ESTIMATION OF THE MAXIMUM OZONE IMPACTS OF OXIDES OF NITROGEN

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Background and Statement of the Problem

When emitted into the atmosphere, many types of volatile chemical compounds can undergo gas-phase chemical reactions that result in the formation of ground-level ozone, which is a serious air quality problem in many areas. However, the amount of ozone formation caused by the emissions of various compounds depends not only on the compound but also on the environment where it is emitted (e.g., see Carter and Atkinson, 1989, Carter, 1994a, Dimitriades, 1999). Ozone impacts can be quantified by "incremental reactivities", which are defined as the change in ozone formed when a small amount of compound is added to the emissions in a particular air pollution episode or scenario, divided by the amount of compound added (Carter and Atkinson, 1989). Note that incremental reactivities are properties both of the compound and episode or scenario in which the compound may be emitted. These can be calculated with airshed models given a model for the atmospheric conditions and chemical mechanisms for the gas-phase atmospheric reactions of the compounds involved with ozone formation (e.g., see Carter, 1994a, RRWG, 1999a, and references therein).

In the case of volatile organic compounds (VOCs), it has been proposed to use "maximum incremental reactivity" (MIR) values to obtain a single ozone impact value for each compound for comparison or regulatory purposes (Carter, 1994a). These are defined as the incremental reactivities of the compounds in scenarios where ozone formation has maximum sensitivities to VOC inputs. This may be appropriate for regulatory applications because it reflects conditions where VOC controls are the most effective for reducing ozone (CARB, 1993; RRWG, 1999b; Dimitriades, 1999). Based on these and other considerations, the California Air Resources Board incorporated MIR values calculated using the methods of Carter (1994a) in several reactivity-based VOC regulations (CARB 1993, 2000). MIR values may also be appropriate to quantify relative ozone impacts of VOCs for life cycle assessment analyses as well, particularly if the objective is to assess the maximum adverse impacts of the emissions of the compounds involved.

As discussed by Carter and Atkinson (1989), the most important single environmental condition that affects the magnitudes of ozone impacts of VOCs is the relative levels of oxides of nitrogen (NO_x) present in the scenarios. VOCs have the highest ozone impacts under conditions where NO_x is abundant and zero impacts when NO_x is absent, because NO_x is required for ozone formation to occur. Because of this, the methodology for deriving MIR values for VOCs is to adjust NO_x inputs in representative scenarios that the ozone formed in the scenarios is the most sensitive to changes in the total VOC inputs in the scenarios, i.e., to yield the highest incremental reactivity of the mixture of VOCs used in the scenario to represent VOC emissions from all sources, and use the incremental reactivities in these "MIR scenarios" as the MIR values for all the VOCs. This is appropriate for deriving MIR values for VOCs because the NO_x inputs that yield the highest incremental reactivities tend to be the same for all compounds.

However, this approach is not appropriate for applications where it is desired to include maximum ozone impacts of oxides of nitrogen (NO and NO_2), because NO_x emissions actually have very large negative impacts on O_3 formation in scenarios where VOCs have the highest incremental reactivities. NO_x emissions have large and positive ozone impacts in scenarios with very low NO_x levels, where VOC impacts on ozone tend to be near zero or negative. Therefore, if it is desired to have a scale that includes maximum ozone impacts of NO_x species, then it is necessary to determine the types of scenarios where these compounds have their highest ozone impacts, and calculate their impacts for these scenarios.

Objectives and Overall Approach

The overall objective of this project is to include maximum ozone impact estimates for NO_x species along with those for VOCs using a methodology that is appropriate for NO_x species yet consistent with that used to derive MIR values for VOCs. The MIR values for VOCs have recently been updated by Carter (2007), using the same scenarios and general methodology as used for the original MIR scale by Carter (1994a), but with using the updated SAPRC-07 mechanism to represent the chemical processes involved (Carter, 2007). The specific objective for this project is to derive maximum ozone impacts for NO_x species that are consistent with the updated MIR values for VOCs given by Carter (2007), but are appropriate for NO_x species. The approach is to adjust the NO_x levels in the scenarios used by Carter (1994a) to yield maximum incremental reactivities of NO_x, and use the average incremental reactivities in these scenarios as the maximum O_3 impacts of these NO_x species.

