated using sophisticated urban airshed models. It must be recognized, however, that the urban airshed models used to predict the impact of these control measures simplify the chemistry and reactivity of the available VOCs by grouping them into a few discrete categories. These oversimplifications can easily distort the true picture and predict an ozone benefit when none actually exists.

VOC Reactivity Technology Forum and Roundtable Discussion September 25, 2007, South Coast Air Quality Management District Headquarters Diamond Bar, CA.

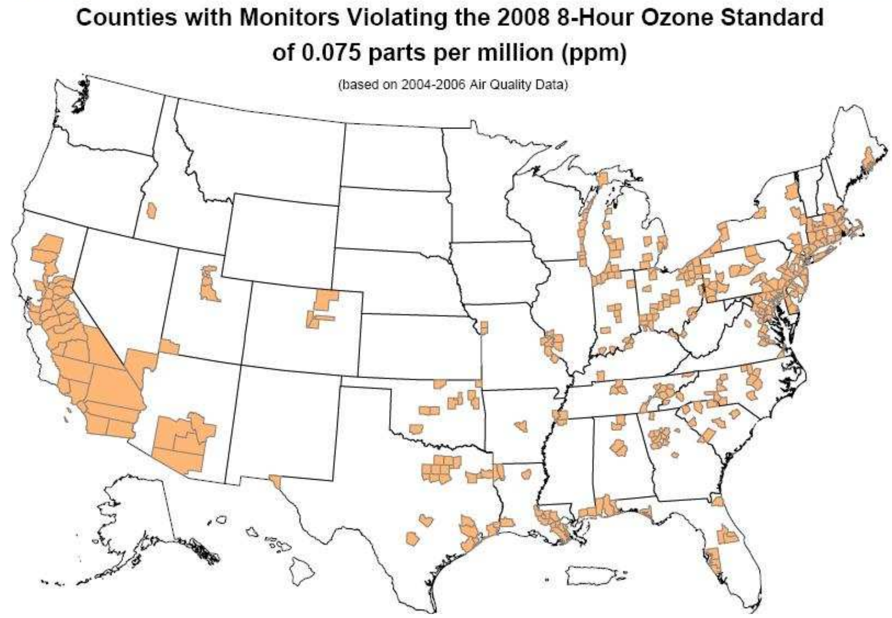
Information presented at the VOC Reactivity Technology Forum and Roundtable Discussion sponsored by the South Coast AQMD has indicated that the ozone-forming potential of many coating categories is actually on the rise. The increase is the result of an overreliance on mass-based standards, which has allowed formulators to select solvents based on solvent strength, not on their actual environmental impact. This lack of true control has led to most categories not achieving the ozone reduction touted by the mass-based VOC adjustment, and in many cases the ozone formation from the coating category actually increased despite a reduction in VOC mass. While some of that increase in ozone forming potential is due to volume growth in the category, a large portion of it is due to a demonstrable increase in the reactivity of the solvents being selected. This unintended consequence of mass-based controls, becomes more severe as the reservoir of potentially controllable solvent VOCs in the product becomes smaller.

A need for new pollutant control ideas

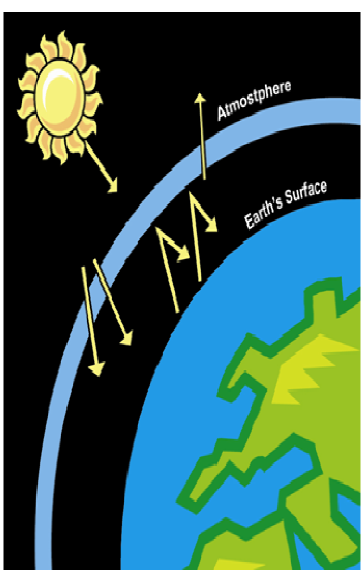
Pollution control regulations in the US have targeted the use and release of solvent VOCs from consumer and commercial products for many years, but the era of fast and easy gains on the ozone problem are quickly coming to an end. The need for new ingenuity and insight into the problems of urban air pollution has never been greater. There is no better example of the increased demands being placed on VOC control policy than the predicted impact of the new national ambient air quality standard for ozone.

In the face of ever stricter ozone standards and the impacts of global warming, the issue of VOC control needs to be reexamined at all levels of government.

The Reactivity Research Working Group (RRWG) was organized in 1998 to conduct research and develop an improved scientific basis for reactivity-related regulatory policies.



The recent reduction of the 8-hr ozone standard from 80 to 75 parts per billion is projected to put 4 times as many counties into ozone nonattainment. Those States affected by the new standard are required to file new SIPs by the year 2013. This will generate an even greater demand for novel VOC control methods, especially in urban areas where ozone concentrations are particularly high.



In fact, there are concerns that we may never be able to achieve total control of urban ozone because of the impacts from global warming. Studies have shown that rising greenhouse gas emissions have caused a temperature increase that will adversely affect our attempts to control ozone in polluted environments. In effect, these studies suggest that large increases in the emission of biogenic VOCs will accompany a shift in the chemistry of smog formation. Together, these changes will lead to an increase in the regional background concentration of ozone. Climate change will also affect the intensity and duration of stagnant air episodes in urban areas and cause more prolonged periods of elevated ozone. The dual impacts of climate change and new ozone control standards mandate that agencies take a new approach to VOC control that will maximize environmental improvement opportunities and minimize the burden to commerce, the community, and the economy.

Reactivity: a rational alternative

VOC control policy in the US has not managed to stay abreast of advances in the science of photochemical reactivity. For many years now scientists, manufacturers, and pollution prevention advocates have argued for the use of reactivity scales in new policy initiatives.

