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# The Ozone Productivity of *n*-Propyl Bromide: Part 2—An Exception to the Maximum Incremental Reactivity Scale

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## ABSTRACT

In an earlier paper the ozone-forming potential of *n*-propyl bromide (NPB) was studied with a new methodology designed to address issues associated with a marginal smog-forming compound. However, the U.S. Environmental Protection Agency (EPA) subsequently revised its policy and now recommends using the Maximum Incremental Reactivity (MIR) scale to rank the ozone-forming potential of all volatile organic compounds (VOCs), including those of marginal ozone productivity. Nevertheless, EPA contemplated exceptions to the box-model-derived MIR scale by allowing use of photochemical grid-model simulations for case specific reactivity assessments. The California Air Resources Board (CARB) also uses the MIR scale and CARB has a Reactivity Scientific Advisory Committee that can consider exceptions to the MIR scale. In this study, grid-model simulations that were recommended by EPA are used to evaluate the incremental ozone impacts of NPB using an update to the chemical mechanism developed in an earlier paper. New methods of analysis of the grid-model output are further developed here to quantify the relative reactivities between NPB and ethane over a wide range of conditions. The new grid-model-based analyses show that NPB is significantly different and generally less in ozone-forming potential (i.e., reactivity) than predicted by the box-model-based MIR scale relative to ethane, EPA's "bright-line" test for non-VOC status. Although NPB has low reactivity compared to typical VOCs on any scale, the new grid-model analyses developed here show that NPB is far less reactive (and even has negative reactivity) compared to the reactivity predicted by the MIR scale.

### IMPLICATIONS

This paper presents the results of continued scientific investigations on the smog-forming potential of NPB, a high-end chlorofluorocarbon replacement solvent. The paper provides an in-depth description of a powerful new methodology that can be used to implement a grid-modeling option to the new EPA policy for granting nonreactive status to compounds that can be shown to be less reactive than ethane. Although NPB can be more reactive than ethane under some conditions, NPB is less reactive than ethane under ozone-peaking conditions and NPB can often reduce ozone (i.e., negative reactivity).

## INTRODUCTION

In an earlier paper[1] the ozone-forming potential of *n*-propyl bromide (NPB) was studied with a new methodology designed to address issues associated with marginal smog-forming compounds. NPB is a replacement for high-end chlorofluorocarbon (CFC) and hydrochlorofluorcarbon (HCFC) solvents. However, these fluorine-containing solvents had been deemed as nonreactive as urban-ozone-forming volatile organic compounds (VOCs) by the U.S. Environmental Protection Agency (EPA). Thus, users of these solvents did not need to report emissions of them as smog-precursors to local air districts. The EPA grants non-volatile organic compound status to marginal smog-forming compounds that can be shown to be equal or less than ethane in ozone-forming potential. Until recently[2] the comparison with ethane could be shown using rate-constant data for the comparative reactions with the hydroxyl (OH) radical, of the candidate VOC with ethane.

Published results for the reaction rate constant of NPB with the OH radical on a weight basis were shown to be statistically significantly less than that of ethane.[1] However, the overall smog formation chemistry of NPB appears to be very unusual compared with typical VOCs and relatively complex because of the presence of bromine. In smog chamber experiments, compared with what would be expected from ethane, NPB initially shows a faster ozone buildup, but then the secondary products that can contain or release bromine atoms tend to destroy ozone such that NPB can eventually have a net overall negative reactivity (i.e., reduce ozone). Bromine-containing compounds have been implicated in atmospheric observations of reduced ozone in areas such as the Arctic and the Dead Sea.[3–6] As discussed by Yang et al.,[6] the main destruction mechanism occurs through a semi-catalytic cycle seen in reactions 1 through 3.

$$Br + O_3 \rightarrow BrO + O_2 \quad (1)$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \quad (2)$$

$$HOBr + h\nu \rightarrow Br + OH \quad (3)$$

which gives a net result in daylight, shown as reaction 4.

$$O_3 + HO_2 \rightarrow OH + 2O_2 \quad (4)$$

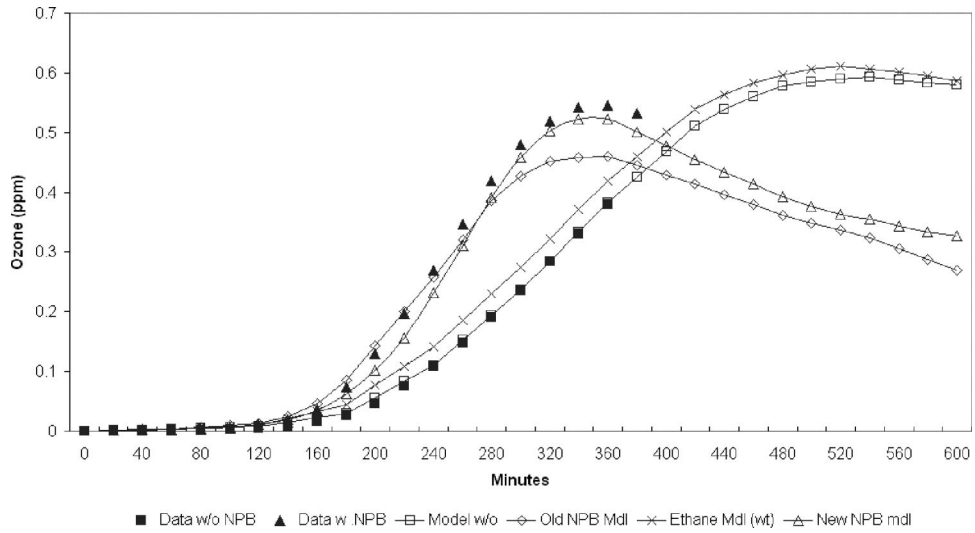


**Figure 1.** Experimental data and modeling results for Bourns College of Engineering–Center for Environmental Research and Technology (CE-CERT) experiment DTC-433.[15] The base experiment used 5.5 ppmC Mini-Surrogate Urban Mixture with 0.37 ppm $NO_x$. When NPB was added, 3 ppm of it was added to the base mixture.

And this net effect not only destroys an ozone molecule as shown here, but a hydroperoxyl radical ($HO_2$) is converted to an OH, which as noted by Whitten[7] is a reversal of the process that typically leads to urban ozone formation. However, this bromine-assisted ozone destruction cycle is clearly most effective when $HO_2$ radicals are most abundant, and this occurs late in the ozone-peaking process when oxides of nitrogen ($NO_x$) are low. The enhanced ozone buildup from NPB observed at high $NO_x$ concentrations (and used in the Maximum Incremental Reactivity [MIR] calculations) is more difficult to explain easily.

The NPB chemistry added to the urban airshed grid model for the previous paper[1] and the Comprehensive Air Quality Model with Extensions (CAMx) grid model used for this paper as well as to simulate the smog chamber experiments with NPB added to surrogate urban mixtures, consists of approximately 70 reactions (by comparison the base ozone chemistry used in CAMx had only 96 reactions). One ozone-enhancement reaction found in the 70 reactions added to treat NPB chemistry is as follows:

$$\mathrm{Br} + OLE \rightarrow BALD + XO2 + \mathrm{HO_2} \qquad (5)$$

where *OLE* is a carbon bond species[8] representing the olefinic bond of terminal olefin compounds (found in all urban mixtures of VOC); *BALD* represents an aldehyde that contains bromine; *XO2* is an operator species representing a conversion of nitric oxide (NO) to nitrogen dioxide ($NO_2$); and the $HO_2$ formed is a new radical. The conversion of NO to $NO_2$ and the formation of a new radical are both important to ozone build-up under high $NO_x$ conditions such as used for the MIR factors.