The NO_x species considered in this work are NO, NO_2, and nitrous acid (HONO). These are the most reactive forms of NO_x present in emissions, and the components of NO_x used in the reactivity assessment scenarios used (Carter, 1994a).

Approach

The scenarios used by Carter (1994a) for deriving the MIR and other reactivity scales consist of the 39 box model scenarios originally derived by Baugues (1990) for ozone regulatory impact assessments using the EKMA model. These were designed to represent the conditions of 39 urban areas in the United States where ozone is a problem at the time these scenarios were developed. The scenarios are out of date but have not been updated since they were used by Carter (1994a). The scenarios as used for reactivity calculations are documented by Carter (1994a) and the input data for the 39 urban areas are given by Carter (1994b). The scenarios with NO_x inputs as derived by Baugues (1990) are referred to as the "Base Case" scenarios. For the purpose of deriving reactivity scales for specified chemical conditions, the NO_x inputs in these scenarios were adjusted to yield the desired chemical conditions, as follows:

- For the MIR scale, the NO_x inputs were adjusted to yield the maximum incremental reactivity of the "Base ROG" mixture used to represent anthropogenic emissions from all sources. These NO_x inputs were about 40% higher than those yielding maximum ozone concentrations in the scenarios, and in most cases were higher than those in the base case scenarios.

- For the MOIR (maximum ozone incremental reactivity) scale, the NO_x inputs were adjusted to yield the highest ozone concentrations in these one day scenarios.

- For the EBIR (equal benefit incremental reactivity) scale, the NO_x inputs were adjusted so that the ozone increase caused by changing total VOC emissions by a certain (small) percentage was the same as changing the total NO_x emissions by an equal percentage. These reflect the highest NO_x conditions where VOC control was at least as effective as VOC control for reducing ozone.

All the other inputs besides total NO_x was the same as in the base case scenarios. For all three cases, the reactivity values for the VOCs in the particular scale was the average of the values calculated for the 39 adjusted NO_x scenarios.

For this work, a fourth type of adjusted NO_x scenario, designated NO_x maximum incremental reactivity (NMIR), was derived for each of the 39 base case scenarios. For these scenarios, the NO_x inputs were adjusted to yield the highest maximum change in ozone caused by varying the total NO_x input in the scenarios. The reactivities in the NMIR scales were the averages of the reactivities for the 39 individual scenarios with NO_x adjusted to yield NMIR conditions.

The NO_x inputs in these reactivity assessment scenarios consisted of mixtures of NO, NO_2 and HONO with ratios that depended on whether the NO_x was present initially or was emitted during the simulation. For each of the 39 scenarios, a certain fraction of NO_x was present initially, with the remainder emitted each hour, with the fraction of NO_x present initially varying from scenario to scenario. For all scenarios the composition of the initially present NO_x was 73.5% NO, 24.5% NO_2, and 2% HONO, and the composition of the emitted NO_x was 94.9% NO, 5% NO_2, and 0.1% HONO. These fractions were derived based on recommendations provided by the California Air Resources Board Staff and input from members of various reactivity advisory committees that were made at the time the first MIR scale of Carter (1994a) was being developed. The higher HONO and NO_2 fractions in the initially present NO_x reflects the expectation that these species would be higher in relatively "aged" mixtures, with the emissions themselves consisting of primarily (~95%) NO. Note that since the fraction of initial NO_x varies from scenario to scenario, the relative composition of NO_x was also variable. On the average the NO_x inputs for the 39 scenarios were 85% NO, 14% NO_2, and 1% HONO.

All the calculations were carried out using the SAPRC07 mechanism documented by Carter (2007). Since this mechanism already represents NO, NO_2, and HONO, it did not need to be modified for this work. Except for the adjustments to derive the NMIR scenarios as discussed above, all the other procedures and scenarios were the same as used to derive the MIR and other reactivity scales given and documented by Carter (2007).

