

Scientific Basis of an Improved EPA Policy on Control of Organic Emissions for Ambient Ozone Reduction

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ABSTRACT

This article describes an effort to re-examine the scientific bases of the existing, more than two decades-old U.S. Environmental Protection Agency (EPA) policy on volatile organic compound reactivity in light of recent scientific knowledge and understanding. The existing policy allows "negligibly reactive" organic emissions, that is, emissions with ambient ozone production potential lower than that of ethane, to be exempted from all ozone regulations. It relies on use of k_{OH} and incremental reactivity data for determining whether an organic compound is negligibly reactive. Recent scientific evidence suggests that (1) exempting the negligibly reactive organic emissions from all regulations is unjustifiable, (2) the choice of ethane as the benchmark organic species for distinguishing reactive from negligibly reactive organics may be inappropriate, (3) the assumptions and methods used for classifying organic compounds as "reactive" and "negligibly reactive" should be reconsidered, and (4) the volatility factor should be considered, more appropriately, in much the same way as the reactivity factor.

IMPLICATIONS

The work described in this article has implications related to EPA's policy on control of organic emissions for ambient ozone reduction. The policy consists of regulations that require inventory and control of organic emissions in ozone non-attainment urban areas, but, for the purpose of encouraging development of environmentally superior alternative products, it also permits exemption of those emissions that are shown to have negligible potential for ambient ozone production. The current policy has been in existence since 1977, with only minor changes to date. Recent research results and understanding, however, suggest that certain elements of the policy need to be updated. These science-dictated revisions will be taken into account in EPA's effort to develop an updated policy that is effective both in enhancing ozone air quality and encouraging development of environmentally superior commercial products.

INTRODUCTION

Photochemical reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in the atmosphere result in formation of photochemical smog, a mixture of oxidants and other hazardous gaseous and particulate pollutants, the most important constituent of which is ozone, a pollutant with adverse effects on human health, vegetation, and materials. This photochemical ozone formation phenomenon has been, for decades, an extensive and persistent urban air pollution problem for which the EPA has had to develop and recommend specific emission control policies and associated implementation regulations.

The purpose of such ozone policies has been not only to impose restrictions and/or reductions of mass of ozone precursor emissions, but also to encourage development of alternative industrial and commercial products with more favorable environmental characteristics. Thus, included in the policies are provisions for excluding from regulation products with adverse, but tolerably small, environmental impacts. The EPA policy specifically includes requirements for inventorying and controlling emissions of photochemically reactive VOCs (those with high potential for producing ozone), but exempts those that are shown to be of negligible reactivity. The part of the policy dealing with reactivity classification of VOC emissions and exemption of the negligibly reactive ones from associated control, inventory, and emission trading regulations is commonly referred to as "VOC reactivity policy." It is a useful policy since, as believed by most—though not all³—experts, the reactivity-based, selective control of VOC emissions is more cost-effective than the indiscriminate, mass-control approach. Also, substitution of less reactive for more reactive organic emissions offers a supplemental control option when all mass control options are exhausted.

During the years following the issuance of the first ozone-related emission control policy, there have been numerous petitions filed with EPA for exempting specific organic emissions from the ozone regulations with the justification that the petitioned emissions are of

negligible reactivity. Those petitions for which the justification was judged to be valid were approved as being in compliance with the EPA policy. However, as new scientific evidence on VOC reactivity was being developed and the petitions were being examined in light of the new evidence, clearly EPA's reactivity policy needed to be re-evaluated and updated consistent with the latest scientific findings and thinking. This led the research and regulatory offices of EPA to undertake an effort to critically review the scientific bases of the existing EPA policy, identify policy weaknesses evidenced by the recent research studies, and search for ways to improve and strengthen the policy. In planning this effort, some of the policy and scientific issues in the VOC reactivity area were recognized to be extremely controversial, hence EPA must solicit and consider extensive input from the outside scientific community.

This report presents the author's perceptions on (1) inconsistencies between existing EPA policy on VOC reactivity and current scientific evidence and understanding, (2) consequent corrective policy revisions needed, (3) associated persisting scientific issues, and (4) new research needed to address such issues. It is offered in the hope of serving as the first step and a focus in EPA's continuing effort to review and improve its policy. In preparing this report, the author strove to take into account prevailing viewpoints within and outside EPA, as well as outside the United States.