EPA[2] has recently joined the California Air Resources Board[9] (CARB) in recommending use of the MIR

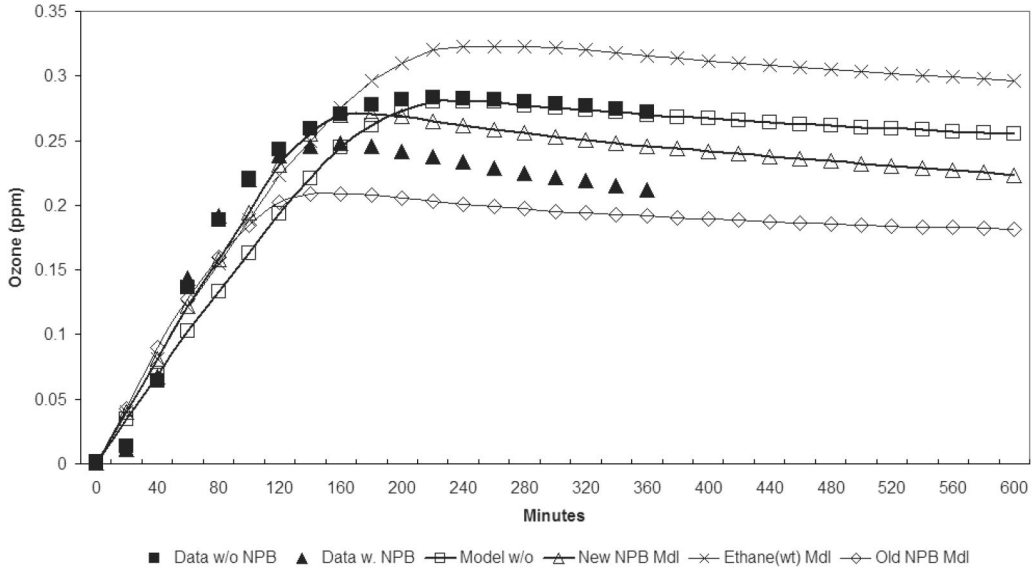


**Figure 2.** Experimental data and modeling results for CE-CERT experiment DTC-424.[15] The base experiment used 4.9 ppmC Full-Surrogate Urban Mixture with 0.12 ppm (low) $NO_x$. When NPB was added, 2.1 ppm of it was added to the base mixture.

**Table 1.** Species names for the Carbon Bond IV (CB4) mechanism with ethane and NPB.

| Species Name | Description | Number of Carbons |
|---|---|---|
| NO | Nitric oxide | 0 |
| $NO_2$ | Nitrogen dioxide | 0 |
| $O_3$ | Ozone | 0 |
| O | Oxygen atom in the $O^3(P)$ electronic state | 0 |
| O1D | Oxygen atom in the $O^1(D)$ electronic state | 0 |
| OH | Hydroxyl radical | 0 |
| $HO_2$ | Hydroperoxy radical | 0 |
| $H_2O_2$ | Hydrogen peroxide | 0 |
| $NO_3$ | Nitrate radical | 0 |
| $N_2O_5$ | Dinitrogen pentoxide | 0 |
| HONO | Nitrous acid | 0 |
| $HNO_3$ | Nitric acid | 0 |
| PNA | Peroxynitric acid ($HNO_4$) | 0 |
| CO | Carbon monoxide | 1 |
| FORM | Formaldehyde | 1 |
| ALD2 | Acetaldehyde | 2 |
| $C_2O_3$ | Acetylperoxy radical | 2 |
| PAN | Peroxyacetyl nitrate | 2 |
| XO2 | NO to $NO_2$ conversion from alkylperoxy ($RO_2$) radical | 0 |
| XO2N | NO to organic nitrate conversion from alkylperoxy ($RO_2$) radical | 0 |
| NTR | Organic nitrate ($RNO_3$) | 1 |
| ETOH | Ethanol | 2 |
| MEOH | Methanol | 1 |
| PAR | Paraffin carbon bond (C–C) | 1 |
| ROR | Secondary alkoxy radical | 0 |
| ETH | Ethene | 2 |
| OLE | Terminal olefin carbon bond (R–C=C) | 2 |
| IOLE | Internal olefin carbon bond (R–C=C–R) | 4 |
| ISOP | Isoprene | 5 |
| ISPD | Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.) | 4 |
| TOL | Toluene and other monoalkyl aromatics | 7 |
| XYL | Xylene and other polyalkyl aromatics | 8 |
| CRES | Cresol and higher molecular weight phenols | 8 |
| $TO_2$ | Toluene-hydroxyl radical adduct | 7 |
| OPEN | Aromatic ring opening product | 4 |
| CRO | Methylphenoxy radical | 7 |
| MGLY | Methylglyoxal and other aromatic products | 3 |
| PANX | Peroxypropionyl nitrate | 3 |
| $CXO_3$ | Propionyl peroxy radical | 3 |
| ETHA | Ethane | 0 |
| NPB | *n*-Propyl bromide | 3 |
| BRAC | 1-Bromo acetone | 3 |
| BALD | 3-Bromo propionaldehyde | 3 |
| $B_2O_3$ | 3-Bromo propionyl peroxy radical | 3 |
| BPAN | 3-Bromo peroxypropionyl nitrate | 3 |
| BR2 | Bromine molecule | 0 |
| BR | Bromine atom | 0 |
| HBR | Hydrogen bromide | 0 |
| BRNO | Nitrosyl bromide | 0 |
| BRN2 | $BrNO_2$ | 0 |
| BONO | BrONO | 0 |
| $BON_2$ | Bromine nitrate, $BrONO_2$ | 0 |

scale[10] to rank the ozone-forming potential of all VOCs, including those of marginal productivity. EPA contemplated exceptions to the box-model-derived MIR scale by allowing use of photochemical grid-model simulations, similar

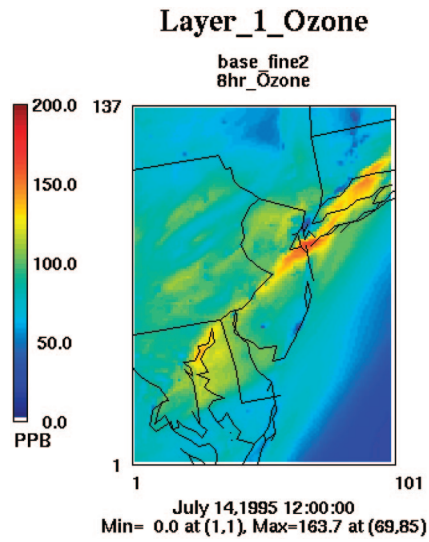


**Figure 3.** CAMx modeling results for 4-km region showing simulated base 8-hr ozone concentration for episode day 8 (July 14).