Results and Discussion

Table 1 lists the NO_x inputs for the various scenarios that gave the maximum sensitivities of O_3 to NO_x inputs in the scenarios, and the incremental reactivities for the NO_x species NO, NO_2, and HONO in these NMIR scenarios. For comparison purposes the NMIR values for the base ROG mixture representing all anthropogenic VOC emissions and CO (a VOC-like compound with the simplest mechanism) are also shown. The incremental reactivities on the table are given on a per molecule basis (moles O_3 formed per mole compound emitted) except for the base ROG mixture, where they are on a mole carbon basis. The NO_x inputs are given relative to the NO_x inputs yielding the maximum ozone concentrations in the scenarios, or MOIR NO_x levels, since this normalizes for effects of other scenario conditions on effective NO_x conditions.

It can be seen from Table 1 that the NO_x levels giving the highest ozone impacts for NO_x (NMIR) are very low, but not zero. On the average, the NO_x levels giving the highest impacts of NO_x range from near-zero up to over 16% of those giving maximum ozone, with the average being about 5% of the maximum ozone levels.

The molar incremental reactivities of the NO_x species in the NMIR scenarios are quite high, being on the order of 16 moles of ozone formed per mole of NO_x species emitted. For comparison purposes, the highest molar reactivities for VOC species in the MIR scale are about 30 for trialkylbenzenes and methacrolates, though the values are much lower for most compounds, and the highest values are only

Table 1.　Relative NO_x input levels and incremental reactivities of selected compounds in scenarios where NO_x inputs are adjusted to yield maximum sensitivity of O_3 to NO_x inputs.

Scenario	NMIR / MOIR NO_x	Incremental Reactivity in NMIR Scale (Mole O_3 / Mole or mole C compound)				
		NO	NO2	HONO	Base ROG	CO
Averaged Conditions	2.2%	14.6	15.3	14.2	-0.012	0.0002
Average City-Specific	4.7%	15.9	16.5	15.5	-0.015	0.0010
Atlanta, GA	4.9%	15.8	16.5	15.4	-0.014	0.0011
Austin, TX	6.8%	14.4	15.1	14.3	-0.015	0.0016
Baltimore, MD	0.3%	15.8	16.5	15.1	-0.012	-0.0001
Baton Rouge, LA	2.8%	15.4	16.1	14.9	-0.014	0.0007
Birmingham, AL	0.4%	17.5	18.3	16.8	-0.014	-0.0002
Boston, MA	16.4%	11.5	12.1	11.6	-0.011	0.0022
Charlotte, NC	12.7%	12.6	13.3	12.8	-0.013	0.0029
Chicago, IL	5.8%	17.5	18.1	17.1	-0.015	0.0012
Cincinnati, OH	6.1%	13.6	14.3	13.4	-0.014	0.0007
Cleveland, OH	1.4%	13.4	14.1	12.9	-0.013	-0.0001
Dallas, TX	5.7%	15.1	15.8	14.7	-0.016	0.0008
Denver, CO	8.3%	16.7	17.4	16.3	-0.016	0.0011
Detroit, MI	5.1%	13.2	13.8	12.8	-0.012	0.0006
El Paso, TX	3.4%	17.1	17.8	16.8	-0.017	0.0009
Hartford, CT	2.1%	16.0	16.7	15.7	-0.013	0.0002
Houston, TX	8.7%	15.3	15.9	15.0	-0.016	0.0014
Indianapolis, IN	5.1%	18.5	19.1	18.2	-0.019	0.0017
Jacksonville, FL	2.4%	18.0	18.7	17.6	-0.012	0.0010
Kansas City, MO	2.1%	15.2	15.9	14.9	-0.012	0.0004
Lake Charles, LA	1.1%	18.1	18.7	17.6	-0.010	0.0007
Los Angeles, CA	0.8%	16.7	17.3	16.3	-0.009	0.0001
Louisville, KY	7.8%	16.1	16.8	15.8	-0.020	0.0016
Memphis, TN	7.5%	16.6	17.2	16.3	-0.018	0.0020
Miami, FL	7.3%	16.7	17.4	16.6	-0.021	0.0023
Nashville, TN	4.1%	19.9	20.5	19.6	-0.022	0.0018
New York, NY	0.0%	14.7	15.4	13.9	-0.013	-0.0002
Philadelphia, PA	7.8%	16.1	16.7	15.7	-0.015	0.0017
Phoenix, AZ	1.3%	19.0	19.7	18.7	-0.014	0.0000
Portland, OR	4.6%	16.9	17.6	16.8	-0.022	0.0019
Richmond, VA	3.6%	15.4	16.1	14.9	-0.013	0.0005
Sacramento, CA	2.4%	21.1	21.8	20.7	-0.018	0.0012
St Louis, MO	3.6%	14.1	14.7	13.6	-0.013	0.0003
Salt Lake City, UT	1.2%	14.9	15.6	14.6	-0.014	-0.0001
San Antonio, TX	3.4%	15.5	16.2	15.3	-0.016	0.0011
San Diego, CA	3.3%	13.5	14.2	13.4	-0.013	0.0010
San Francisco, CA	2.9%	17.0	17.6	16.5	-0.012	0.0006
Tampa, FL	3.1%	16.0	16.6	15.6	-0.017	0.0010
Tulsa, OK	11.1%	14.3	14.9	14.2	-0.018	0.0028
Washington, DC	4.9%	13.5	14.1	13.1	-0.014	0.0005