EVOLUTION OF CURRENT POLICY

The initial version of the current policy was issued in 1971 as part of EPA's guidance to states for preparation of State Implementation Plans (SIP) for ozone attainment. In that version, EPA emphasized reduction of total mass of organic emissions, but it also offered that "substitution of one compound for another might be useful where it would result in a clearly evident decrease in reactivity and thus tend to reduce photochemical oxidant formation." This latter statement encouraged states to promulgate SIPs with organic emission substitution provisions similar to the Los Angeles District's Rule 66, which allowed many VOC species with appreciable, but tolerable, adverse effects to be exempted from control.

The exempt status of many of those organic emission species was questioned a few years later, when research results revealed pollutant transport conditions enhance ozone formation so as to make those organics act as significant ozone producers. This led EPA to issue, in 1977, a Recommended Policy on Control of Volatile Organic Compounds,⁶ offering its own, much more limited list of exempt organic compounds. Specifically, in the recommended policy EPA judged only 12 organic compounds to be of negligible reactivity and, of those,

only four qualified for exemption. At that time, EPA elected not to craft a definition of "negligibly reactive" that included test methods or other indices of reactivity, because of the substantial commitment that such a definition would require on the part of EPA for time and resources. Thus, the responsibility for proving the negligibly reactive nature of an organic emission species was intended by EPA to rest outside the agency. However, regardless of that intention, EPA later did support development of protocol methods for reactivity-testing organic compounds and offered them, unofficially at least, for public use. Those methods, known as the " k_{OH} "⁷ and Incremental Reactivity (IR)⁸ methods, are now routinely used for comparing the reactivity of an organic compound with that of ethane, which is the compound whose reactivity is used by EPA as the borderline separating reactive from negligibly reactive organics. Comparisons are made on a per-mole basis, but, in at least one case, EPA accepted a judgment based on a per-unit-weight basis comparison. These methods were used extensively during recent years to assess the reactivity of previously unstudied organics. As a result, several tens of compounds, mostly in the halocarbon family, were added to the list of negligibly reactives.

Finally, in 1992, EPA simplified its selective organic emission control policy by generalizing the definition of VOC to denote organic compounds with significant potential for ozone formation, and by declaring all organic emission species to be VOCs, except those that were "adequately shown, and determined by EPA," to be negligible ozone producers and, hence, non-VOCs⁹.

The analysis and discussion given here have been structured in terms of components dealing with five key elements of the EPA policy in its current form. Perceived weaknesses and related scientific issues are discussed and recommendations for improvement are offered separately for each component. The subjects of these five policy elements are (1) exemption of organic emissions on reactivity bases, (2) ethane reactivity "bright line," (3) reactivity classification guideline methods, (4) universal validity of reactivity scales, and (5) emission volatility.

Exemption of Organic Emissions on Reactivity Bases

This policy element mandates that the non-VOC emissions may be exempted from the ozone-related control and inventory requirements and must not be used in emissions netting, offsetting, or trading. One important implication arising from the inventory requirement exemption is that non-VOC organic emissions cannot be included in model computations of emission control requirements. The importance of this implication will be discussed later.

Exempting from the ozone regulations the specific organic emissions identified by EPA as negligibly reactive has been justified, to date, based on two early judgments. The first judgment was that while nearly all organic compounds are capable of producing ozone, not exempting from the control requirement (and, by extension, from the inventorying requirement) those compounds that produce only negligible amounts of ozone would be impractical and/or not cost-effective.