to those done by Carter, Tonnesen, and Yarwood,[11] for case-specific reactivity assessments. CARB has a Reactivity Scientific Advisory Committee[12] that can consider exceptions to the MIR scale and CARB itself has recently been using a grid-model to assess the reactivity of carbon monoxide (CO) under ozone-conducive conditions.[13] In this study, the same EPA-recommended[2] grid-model simulations of Carter, Tonnesen, and Yarwood are used to evaluate the incremental ozone impacts of NPB using a minor update to the chemical mechanism of Whitten et al.[1] New methods of analysis of the grid-model output are further developed here to quantify the relative reactivities between ethane and NPB. The new methods of analyses show that NPB, relative to ethane, is significantly different in ozone-forming potential (i.e., reactivity) than predicted by the MIR scale. However, although NPB has low reactivity compared with typical VOCs on any scale, this

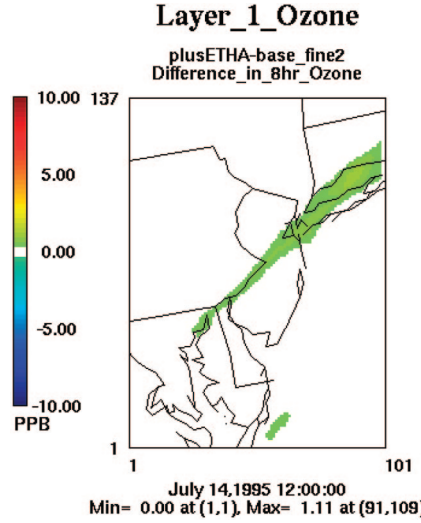


**Figure 4.** CAMx modeling results for 4-km region showing the simulated changes to the base 8-hr ozone concentrations when surface anthropogenic VOCs are increased by 10 wt % as ethane for episode day 8 (July 14).

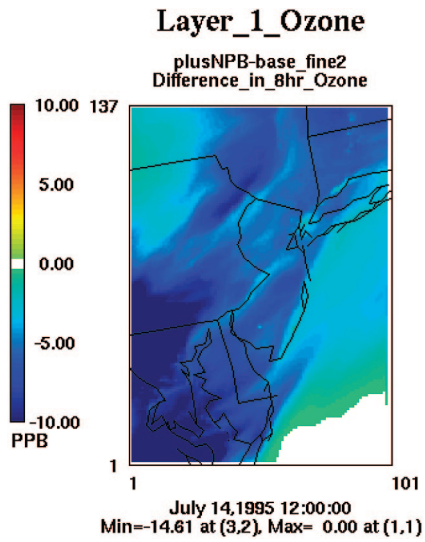


**Figure 5.** CAMx modeling results for 4-km region showing the simulated changes to the base 8-hr ozone concentrations when surface anthropogenic VOCs are increased by 10 wt % as NPB for episode day 8 (July 14).

new grid-model analysis finds that NPB is far less reactive (and even has negative reactivity) compared with ethane as predicted by the MIR scale.

The previous grid-modeling study by Carter, Tonnesen, and Yarwood found that grid-model tests confirmed that box-model-derived MIR factors give satisfactory relative reactivities for most VOCs over a wide range of conditions and ozone metrics. However, that work found a "consistent bias" for slower reacting species, such as ethane and CO, with the grid-model finding greater ozone-forming potential than predicted by the MIR scale. Here we show that the opposite bias is also possible for slower reacting species, namely that the MIR scale can overestimate rather than consistently underestimate the ozone-forming potential of a low-reactivity compound, namely NPB ($CH_3CH_2CH_2Br$). The latest MIR values for ethane and NPB are 0.31 and 0.35 g ozone per gram VOC, respectively.[14]

## RESULTS

The previous paper by Whitten et al.[1] developed a mechanism for the atmospheric degradation of NPB but noted that some relevant publications had become available too late to be included in their smog chamber testing and grid-model simulations. Thus, as the first part of this new study, the information given in these publications was used to make a minor update to the NPB chemistry and retest it against the data from the six smog chamber experiments of Carter et al.[15] It was found that the updated chemistry did a slightly better job of predicting all of the available smog chamber data. The updated NPB reaction set was then incorporated into the CAMx grid model for this study.

The main upgrade to the NPB chemistry stems from the work of Gilles et al.,[16] who measured the initial product distribution of the OH radical reactions (reactions 6–8) that can abstract hydrogen atoms from three different sites in the NPB molecule.

$$OH + CH_2BrCH_2CH_3 \rightarrow CH_2BrC^{\cdot}HCH_3 \quad (56\%) \quad (6)$$

$$\rightarrow C^{\cdot}HBrCH_2CH_3 \quad (32\%) \quad (7)$$

$$\rightarrow CH_2BrCH_2C^{\cdot}H_2 \quad (12\%) \quad (8)$$

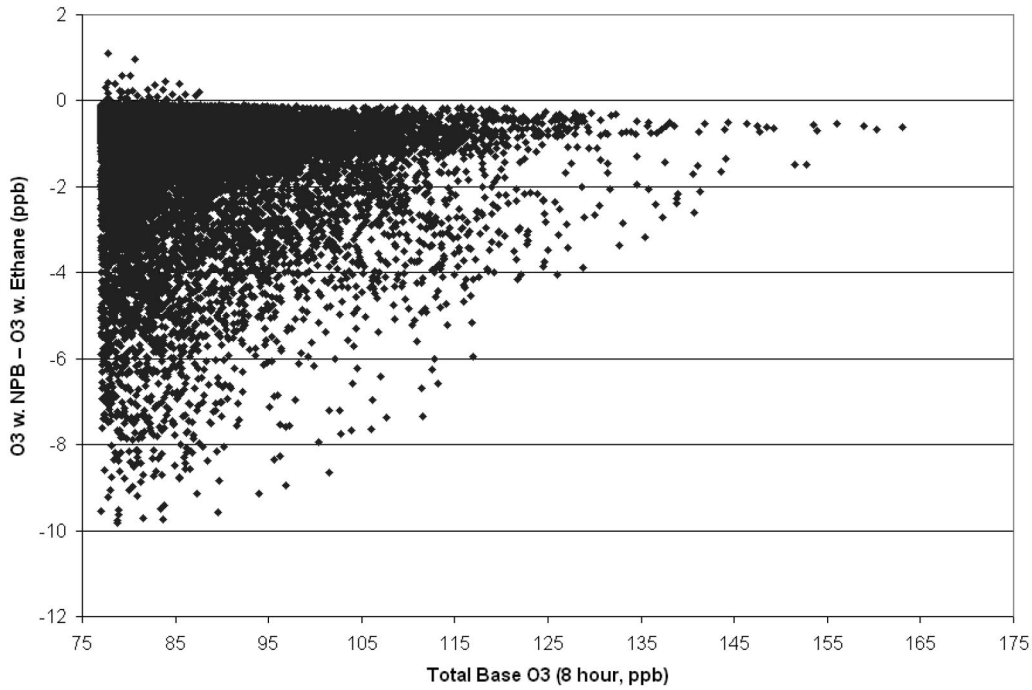


**Figure 6.** The ozone changes (in ppb) comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC. Shown are the highest 30,000 total ozone grid cells simulated in the 12-km fine-grid region for episode day 6 (July 12).