about 10 on a per carbon basis. Of the NO_x species. NO_2 has the highest molar reactivities in the NMIR scale, with that for NO being about 0.6 - 0.7 less regardless of conditions (or NO_x inputs). This difference reflects the fact that NO reacts with O_3, which means that all else being equal it should it should form up to one molecule less O_3 than NO_2. HONO rapidly forms NO when it reacts, so it should have similar reactivity of NO in scenarios where O_3 is primarily sensitive to NO_x inputs. The fact that that the molar reactivity of HONO is slightly different than that of NO (usually but not always lower) reflects the impact of the radical initiation caused by HONO photolysis on O_3 formation in the scenario. The generally negative apparent impact of the radical initiation can be attributed to the higher radical levels causing more reactions of VOC species forming intermediates that remove NO_x from the system, via processes such as PAN or organic nitrate formation. This is the reason that the base ROG has negative incremental reactivities in these NMIR scenarios. On the other hand, the NMIR reactivity of CO generally not negative (though is very close to zero) because the reactions of CO do not have processes that cause NO_x removal from the system.

Although reactivities quantified on a molar basis, such as shown on Table 1 are more meaningful from a mechanistic standpoint, for most regulatory and other practical applications a mass-based quantification, with reactivities in units of grams O_3 per gram compound emitted, is more appropriate. This is because emissions are generally quantified on a mass basis. The conversion of incremental reactivities from molar basis to mass basis is as follows:

$$IR \text{ (grams } O_3 \text{ per gram VOC} = IR \text{ (Moles } O_3 \text{ per mole VOC) x } \frac{47.9982 \text{ (grams } O_3 \text{ per mole } O_3)}{MW_{VOC} \text{ (grams per mole VOC)}}$$

(However, if emissions are quantified on a molar basis, then molar reactivities should obviously be used.) In grams O_3 per gram compound units, the average city-specific NMIR incremental reactivities of the NO_x species are as follows:

NO: 25.37
NO_2: 17.24
HONO: 15.85

Note that the conversion involves applying a constant factor for each compound, which is inversely proportional to the molecular weight, and therefore does not affect the scenario-to-scenario variability shown in Table 1. The molar reactivities of NO are the highest because it has the lowest molecular weight, with the molecular weight difference being more important than the molar reactivity difference shown on Table 1.