The second judgment was that there is, indeed, a significant number of organic compounds that are not capable of producing appreciable ozone. That judgment was based on results from an EPA smog chamber study⁵ conducted during 1975-76, the objective of which was to develop a rationale for defining a borderline reactivity level separating negligibly reactive organic compounds from reactive ones. The researchers in that study understood that such a rationale could not be developed without a compromise, given that nearly all organic compounds were thought to have a potential for forming ozone, and (if scientific criteria alone were to be used) the distinction between reactive and negligibly reactive organics would have to be largely arbitrary. In searching for a compromise, the researchers felt the arbitrariness of the borderline level would be reduced somewhat, if that level were to be related somehow to the ambient ozone air quality standard, which at that time was 0.08 ppm O₃. This led them to define negligibly reactive organics as those which, when present in the atmosphere *each alone* at ambient concentrations comparable with those occurring in the most polluted urban atmospheres (i.e., Los Angeles during the smog season), and under optimum VOC-to-NO_x ratio and irradiation time conditions, will not produce ozone concentrations exceeding the ozone air quality standard. Based on that definition, the researchers designed a smog chamber test program in which (a) a number of selected, low-reactivity organic compounds were irradiated individually in the chamber at the concentration of 4 ppm (mole/mole) and the VOC-to-NO_x mole ratio of 20, until the ozone concentration peaked, and (b) resultant peak ozone concentrations were measured and compared with the 0.08-ppm value. Results were interpreted to mean that, if all organic pollutants present in a severely polluted U.S. urban atmosphere (such as the Los Angeles atmosphere during smog season) were to be replaced by an equimolar concentration of ethane or other equally or less reactive organic, then ozone levels in that atmosphere could not exceed the ozone standard, even under prolonged irradiation and favorable VOC-to-NO_x conditions. Based on those results, organic compounds that are equally as, or less reactive than, ethane could be assumed to be negligibly reactive.

Those two judgments are no longer entirely valid bases for this part of the EPA policy. Researchers now believe that, while sufficiently unreactive organic emissions should be exempted from ozone-related control for practical reasons, exempting such emissions from the inventory requirement is not, for the following reason. Control-exempt organics could, at least conceivably, accumulate in the atmosphere (due to growth) at levels that ultimately would be high enough—higher than the Los Angeles smog season levels—for many of them to cause ozone exceedances. Therefore, control-exempt organic emissions should be considered in computing control requirements. This, of course, requires that they be inventoried. In conclusion, the privileged treatment currently accorded the non-VOC organic emissions is partly unjustified, constituting a weakness of this component of the EPA policy. The recommendation offered here is that all organic emissions, regardless of reactivity, be inventoried to allow the option of considering them in development of ozone control strategies. If exemptions must be allowed, then the exempt organics that should be allowed are only those with reactivities that are not significantly greater than zero. Such organics would probably include certain freon¹ and other comparably reactive organics, as well as those of negative reactivity under virtually all typical conditions.

Ethane Reactivity "Bright Line"

According to the existing EPA policy, organic emissions with reactivity equal to or lower than that of ethane—that is, at or below the ethane reactivity "bright line"—shall be exempted from the ozone regulations as being negligibly reactive. This policy element has been neither explicitly described nor officially issued by EPA. Rather, it acquired policy status when EPA began to use the comparison with ethane as the basis for judging whether an organic emission species should be subject to, or excluded from, the ozone regulations. The rationale behind this EPA practice is derived from the fact that ethane is the most reactive species of those identified by EPA as being negligibly reactive.⁶

Associated with this policy element are four questions at issue:

- (1) Should a bright line, rather than a band, be used as the boundary between the reactive and negligibly reactive organic compound classes?
- (2) Should ethane continue to be the boundary reactivity species?
- (3) For identification of negligibly reactive organic compounds, should the comparison with ethane—or some other benchmark species—be made on a per-unit-weight or a per-mole basis?
- (4) Is the distinction between reactive and negligibly reactive organic compounds really necessary?

Use of a bright line—rather than a band—may be viewed as a weakness in the EPA policy because it leads to the unreasonable conclusion that two organic emission species that are only slightly different in reactivity could be lying one below and one above the bright line. That is, one could be subject to, and the other exempt from, regulations. The use of a band centered over the benchmark species reactivity and bounded by the uncertainty bounds may be better justified than the use of a bright line. For the special case of organics whose reactivities lie within the band, a weight-of-evidence approach could be used to assign a VOC or non-VOC status. For example, a non-VOC status would be granted to those organic emissions that would be used to replace other, clearly more reactive ones—a viable approach, but one not necessarily without problems. An alternative method that avoids the problem with organics lying near the bright line is the “continuous reactivity adjustment” method used in California’s Clean-Fuel/Low Emissions Vehicle regulatory program.¹² By this method, the non-methane organic emissions from automobiles are treated as VOCs, with environmental effects measured by their reactivity-weighted amounts. All these methods of using the reactivity concept in regulatory organic emission programs have varying merits and difficulties. Scientific issues associated with obtaining a valid, acceptably accurate measure of an organic compound’s reactivity presents a common difficulty. There are also regulation implementation issues, such as enforceability, proprietary concerns, and regulatory complexity. Therefore, before EPA revises its reactivity-based control regulations, it must first solicit and consider input from the industrial, governmental, and academic communities on all scientific and policy issues in this subject area.