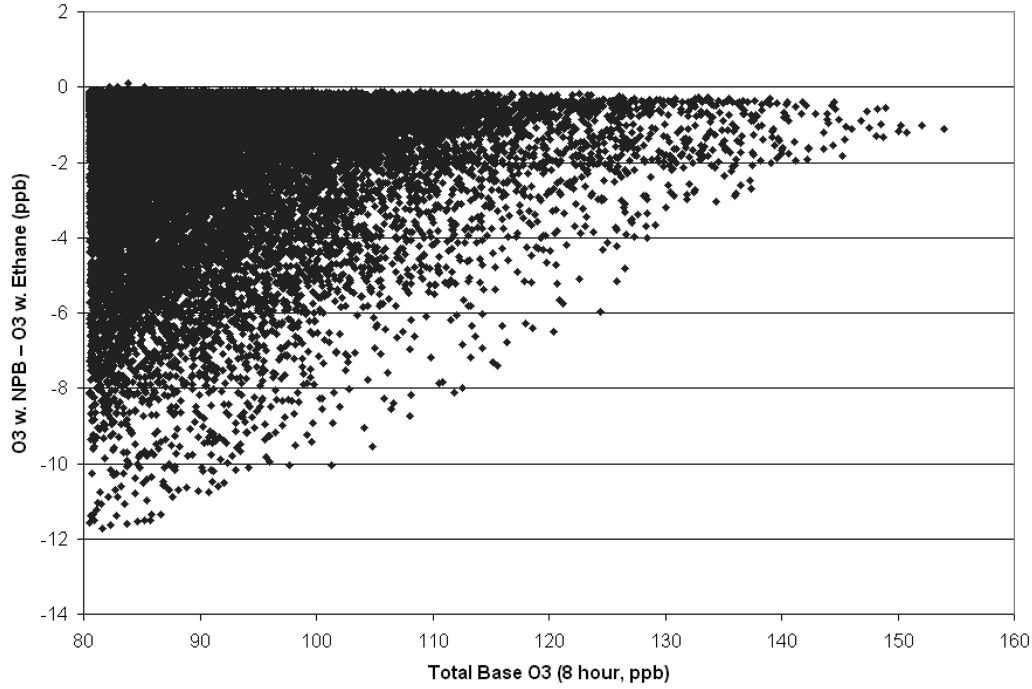


**Figure 7.** The ozone changes (in ppb) comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC. Shown are the highest 30,000 total ozone grid cells simulated in the 12-km fine-grid region for episode day 7 (July 13).

The impact of this new product distribution and other minor changes (the next most important being the photolysis rate for bromoacetone) are shown in Figures 1 and 2 (Figures S1–S4 are available in the supplemental data published at http://secure.awma.org/onlinelibrary/samples/10.3155-1047-3289.58.7.891_supplmaterial.pdf). Compared with observed chamber data, the older model impacts (also included in these figures) from the previous paper[1] tended to overpredict the initial ozone increase, but underpredict observed peak ozone increases and final ozone decay rates. The updated NPB mechanism is seen to come much closer to observed peak ozone increases and decay rates. The species used in the new reaction mechanism for NPB are listed in Table 1 (the full reaction mechanism for NPB is listed as Table S1 in the supplemental data).

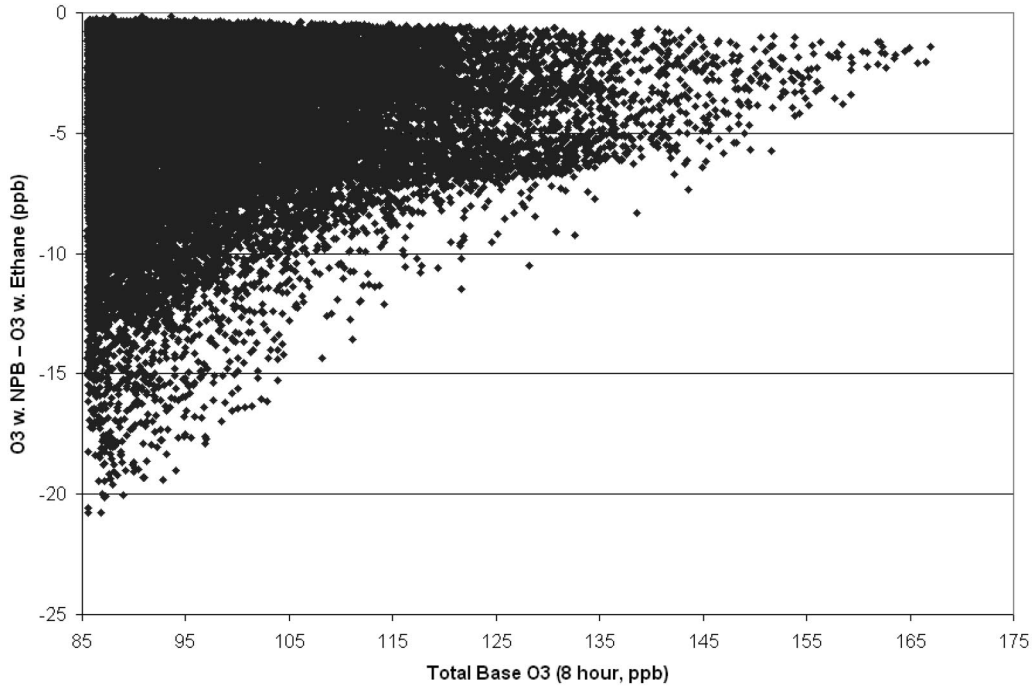


**Figure 8.** The ozone changes (in ppb) comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC. Shown are the highest 30,000 total ozone grid cells simulated in the 12-km fine-grid region for episode day 8 (July 14).