Evidence exists that mass-based reformulation has resulted in products with a higher ozone formation potential than their predecessors.

Regulating chemicals according to their ability to contribute to ozone formation has the potential for dramatically impacting urban ozone levels. The adoption of this new approach has met with considerable resistance, however. Although some rules have been passed at the State and Federal level that incorporate the principles of reactivity, there has been a belief by many that the old mass-based controls provide greater benefit.

The USEPA 's 2005 Interim Guidance encouraged states to consider recent scientific information on reactivity in the development of their SIPs.

The current philosophy seems to be that reactivity should not be considered until all opportunities for mass-based controls have been exhausted. But this policy of forcing ever tighter restrictions on the use of solvent VOCs is shortsighted and ignores the benefits that can be accrued when reactivity is used early in the process. It is based entirely on the belief that as long as manufacturers can reformulate, mass reductions are the best option. Indeed, the recent passage of the photochemical reactivity-based Aerosol Coatings Rule by the State of California was only possible after first determining that product reformulation was not an option. The USEPA has also published a photochemical reactivity based Aerosol Coatings Rule that is anticipated to be finalized in 2009.

Under some circumstances mass-based reductions would seem to be a reasonable alternative, if there was a method to ensure that the VOC decreases were equally distributed among high and low reactivity solvents. This would ensure that the mass reductions actually resulted in a decline in ozone formation. Unfortunately, this is not always the case, and there is no guarantee that the products of tomorrow will actually achieve the desired result of lowering urban ozone levels.

As noted earlier, evidence presented at the VOC Reactivity Technology Forum and Roundtable Discussion showed that mass-based reformulation has resulted in products that have a higher ozone formation potential than their predecessors. This unanticipated effect occurs because product designers have seen a performance advantage when low reactivity VOCs are preferentially removed from reformulated products. The result is an increased percentage of highly reactive VOCs and an overall greater ozone-forming potential for the product. Adopting a reactivity-based VOC control policy would prevent this unintended effect and ensure that all product reformulations actually result in a benefit to the environment. The continued push for mass reductions from consumer and commercial product categories does not guarantee that urban ozone levels will actually decline.

A shift in VOC control policy to a scheme that promotes the use of reactivity-based limits would have a number of ancillary benefits that should also be considered. These include:

- *easier prioritization of potential control measures using reactivity metrics;*
- *the identification of more cost-effective approaches to solvent VOC control;*
- *the development and use of more robust urban air shed models to identify control options and track progress on ozone attainment;*
- *an incentive to further speciate emissions inventories, which allow a more accurate identification of potential control VOC options;*

- *the creation of more substitution options for product formulators resulting in more effective and efficient products.*

The first step in designing a regulation based on reactivity is to select the most appropriate reactivity scale.

Although some criticisms have been levied against the use of reactivity-based standards, they are generally speculative and easily addressed in any future policy initiatives. For instance, the claim that reactivity-based controls will allow greater use of less reactive, but highly toxic, solvents is difficult to substantiate, since manufacturers routinely screen and eliminate highly hazardous chemicals from their product formulations. Another criticism that has been cited is the belief that reactivity-based controls will lead to greater use of low reactivity VOCs that can be transported out of an area only to cause downwind increases in ozone formation. Studies have shown, however, that this is not the case and that the ozone reductions realized by the upwind elimination of highly reactive VOCs are far greater that the increases resulting from downwind formation.

In the face of increasingly difficult compliance demands on State governments, reactivity-based controls provide a scientifically vetted and highly innovative approach to VOC control. The path has been cleared for the incorporation of reactivity metrics into State pollution control plans. The primary roadblock to widespread adoption is the failure to fully understand and appreciate the relative strengths afforded by this state-of the art approach to ozone abatement. The sooner these advantages are recognized, the faster we can realize real improvements in urban ozone levels throughout the country.

Summary

VOC Reactivity Technology Forum and Roundtable Discussion September 25, 2007, South Coast Air Quality Management District Headquarters Diamond Bar, CA.

The current approach to the control of solvent VOCs focuses on mass-based reductions to extract as much VOC as possible from a product category before looking at the feasibility of using reactivity-based controls. This tactic, however, can have negative environmental consequences by forcing product formulators to select alternative VOCs without any regard to their ozone-forming potential. This trend was recently illustrated at the VOC Reactivity Technology Forum where an analysis of past regulatory initiatives showed that strict reliance on mass -based VOC controls has led to an overall increase in the ozone-forming potential of some products as manufacturers choose more efficient, but more highly reactive, VOCs to reformulate their products. The failure to adopt reactivity-based controls on a wide spread basis represents a missed opportunity that could yield far greater environmental benefit than the present approach.

Over twenty different photochemical reactivity scales have been developed to meet any particular regulatory need.

Drawbacks in the current VOC control policy can be prevented with a more aggressive move towards a reactivity-based VOC control plan at both the regional and national level. State agencies in charge of pollution planning must become more willing to entertain alternatives to the rigid and restrictive nature of the mass-based measures currently in use. Adoption of a more robust and technically justified reactivity scheme provides an alternative that can reap benefits far into the twenty-first century.

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Please visit www.americanchemistry.com/solvents for more information about other solvent topics.

Reading List

The following reading list provides more information on many of the topics discussed in this white paper.

Avery, R. J. (2006). Reactivity-based VOC control for solvent products: More efficient ozone reduction strategies. Environmental Science & Technology **40**, 4845-4850.

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