The second question at issue is whether the reactivity benchmark species should be ethane. To understand this issue, one must first understand the reasoning EPA used in identifying the negligible reactivity organics to be exempted from the VOC definition. That reasoning was derived from the results of the 1975–76 EPA study previously described. The data from that study showed propane formed a peak ozone concentration equal to 0.08 ppm, and based on that finding, the researchers offered that “unreactive organics are defined as those with reactivities lower than the reactivity of propane.” Based on that, and presumably to ensure achievement of the standard, the EPA authors of the 1977 policy developed a list of negligibly reactive organics which consisted of ethane—an organic with nearly one-third the reactivity of propane—and all other organic compounds with reactivity equal to or less than that of ethane.

The preceding interpretation of the data from the 1975–76 study provided a justification for the selection of ethane as the reactivity benchmark, but it did not include two relevant and important qualifications, an omission that is perceived as a weakness of this policy rule with significant implications, as discussed later. The first qualification is that the use of ethane as the benchmark is valid, provided the reactivity comparison with ethane is conducted on an *equimolar concentration basis*. Obviously, had the comparative testing in the smog chamber study previously cited⁹ been conducted using, for example, equal weight concentrations, then some other organic species would have been selected as the reactivity benchmark.

The second qualification is that organic species equally as or less reactive than ethane are negligibly reactive *only as long as they occur in the atmosphere at concentration levels not exceeding 4 ppm (mole/mole)*. Again, had the cited smog chamber testing been done at higher (than 4 ppm) or lower initial organic concentrations, more or less ozone would have been produced and, instead of ethane, a lower or higher reactivity organic would have been selected as the reactivity benchmark.

Another weakness of this policy rule arises from the uncertainties of the smog chamber data used as a basis of the rule. Those data, taken in a study performed more than two decades ago, are now known to have uncertainties associated with chamber artifact phenomena and the unrealistic conditions used in smog chamber studies at that time. Particularly important is the realistic conditions factor, as attested by current knowledge that when low reactivity organics are irradiated in the presence of realistic VOC mixtures, they produce, as a rule, much more ozone¹³ than when irradiated alone, as was done in the EPA smog chamber study of 1975–76. The significant implication from this knowledge is that the reactivity benchmark species should not be ethane, but a species of lower reactivity.

Finally, note that EPA has recently revised the ozone air quality standard from a one-hour average-ozone-concentration value to an eight-hour average value.¹⁴ This obviously requires that the definition of “negligibly reactive organic” be revised and a new reactivity benchmark species be selected.

In conclusion, reactivity classification of organics and selection of a reactivity benchmark are issues that must be restudied using much improved current methodology (discussed below). Furthermore, and equally important, consideration should be given to the implications raised by a classification that is too conservative or too permissive. For example, use of a less-reactive-than-ethane benchmark species would result in increased environmental benefits, but such increased conservatism

would also tend to lessen the incentive for the industry to develop lower-reactivity substitute products. Clearly, an analysis is needed, with engineering, economic, and scientific inputs from the industrial, governmental, and academic communities, before EPA can select and adopt an optimum reactivity classification scheme.

The third question—whether organic compounds should be compared with ethane on a per-unit-weight or a per-mole basis—is raised as a challenge to EPA's use, in at least one case, of the per-unit-weight basis with the justification that it is consistent with agency practices in the emission inventory and emission standards areas. Use of the per-unit-weight basis in the reactivity area is of questionable validity for reasons that, as previously explained, are related to the selection of ethane as the boundary species separating reactive from negligibly reactive organics and the qualifications of such a selection. To reiterate, the per-mole basis must be used, since the ethane was selected out of *arbitrary* comparison of organic compounds. Use of the per-unit-weight basis for comparison of organic compounds with ethane has the significant consequence of tending to cause reactive, high-molecular-weight VOCs to be classified as negligibly reactive, in conflict with the molar reactivity data.