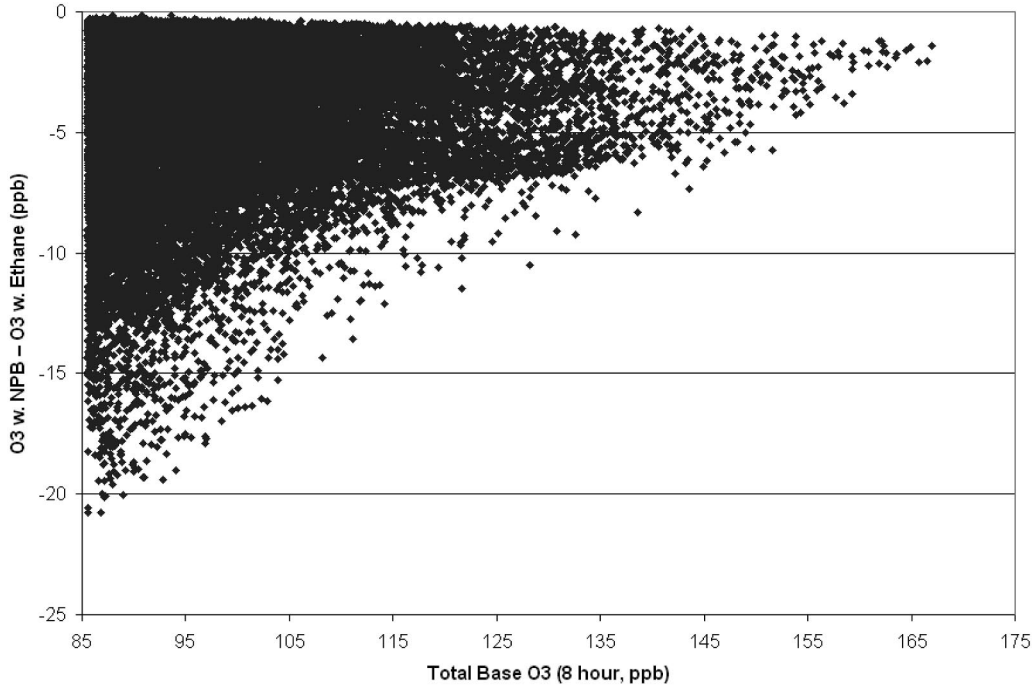


**Figure 9.** The ozone changes (in ppb) comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC. Shown are the highest 30,000 total ozone grid cells simulated in the 12-km fine-grid region for episode day 9 (July 15).

Grid-modeling was performed using version 4.2 of the CAMx, with modeling databases used by Carter et al.[11] for reactivity assessments contributed to EPA's Reactivity Research Working Group. As described by Carter et al.,[11] the model has nested 36-, 12-, and 4-km resolution grids. The 36-km grid covers more than half of the lower 48 states east of the Rocky Mountains, the 12-km grid covers a region extending from Memphis to Boston, and the 4-km grid covers the northeast corridor including Washington, Philadelphia, and New York City. The overall 9-day episode that forms the base for these simulations occurred during July 1995. The model is started on July 7 and runs through the July 15. The first 4 days are run using only the 36-km resolution as a "spin-up" to remove the influence of the model initial conditions. The last 5 days continue with two-way nested 36-, 12-, and 4-km resolutions used and the 12- and 4-km areas are used for the analyses presented here.

The incremental ozone impacts of NPB were compared with the incremental ozone impacts of ethane by adding either of these compounds to the model emissions at 10 wt % of the total surface anthropogenic VOC emissions. Ethane was used in this comparison because EPA has considered compounds that are no more reactive than ethane to be "low reactivity" and exempt from the definition of VOC.[2] Figures 3–5 (Figures S5–S13 are available in the supplemental data) show maps of the 4-km grid area for the base-case peak 8-hr ozone formation, then differences between the base simulation and the addition of ethane, and then as NPB. For this episode the maps indicate that adding ethane always increases peak 8-hr ozone whereas adding NPB tends mostly to reduce peak 8-hr ozone.

The method for evaluating reactivity that was developed here involves looking at all 8-hr ozone values for each day in both the 12- and 4-km grid regions. Because of limitations of the spreadsheet software, only the 30,000 grid-cell-hours with the highest 8-hr ozone can be displayed in the figures for each day, but statistics are developed without this 30,000 limitation and these statistics are shown in tables that accompany each figure. The grid-cell-hours with 8-hr ozone above 75–85 ppb are considered to be the main grid cells of interest in developing

**Table 2.** Statistical information relevant to Figure 6 that shows the differences in 8-hr ozone concentrations between adding equal weight amounts of ethane or NPB for the 12-km region on episode day 6 (July 12) for all grid cells having 75-ppb base ozone or higher.

| Ozone Range | 75–85 | 85–95 | 95–105 | 105–115 | 115–125 | 125–135 | 135–145 | 145–155 | 155–165 |
|---|---|---|---|---|---|---|---|---|---|
| Cells | 22,089 | 8,287 | 2,494 | 871 | 279 | 73 | 26 | 9 | 4 |
| Max Δ | 1.099 | 0.388 | −0.137 | −0.15 | −0.164 | −0.287 | −0.494 | −0.529 | −0.534 |
| Min Δ | −10.25 | −9.564 | −8.963 | −7.633 | −5.964 | −4.054 | −3.181 | −1.489 | −0.657 |
| Mean | −0.948 | −0.985 | −1.196 | −1.437 | −1.382 | −1.128 | −1.422 | −0.810 | −0.596 |
| Median | −0.545 | −0.599 | −0.784 | −0.948 | −0.84 | −0.721 | −1.388 | −0.636 | −0.596 |
| SD | 1.183 | 1.133 | 1.152 | 1.241 | 1.194 | 0.965 | 0.857 | 0.386 | 0.051 |
| Cells > 0 | 35 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Percent > 0 | 0.158 | 0.072 | | | | | | | |

**Table 3.** Statistical information relevant to Figure 7 that shows the differences in 8-hr ozone concentrations between adding equal weight amounts of ethane or NPB for the 12-km region on episode day 7 (July 13) for all grid cells having 75 ppb base ozone or higher.

| Ozone Range | 75–85 | 85–95 | 95–105 | 105–115 | 115–125 | 125–135 | 135–145 | 145–155 |
|---|---|---|---|---|---|---|---|---|
| Cells | 23,711 | 12,674 | 5,093 | 1,662 | 553 | 274 | 97 | 17 |
| Max Δ | 0.111 | 0.008 | −0.095 | −0.112 | −0.168 | −0.239 | −0.309 | −0.546 |
| Min Δ | −12.154 | −11.511 | −10.045 | −8.742 | −7.389 | −5.159 | −2.882 | −1.822 |
| Mean | −1.542 | −1.534 | −1.533 | −1.528 | −1.532 | −1.357 | −1.198 | −1.078 |
| Median | −0.684 | −0.860 | −0.951 | −0.991 | −1.115 | −1.161 | −1.110 | −1.069 |
| SD | 1.946 | 1.730 | 1.579 | 1.414 | 1.301 | 0.989 | 0.662 | 0.311 |
| Cells > 0 | 5 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| Percent > 0 | 0.021 | 0.008 | | | | | | |

ozone air-quality management strategies. Grid cells with base-case 8-hr ozone below 75 ppb were excluded from the analysis. The incremental ozone impacts of NPB and ethane were compared by calculating the difference in 8-hr ozone between adding NPB or ethane (i.e., ozone with NPB minus ozone with ethane) for all grid cells in the 12- and 4-km grid regions.