Note that although NO and NO_2 have negative ozone impacts in the MIR scale used for VOCs, HONO has a relatively high impact in the MIR scale because of the fact that it rapidly forms OH radicals, which causes more O_3 formation in high NO_x conditions. The MIR value for HONO is calculated to be 6.94 grams O_3 per gram HONO. This is relatively high but not as high as the NMIR value for HONO, which is 15.85. Therefore for regulatory and life cycle assessment applications we recommend using the NMIR and not the MIR value for HONO as well as for NO and NO_2.

Conclusions and Recommendations

It is recommended that for regulatory or life cycle impact assessment applications where NO_x impacts need to be evaluated using the same scale as VOC impacts, and where the MIR scale is used for evaluating VOC impacts, the NO_x impacts used should be those derived for the NMIR scale as discussed above. For the SAPRC-07 reactivity scale given by Carter (2007) the NMIR values of 25.37, 17.24, and 15.85 grams O_3 per gram compound for NO, NO_2, and HONO respectively be added to the MIR values

given for the VOCs. These values are being added to the SAPRC-07 reactivity tabulations available at the SAPRC mechanism web site at http://www.cert.ucr.edu/~carter/SAPRC.

Note that regardless of whether one is considering VOCs or NO_x, the units used to quantify the reactivity should be consistent with the units used to quantify the emissions of the compound. If the emissions are quantified on a mass basis then the mass-based reactivity units, given above, should be used. If they are quantified on a molar basis, then mole based reactivity units should be used.

If one is interested in quantifying the impact of NO_x, then the speciation of the NO_x needs to be specified. This depends on the NO_x source and how emissions from that source are quantified, a discussion of which is beyond the scope of this document. In any case, as with VOCs, the incremental reactivity of the mixture is the same as the linear combination of the reactivities of the components, with weight fractions being used if reactivities are quantified on a mass basis or mole fractions are used if they are quantified on a molar basis. NO_x is generally considered to be a mixture of NO and NO_2, so the fraction of each needs to be specified for estimating the impact of NO_x. (A small amount of HONO is included with the NO_x inputs in the reactivity scenarios of Carter [1997a,b], but usually this is not considered when quantifying NO_x emissions. The HONO contribution is relatively unimportant in this application in any case.) For some emissions applications the molecular weight of NO_2 is used to derive mass NO_x emissions from molar emissions data, even though NO_x is mostly NO. In those cases, the recommended procedure is to either use molar quantifications so the molecular weight does not matter, or to re-derive the molecular weight to be the appropriate value based on the NO_x speciation assumed to be appropriate for the source.

References

Carter, W. P. L. and R. Atkinson (1989a): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environ. Sci. Technol., 23, 864.

Carter, W. P. L. (1994a): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," J. Air & Waste Manage. Assoc., 44, 881-899.

Carter, W. P. L. (1994b): "Calculation of Reactivity Scales Using an Updated Carbon Bond IV Mechanism," Report Prepared for Systems Applications International Under Funding from the Auto/Oil Air Quality Improvement Research Program, April 12.

Carter, W. P. L. (2000): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at http://cert.ucr.edu/~carter/absts.htm#saprc99 and http://www.cert.ucr.edu/~carter/reactdat.htm.

Carter, W. P. L. (2003): "The SAPRC-99 Chemical Mechanism and Updated VOC Reactivity Scales, Updated and Corrected Data as of February 5, 2003," Available at http://www.cert.ucr.edu/~carter/reactdat.htm.

Carter, W. P. L. (2007): "Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales," Final report to the California Air Resources Board Contract No. 03-318. August. Available at www.cert.ucr.edu/~carter/SAPRC.

Dimitriades, B. (1999): "Scientific Basis of an Improved EPA Policy on Control of Organic Emissions for Ambient Ozone Reduction," J. Air & Waste Manage. Assoc. 49, 831-838

RRWG (1999a): "VOC Reactivity Policy White Paper," Prepared by the Reactivity Research Work Group Policy Team, October 1. Available at http://www.narsto.org/section.src?SID=10.

RRWG (1999b): "VOC Reactivity Science Assessment: Executive Summary", Prepared by the Reactivity Research Working Group Science Team, May 5, Available at http://www.narsto.org/section.src?SID=10.