To further clarify, it is *not* advocated here that the per-mole basis must be the one to use. The author's intent is merely to caution that, for comparing organic species with the benchmark species for reactivity-classification purposes, the per-mole basis must be used, if ethane is the benchmark species. If the weight basis must be used, then a reactivity benchmark species other than ethane must be selected and used. In fact, a rough estimate of the reactivity level of such a benchmark can be computed simply from the 1975-76 EPA study⁹ data, as follows. Given that the molecular weight of the average VOC species in an urban atmosphere is 69⁵, 2.3 times greater than that of ethane, *on a per unit weight basis* the reactivity borderline separating reactive from negligibly reactive organics should be at a level 2.3 times lower than that of the ethane reactivity. This lessens, but does not remove, the problem related to the choice of the basis used to compare reactivities of organic compounds. Compounds with a molecular weight greater than 69 still may be classified differently depending on whether the weight basis or the mole basis is used for the comparison with the benchmark. In fact, this problem is unavoidable and constitutes a conceptual weakness of the part of the policy that calls for classifying organic emissions into VOCs and non-VOCs based on comparison with a given organic compound's reactivity.

The final question, whether the distinction between reactive and negligibly reactive organic compounds is

really necessary, is to a large extent—but not totally—of a policy nature, governed mainly by socioeconomic considerations. If such a distinction must be made, then it also should have a fairly concrete and reasonable scientific justification. One such classification would be, for example, the one in which the negligibly reactive organics are those whose reactivities are not significantly greater than zero. This would be tantamount, however, to an extremely conservative policy. To lessen the problem, consideration should perhaps be given to allowing credit for substituting low-reactivity VOCs for substantially more reactive ones. In such a policy, the terms significantly and substantially would be defined by the agency alone or in consultation with other sectors.

Reactivity Classification Guideline Methods

Existing EPA guidelines for reactivity-classifying organic emissions are unofficial. They are surmised from EPA practices in which the k_{OH} method⁷ is used for identifying negligibly reactive organics and Carter's Maximum Incremental Reactivity (MIR) method⁸ for ascertaining reactivities higher than that of ethane. The k_{OH} method is based on measurement of the rate constant of the reaction of hydroxyl radicals (OH) with the organic species and comparison with the rate constant for the OH reaction with ethane. Carter's method uses a smog chamber-tested chemical mechanism model to compute reactivities for a given set of ambient conditions. Both guideline methods have weaknesses.

When the first guideline method, the k_{OH} method, was conceived, organic compounds with a k_{OH} value lower than that of ethane were assumed to also have lower ozone production potentials. That assumption was based on the belief that the rate-determining step in the ozone-producing photodegradation of an ambient organic pollutant was the reaction of the organic with OH—the first step of the photodegradation process. That assumption, however, is now being questioned. To explore the validity of this assumption, the author compared MIR reactivities with k_{OH} reactivities for some 370 organic species,⁶ using reactivity values in ethane equivalent units. The comparison showed the MIR values to be higher—and, in some cases, considerably higher—than the respective k_{OH} values for some 40 organic species (within the paraffin, aromatic, ketone, and halocarbon families). Based on that fact, one cannot rule out the existence of organic species with lower-than-ethane k_{OH} reactivities but higher-than-ethane MIR reactivities. Evidently, the chemistry following the initial OH reaction step can be sufficiently potent (in terms of ozone production) to more than offset the effect of the low OH reaction rate.