Figures 6–9 show how the envelopes of ozone increment for adding NPB versus adding ethane depend upon the base-case 8-hr ozone in the 12-km grid. For example, in Figure 6 for the first day analyzed (July 12) only a few points of the top 30,000 are positive (i.e., NPB has more ozone impact than ethane) and these are associated with low base-case ozone values. Table 2 presents the statistical analysis in bin form for all 34,132 grid cells with 8-hr ozone over 75 ppb in the 12-km region on this simulation day. The lowest bin (75–85 ppb base 8-hr ozone) has over 20,000 grid cells, of which only 35 (or 0.16%) show NPB to generate more ozone than ethane. In the second bin of Table 2 there are still over 8000 grid cells, but only 6 (down to 0.07%) show NPB to be more reactive. All higher ozone concentration cells (over 3700 of them) with ozone ranging up to 163 ppb, show NPB to generate less ozone than ethane. On the second day analyzed (July 13, Figure 7) the episode is further developed and, on average, ozone values are somewhat higher (the 30,000 highest start above 80.5 ppb rather than 77 ppb as was seen in Figure 6). In Figure 7 there are only a couple of points seen from the top 30,000 in which adding NPB makes more ozone than adding ethane. Table 3 provides the statistics (based on all 44,081 cells having 8-hr ozone levels over 75 ppb) confirming what Figure 7 shows. Again, these few points are associated with low base-case ozone values among the top 44,081. For the next day (July 14, Figure 8 and Table 4) it is seen that zero cell-hours (out of the 56,211 analyzed for Table 4) have ozone impacts of adding NPB that are greater than the ozone impact of adding ethane. Moreover, some cells (albeit with ozone levels far lower than the highest concentrations) show that ozone can be as much as 20 ppb less compared with adding ethane. The episode has by this time progressed such that the top 30,000 cell-hours begin at 85.5 ppb. On the final day (July 15; Figure 9 and Table 5) of the episode there are again zero cells among the 31,577 grid cells with ozone over 75 ppb where the NPB impacts exceed those of an equal addition of ethane by weight. Moreover, Figure 10 and Table 6 show that all but 37 of the top 31,577 grid cells have lower 8-hr ozone than even the base case. That is, in virtually all 31,577 of the higher ozone concentration 12-km grid cells on July 15, the addition of NPB actually reduces ozone compared even to the base case.

The 4-km grid area (the northeast corridor) shows similar results to the 12-km grid presented above, and most of the analyses are provided in the supplemental data as Figures S14–S17 and their related statistical Tables S2–S5. But the first analysis day of July 12 is interesting and is included here as Figures 11 and 12 with Tables 7 and 8. This analysis shows over 2% of the 4-km grid cells with 8-hr ozone exceeding 75 ppb in which the impacts of NPB do exceed those of ethane (the 12-km region on this day showed only ~0.1% of cells with NPB impacts exceeding ethane). However, in this 4-km region on July 12 the episode is not fully developed because less than 10,000 cells with simulated 8-hr ozone values exceed 75 ppb. Moreover, from Figure 12, it can readily be seen that the highest NPB impacts are associated with cells that show negative ozone impacts when $NO_x$ emissions are increased. Ozone reduction with increased $NO_x$ is associated with the definition of

**Table 4.** Statistical information relevant to Figure 8 that shows the differences in 8-hr ozone concentrations between adding equal weight amounts of ethane or NPB for the 12-km region on episode day 8 (July 14) for all grid cells having 75-ppb base ozone or higher.

| Ozone Range | 75–85 | 85–95 | 95–105 | 105–115 | 115–125 | 125–135 | 135–145 | 145–155 | 155–165 | 165–175 |
|---|---|---|---|---|---|---|---|---|---|---|
| Cells | 25,205 | 15,687 | 8,055 | 4,147 | 1,892 | 789 | 286 | 111 | 36 | 3 |
| Max Δ | −0.12 | −0.13 | −0.31 | −0.40 | −0.52 | −0.61 | −0.70 | −1.00 | −1.21 | −1.42 |
| Min Δ | −24.32 | −20.78 | −17.88 | −14.33 | −11.49 | −10.51 | −8.30 | −6.17 | −3.85 | −2.11 |
| Mean | −4.34 | −4.34 | −3.99 | −3.76 | −3.73 | −4.08 | −3.48 | −3.07 | −2.12 | −1.85 |
| Median | −2.91 | −3.28 | −3.25 | −3.17 | −3.37 | −3.86 | −3.48 | −2.83 | −1.86 | −2.03 |
| SD | 4.16 | 3.62 | 2.84 | 2.28 | 2.03 | 1.92 | 1.63 | 1.22 | 0.75 | 0.38 |
| Cells > 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

**Table 5.** Statistical information relevant to Figure 9 that shows the differences in 8-hr ozone concentrations between adding equal weight amounts of ethane or NPB for the 12-km region on episode day 9 (July 15) for all grid cells having 75-ppb base ozone or higher.

| Ozone Range | 75–85 | 85–95 | 95–105 | 105–115 | 115–125 | 125–135 | 135–145 | 145–155 | 155–165 | 165–175 | 176.5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cells | 14,726 | 8,961 | 4,494 | 2,053 | 780 | 305 | 131 | 78 | 38 | 10 | 1 |
| Max Δ | 0.34 | −0.09 | −0.10 | −0.22 | −0.24 | −0.29 | −0.30 | −0.34 | −1.28 | −0.88 | −8.31 |
| Min Δ | −25.6 | −26.4 | −27.0 | −23.3 | −21.5 | −18.0 | −12.2 | −9.6 | −9.8 | −9.3 | −8.3 |
| Mean | −4.31 | −5.08 | −5.06 | −4.87 | −5.04 | −4.42 | −4.46 | −4.53 | −4.75 | −7.66 | −8.31 |
| Median | −2.65 | −3.31 | −3.10 | −2.83 | −2.80 | −2.73 | −2.91 | −2.92 | −3.03 | −8.06 | −8.31 |
| SD | 4.29 | 4.63 | 4.60 | 4.39 | 4.35 | 3.55 | 3.32 | 3.16 | 3.20 | 1.68 | 0.00 |
| Cells > 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Percent > 0 | 0.007 | | | | | | | | | | |

**Table 6.** Statistical information relevant to Figure 10 that shows the differences in 8-hr ozone concentrations between the base case and adding NPB (10% of the total base VOC) weight addition to the base VOC for the 12-km region on episode day 9 (July 15) for all grid cells having 75-ppb base ozone or higher.

| Ozone Range | 75–85 | 85–95 | 95–105 | 105–115 | 115–125 | 125–135 | 135–145 | 145–155 | 155–165 | 165–175 | 176.5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cells | 14,726 | 8,961 | 4,494 | 2,053 | 780 | 305 | 131 | 78 | 38 | 10 | 1 |
| Max Δ | 0.99 | 0.71 | 0.64 | 0.31 | 0.03 | −0.09 | −0.04 | 0.02 | −0.88 | −2.99 | −8.00 |
| Min Δ | −25.4 | −26.3 | −26.9 | −23.1 | −21.0 | −17.5 | −11.8 | −9.31 | −9.51 | −8.91 | −8.00 |
| Mean | −4.17 | −4.91 | −4.86 | −4.63 | −4.77 | −4.16 | −4.19 | −4.25 | −4.48 | −7.34 | −8.00 |
| Median | −2.49 | −3.12 | −2.88 | −2.59 | −2.49 | −2.44 | −2.73 | −2.76 | −2.82 | −7.68 | −8.00 |
| SD | 4.28 | 4.62 | 4.59 | 4.38 | 4.34 | 3.57 | 3.32 | 3.17 | 3.20 | 1.64 | 0.00 |
| Cells > 0 | 18 | 8 | 7 | 2 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| Percent > 0 | 0.12 | 0.09 | 0.16 | 0.10 | 0.13 | | | 1.28 | | | |

Carter's MIR condition. Thus, the conditions that are most "MIR-like" on July 12 do show ozone impacts from NPB that approach those from the high-$NO_x$, single-cell, single-day box-model simulations done by Carter and Tuazon.[17] However, a single-day box-model is unable to account for the multiday, regional-scale ozone impacts of NPB that contribute to its incremental ozone impact for even the most MIR-like grid cells in a grid model simulation.

