MEMORANDUM

National Volatile Organic Compound Emission Standards for Aerosol Coatings

Review of the Technical Basis for use of the One-dimensional MIR Scale in the National Volatile Organic Compound Emission Standards for Aerosol Coatings

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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Research Triangle Park, NC 27711

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Research and Development

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SUBJECT: **Review of the Technical Basis for use of the One-dimensional MIR Scale in the National Volatile Organic Compound Emission Standards for Aerosol Coatings**

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I have reviewed the literature on reactivity to determine if it supports the use of a reactivity-based control for aerosol coatings, and in particular, the use of a single, one-dimensional, box model-based Maximum Incremental Reactivity (MIR) scale for national applicability. While I believe that we should continue to do more research work in this area to ensure that the best possible metric/scale is being employed, there's evidence that, given what we already know, EPA can already make a compelling case for considering reactivity as a basis for VOC control. While no single scale will be a perfect predictor of ozone in every location at every time, a single one-dimensional, box model-based MIR scale, is remarkably consistent with the more complex, three-dimensional, Air Quality Model-based scales. The three-dimensional scales are attractive for their robustness and general applicability, but at the current time, the one-dimensional MIR

scale has several advantages. We have a history of implementation and scientific review, as well as existing product formulations using the MIR, based on the 2001 CARB rule. We have peer-reviewed values for over 800 compounds based on the box model MIR, but for only about 30 explicit compounds from the three-dimensional models. Because it is much easier to implement, the box model-based MIR scale gives us a way to easily incorporate updates to the chemical mechanism and information on new chemical species that are not part of the existing 800 compounds.

In the following pages, I list four of the technical questions that we need to address in order to proceed with use of one-dimensional MIR values in a national regulation, and summarize how the scientific literature addresses these issues. Based on this review, I believe it is reasonable to proceed with the regulation, with the caveat that we allow the flexibility to modify the scale as the science improves. I include a more detailed discussion, plots, and references in an attached report to this memo.

Question 1: Does the mechanism used to derive MIRs accurately characterize ozone formation from individual VOCs?

In general, the SAPRC99 chemical mechanism which has been used to predict the reactivity of ozone formation for VOCs, and derive the MIRs, has been shown to be a valid predictor of ozone formation under controlled evaluation studies. Ozone formation in the atmosphere is a complex process and there is still some uncertainty in the mechanism predictions. While the mechanisms may underpredict ozone at low VOC/NOx ratios, which are of most interest to this regulation, use of SAPRC99 minimizes this bias, and the bias errs on the side of being slightly conservative. There is some uncertainty in the detailed chemical mechanisms used to calculate reactivities of individual VOCs, but for the compounds used most often in aerosol coatings, this uncertainty is estimated to be largely limited to categories 1 or 2. I believe this is equal to (probably less than) the uncertainties involved in overall calculations of ozone changes due to mass reductions.

Question 2: Is the MIR a reasonable way to define reactivity?

All of the different metrics that have been proposed, approximately 4 box model-based metrics and 8+ three-dimensional metrics, give generally consistent predictions in the relative ranking of reactivities. None of the detailed studies performed to date have shown serious deficiencies in the long-used MIR metric. The aldehydes are sometimes outliers, but these are not important components of aerosol coatings.

The MIR describes ozone formation in areas where ozone is most sensitive to VOC emissions, in upwind areas with high emissions. It is complementary to NOx control programs which address ozone formation in NOx-limited areas. The box model-based MIR scale gives the largest difference between the high reacting compounds and the lower reacting compounds than any of the other scales. On the negative side, this allows a larger amount of overall mass to possibly be emitted in a reactivity-limited solvent, as compared with an equal mass-restricted solvent, which would benefit ozone in the immediate area, but may increase ozone slightly downwind (see Question 4 for further discussion). On the positive side, it provides more incentive for manufacturers to use low-reactivity chemicals in aerosol coatings – the major goal of this policy.

In addition, the MIR has a long history of use and analysis, and is the basis of some existing paint formulations under California law. Given the uncertainties inherent in any air quality modeling, is a reasonable way to characterize reactivity. The three-dimensional AQM metrics are arguably more robust, but there are no detailed reactivity scales yet available for all of the possible chemicals involved in aerosol coatings using AQMs.

Question 3: Does a single MIR scale account for potential spatial variability across the United States?

Several three-dimensional modeling studies have shown that spatial variations in reactivity are generally found to be small, and averaging time used in calculation of the scale (whether 1 hour or 8 hours) makes little difference in the values. When viewed on a relative basis, as is applicable for solvent mixtures, the one-dimensional, city-specific MIR values are approximately the same for the 39 different cities studied. This gives us confidence that one metric and scale can be used with equal applicability throughout the country.

Question 4: Is the large effective range of the MIR scale a potential problem when replacing high reactivity compounds with lower reactivity chemicals?

A major benefit as well as a concern with the use of MIR is its large effective range. The box model-based MIR scale gives the largest difference between the high reacting compounds and the lower reacting compounds. This means that a substitution using MIR would result in a larger permissible amount of mass than using another metric, i.e. the MOIR. Compared with an equal mass-restricted solvent, would benefit ozone in the immediate area but may have some disbenefits downwind.

Current studies indicate that some increases in ozone due to increased mass of low-reacting compounds are possible, but the studies have only looked at very extreme cases (i.e. substitution of all VOCs with equal-ozone amounts of ethane, tracking ozone formation downwind from substitutions only in an urban area). While ozone could increase due to these upwind substitutions, the increases tended to be much smaller (by a factor of 12-20) than the magnitude of concurrent ozone decreases. The substitutions had a larger effect on reducing the higher ozone concentrations than they did on increasing downwind concentrations. Even in these extreme cases, the benefits for ozone (reduction in ozone peak) were significant.

Inherent in this rule is a reduction in ozone equivalent to a reduction in mass, therefore the substitutions will be done on a less-than-equal ozone basis, relative to the pre-rule mixture. Realistic changes in formulation, especially if limited to aerosol coatings are unlikely to result in a noticeable increase in ozone downwind, given that downwind areas are usually NOx-limited, so small amounts of additional VOCs won't influence ozone formation much.

More detailed and realistic studies are needed to determine whether any potential increase in mass due to reactivity-based VOC limits are truly a problem.