Carter's smog chamber/modeling method has a validity advantage over the k_{OH} method in that the reactivity data it produces are more direct measures of ozone

potential. However, it also has weaknesses. Namely, it is based on use of Empirical Chemical Modeling Approach (ECMA) a single-cell box model that treats atmospheric processes with inadequate detail and simulates only one-day ozone episodes (in some urban areas ozone episodes are of multi-day duration); uses a chemical mechanism that is outdated; and uses unrealistic scenarios of urban conditions.^{17,18}

More recently, McNair and co-workers⁸ developed a new modeling method that has the following advantages over the Carter method: (1) it is based on use of a three-dimensional airshed model capable of simulating multi-day ozone episodes; (2) it uses realistic conditions; and (3) it is equipped with a recent-version—though condensed—chemical mechanism. Its disadvantages compared with the Carter method are its tediousness and costliness, and the difficulty—inherent to airshed models—of accommodating an explicit (i.e., non-condensed, hence more detailed) chemical mechanism.

Finally, there is also a method developed in Europe by Derwent and co-workers^{9,20} that uses a photochemical trajectory model and that has the uniqueness of being equipped with an extremely detailed master chemical mechanism containing some 7,100 reaction steps and 2,400 chemical species. Notwithstanding the fact that many of the requisite reaction rate constants have not been measured—only theoretical estimates are available—that mechanism derives an amount of credibility from its highly detailed nature and its good agreement with other, smog chamber-tested mechanisms. This especially is true when applied on low-reactivity organics for which the experimental reactivity measurement methods are known to be unreliable.

Ideally, the method for determining reactivities should be one that combines the strengths of the methods described here: namely, the combined smog chamber testing and modeling approach conceived by Carter, the application of airshed models introduced by McNair and co-workers, and the emphasis on chemical mechanism detail advocated by Derwent and co-workers. In practice, such a combination is precluded due to computer capability limitations and cost. One conceivable compromise would be a method that uses a current science airshed model—for instance, the EPA-developed Models-3,²¹ equipped with a late-version explicit mechanism—and sets of detailed, well-documented urban and regional conditions for a number of ozone episodes in several urban/regional areas in which ozone is sensitive to the VOC factor. An effort to develop such a method and make it available for public use, especially in cases in which the reactivity evidence obtained with the existing methods is equivocal and critically needed, is strongly recommended.

Consistent with this, the author strongly advises also that EPA develop and sustain a program of laboratory and modeling studies on the atmospheric chemistry of important (high emission volume) ambient organics of not well-known atmospheric chemistry. Finally, the author also perceives a pressing need for a practical, inexpensive method to obtain reactivity estimates for ambient organics of relatively low importance and unknown atmospheric chemistry. One such recent method, proposed for estimating upper limit reactivities,²² should be useful as a screening method for identifying very low reactivity organics.

Universal Validity of Reactivity Scales

The EPA policy now in use is based on the assumption that its current classification of ambient organics into VOCs and non-VOCs is universally valid and independent of pollutant transport, ambient VOC composition, VOC-to-NO_x ratio, and other ambient conditions. However, the photochemical ozone formation chemistry is such that the reactivities of organic species vary with ambient conditions. This obviously raises questions about the practicality of a reactivity scale that is not universally valid. Research is needed to better understand the variation of reactivity with ambient conditions, and to either develop a more effective way of classifying organics by reactivity, or conceive other ways of applying the reactivity concept in ozone control strategies. Consideration should be given, for example, to the fact that the uncertainties introduced by the ambient conditions variability factor are much smaller for relative reactivities and, by extension, for estimates of emission substitution benefits.² This underscores the rationality of policies that encourage development of organic products of lower—though not necessarily negligible—reactivity under all conditions, that is, policies that place the emphasis on relative rather than absolute reactivities.

Emission Volatility

The existing EPA policy and, specifically, its VOC definition rule,⁹ distinguishes between VOC and non-VOC emissions and cites reactivity as the basis for the distinction. The policy, however, does not include volatility-specific rules, and neither is there explicit volatility language included in EPA's VOC definition rule. Therefore, unlike the reactivity factor, the current EPA policy and associated regulations ignore the volatility factor, even though the two factors have analogous effects. Thus, there are volatile and negligibly volatile—as there are reactive and negligibly reactive—organic emissions contributing significantly and negligibly, respectively, to atmospheric ozone formation. Recognizing this distinction in the case of reactivity, but not in the case of volatility, appears to be an inconsistency of the EPA policy.