For the next 3 days (July 13–15), the 4-km area shows far fewer grid cells with NPB impacts that exceed those

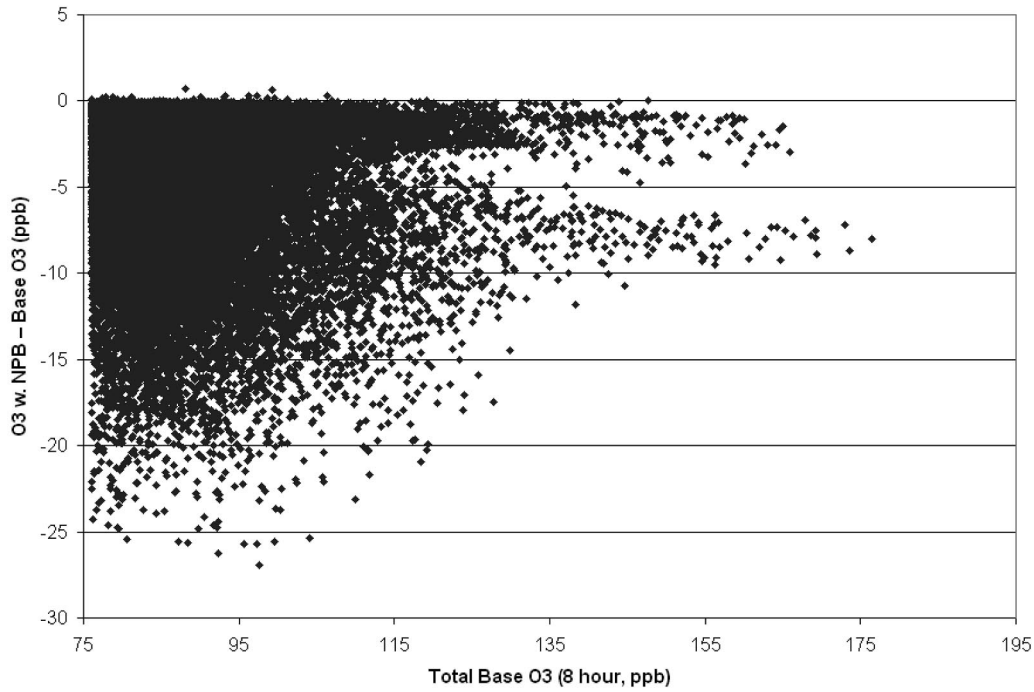


**Figure 10.** The ozone changes (in ppb) comparing the NPB (10% of the total base VOC) weight addition to the base VOC. Shown are the highest 30,000 total ozone grid cells simulated in the 12-km fine-grid region for episode day 9 (July 15).

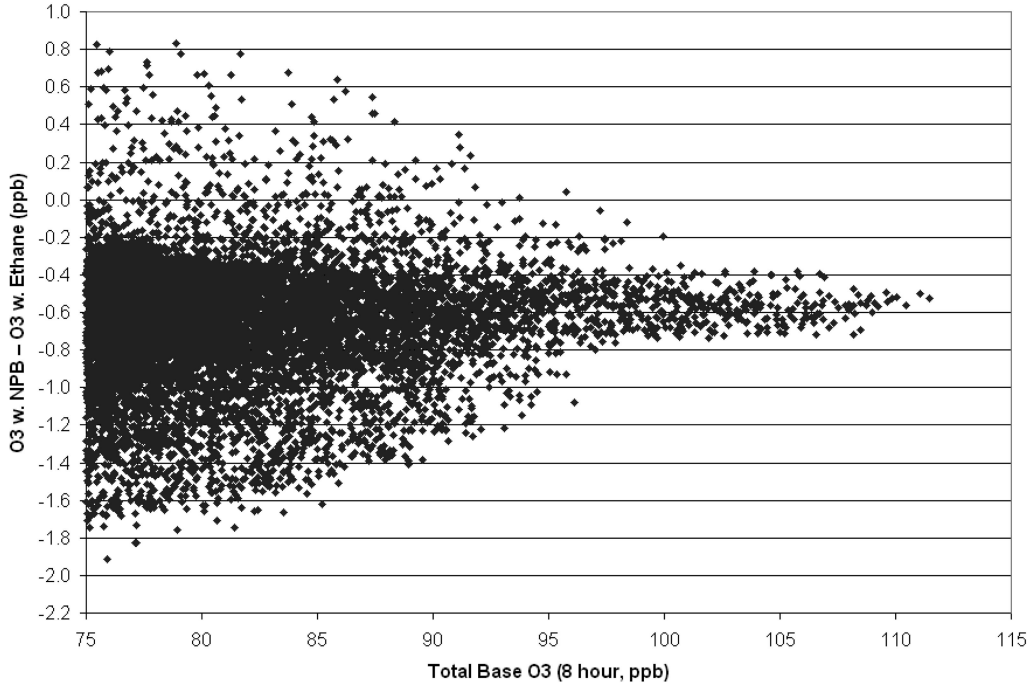


**Figure 11.** The ozone changes (in ppb) comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC. Shown are all 9786 total ozone grid cells greater than 75 ppb simulated in the 4-km fine-grid region for episode day 6 (July 12).

from ethane than on July 12 (Figure 11 and Table 7). Figures S14–S17 (which show the 4-km grid results for these 3 days) are available as supplemental data. On July 13, total ozone concentrations are beginning to increase as the episode progresses, because there are 23,766 cell-hours with simulated 8-hr ozone values greater than 75 ppb compared with only 9787 on July 12. On the third analysis day (July 14), the episode has developed dramatically and zero grid cells show NPB impacts exceeding those from ethane among the 35,052 cells showing simulated 8-hr ozone values over 85 ppb. Then for the final day (July 15) there are again zero cells with ozone impacts from NPB greater than from ethane. Moreover, for this day of this episode, essentially all (99.8%) NPB impacts are negative, relative to even the base-case ozone values. Figure 13 and Table 9 show that the highest ozone values rarely correspond to MIR-like conditions that themselves always show, because of Carter's methodology, that $NO_x$