Ambient organics do not participate in the atmospheric ozone formation process unless they exist in the gas phase. Distribution of an ambient organic pollutant in the gas and particle phases depends on the pollutant's volatility, molecular polarity, solubility in water, reactivity, and nature of the surface of the atmospheric particles with which the organic comes in contact. In general, organics with vapor pressures within the range 10^{-7} to 10^{-8} Torr, commonly referred to as semi-volatiles, occur in both the gas and particle phases. For such organics, obtaining emission and ambient concentration data relevant to the atmospheric ozone formation phenomenon is not easy. Measurement results need to be adjusted to reflect the phase distribution of such organics in the atmosphere—which may be different than that in the emissions stream—and the fact that part of the particulate organic material in the atmosphere will eventually volatilize and participate in the gas-phase ozone formation process.

SUMMARY AND CONCLUSIONS

To deal with the photochemical ozone problem in urban areas, EPA developed and recommended an organic emissions control policy that took into account emission reactivity. The highlights of this reactivity-related component of the policy are that (1) it calls for classifying organic compounds into reactives or VOCs and negligible reactives or non-VOCs, with the reactivity of ethane being the boundary separating the two classes; (2) it requires the VOCs be subject to control and inventory regulations; and (3) it exempts the non-VOCs from such regulations and prohibits their use in emissions netting, offsetting, or trading. The belief now is that that policy and some associated official and/or unofficial regulations need to be revised consistent with recent scientific data and understanding.

In reactivity classifying an organic compound, EPA's unofficial regulatory practice has been to compare the compound's reactivity with that of ethane using k_{OH} or MIR data on a per-mole or a per-unit-weight basis. The k_{OH} , however, is no longer believed to be a valid indicator of an organic compound's ozone production potential, and the MIR data used to date are now thought to have weaknesses associated with the EKMA modeling method used to obtain them. Also, use of the per-unit-weight basis is inconsistent with the selection of ethane as the reactivity benchmark, and creates a bias that causes reactive, high molecular weight organics to be classified as negligibly reactive.

For more reliable reactivity classification of organic compounds and estimation of emission substitution benefits, new, more accurate incremental reactivity data must be obtained and the possibility of needing a new reactivity benchmark should be explored. The requisite data

should be obtained by using a modeling method that uses an airshed model, a smog chamber-tested explicit chemical mechanism, and well-documented ambient conditions for several ozone episodes in a variety of non-attainment urban/regional areas. Also, organics should be compared with the benchmark species on a basis consistent with that used to select the benchmark species.

The latest scientific understanding is that many of the organic compounds identified by EPA as non-VOCs have greater significance as ozone producers than assumed by EPA, to the extent that exempting them from control regulations, especially the inventory requirement, is not justifiable. The author submits that if a distinction between VOCs and non-VOCs must be sustained, then non-VOCs should be defined as those whose reactivities and volatilities are not significantly greater than zero. Recent scientific evidence indicates further that, while the absolute reactivities of organic compounds are subject to fairly large uncertainties due to uncertainties in the atmospheric chemistry of the organics and the effect of varying ambient conditions, the uncertainties of relative reactivity data are substantially smaller. This supports regulatory policies that encourage emission substitution as an approach to ambient ozone reduction to complement the emission mass reduction strategy.

In conclusion, the scientific evidence currently available supports a reactivity policy that

- (1) may allow blanket exemption from ozone regulations for those organic emissions whose reactivities/volatilities are not significantly greater than zero;
- (2) values benefits from substitution of less reactive/volatile organic emissions for more reactive/volatile ones; and
- (3) requires that the reactivity data used to support substitution benefits and "exemptibility" shall be validated using continually updated airshed modeling methods.

Such a policy requires also that a continuing program of laboratory and modeling studies be developed, encouraged, and sustained to reduce uncertainties in the areas of ozone-related atmospheric chemistry of organic pollutants, organic emission composition, and reactivity modeling.

Finally, the advantages of a reactivity-based emission control policy over the total mass reduction approach, and the specific reactivity policy aspects discussed here, have been subjects of scientific controversy, with the scientific community being divided generally between reactivity advocates and reactivity skeptics. Therefore, in reviewing its policy and contemplating changes, to ensure credibility, EPA must solicit and use input from the scientific community at large and strive to develop a consensus judgment.

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