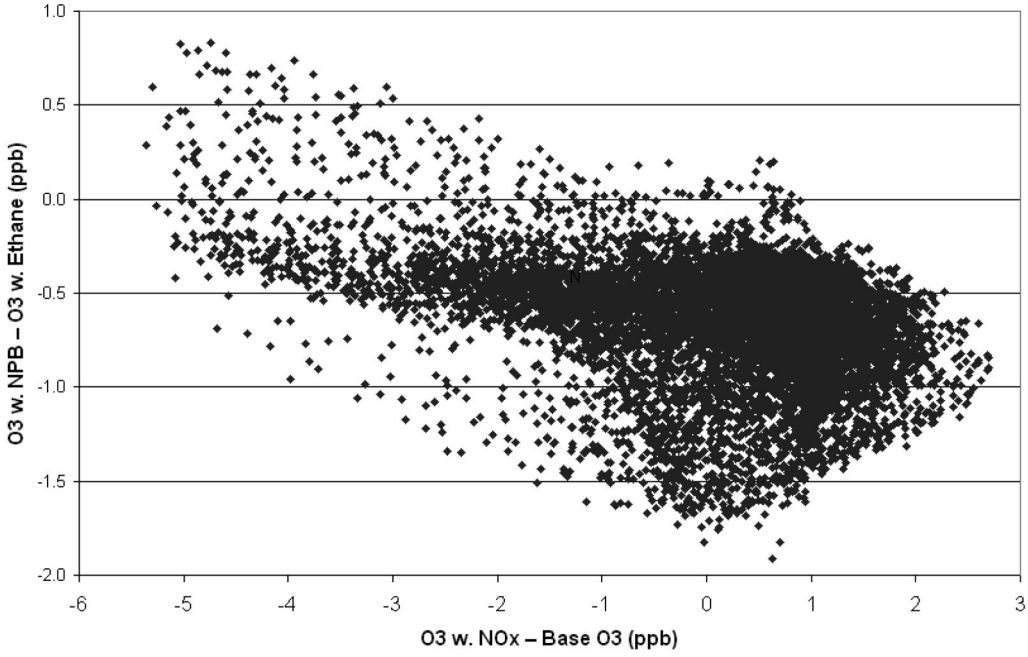


**Figure 12.** The ozone changes (in ppb) comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC. Shown are all 9786 total ozone grid cells greater than 75 ppb simulated in the 4-km fine-grid region for episode day 6 (July 12) plotted against the changes in ozone in those cells from adding the same weight addition as $NO_x$.

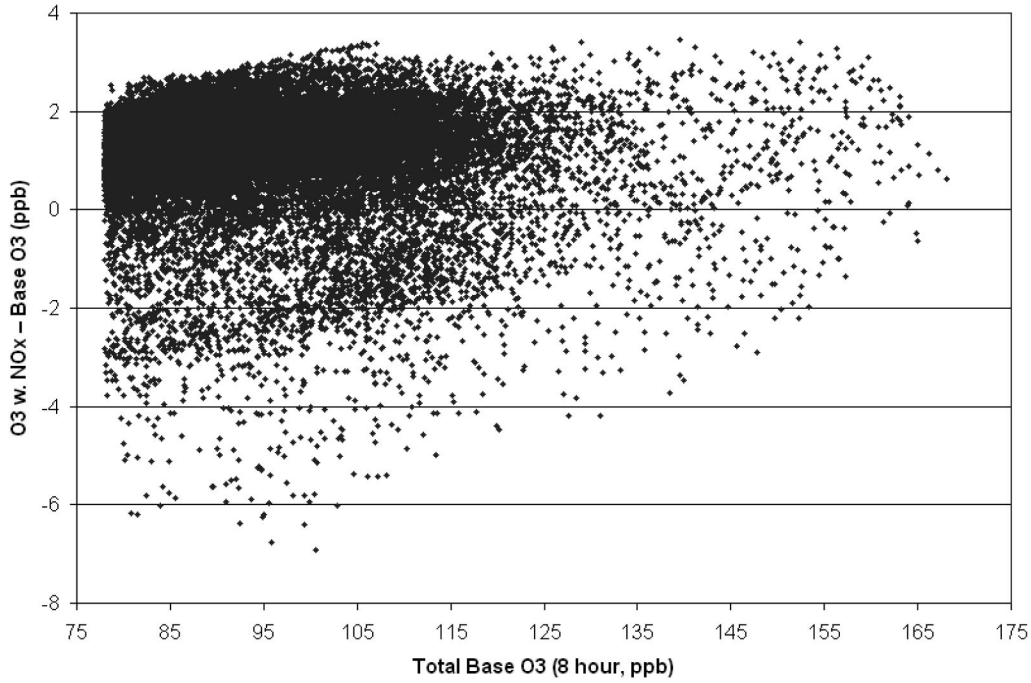


**Figure 13.** The ozone changes (in ppb) comparing an $NO_x$ (10% of the total base VOC) weight addition to the base $NO_x$ plotted against the base ozone in those cells. Shown are the highest 30,000 total ozone grid cells greater than 75 ppb simulated in the 4-km fine-grid region for episode day 9 (July 15).

additions must reduce ozone. Additionally, Figure 13 shows that none of the very highest ozone values show negative ozone response to $NO_x$ addition.

## DISCUSSION

A new means to evaluate low-reactivity compounds has been demonstrated here for the case of NPB. This new technique utilizes results from multiday, multiscale regional grid-modeling as suggested by EPA[2] under conditions of a major ozone episode as used to develop State Implementation Plans (SIPs) to reduce ozone. The model is run using as much as a 10% increase in the VOC emissions by weight for the specific compound being tested. For cases such as NPB in which comparisons to ethane are important, the model is also run with 10 wt % increase in VOC as ethane. If necessary to characterize ozone response of grid cells to VOC and $NO_x$, the model can be run with the $NO_x$ added at 10 wt % of the VOC emissions.

In the regions of higher grid resolution (that generally also contain the highest ozone concentrations seen during the episode) differences in 8-hr ozone concentrations between the base case (or ethane added case) and the simulation with the test VOC (or NOx) are analyzed. The analysis should focus on the highest ozone grid cells that are relevant to ozone nonattainment (e.g., 8-hr ozone above 75 ppb). These comparison values are plotted against the total base ozone found in the same cells as the comparisons. Statistical analyses can also be performed that quantify the extent of impacts shown by the plots. In this present study the addition of NPB generally produced less ozone than equal weight additions of ethane even for

**Table 7.** Statistical information relevant to Figure 11 that shows the differences in 8-hr ozone concentrations between adding equal weight amounts of ethane or NPB for the 4-km region on episode day 6 (July 12) for all grid cells having 75-ppb base ozone or higher.

| Ozone Range | 75–85 | 85–95 | 95–105 | 105–115 |
|---|---|---|---|---|
| Cells | 7,143 | 2,147 | 428 | 69 |
| Max Δ | 0.830 | 0.641 | 0.039 | −0.382 |
| Min Δ | −1.912 | −1.621 | −1.080 | −0.716 |
| Mean | −0.670 | −0.640 | −0.556 | −0.574 |
| Median | −0.627 | −0.619 | −0.558 | −0.569 |
| SD | 0.348 | 0.296 | 0.132 | 0.079 |
| Cells > 0 | 161 | 51 | 1 | 0 |
| Percent > 0 | 2.25 | 2.38 | 0.23 | |

**Table 8.** Statistical information relevant to Figure 12 that shows the differences in 8-hr ozone concentrations ozone changes (in ppb) in the 4-km fine-grid region for episode day 6 (July 12), comparing an NPB addition to an equal (10% of the total base VOC) weight addition of ethane to the base VOC plotted against the changes in ozone in those cells from adding the same weight addition as $NO_x$.

| Ozone Due to $NO_x$ Add | −4 to −6 | −2 to −4 | 0 to −2 | 0 to + 2 | +2 to + 4 |
|---|---|---|---|---|---|
| Cells | 174 | 690 | 2,824 | 5,956 | 143 |
| Max Δ | 0.830 | 0.735 | 0.318 | 0.208 | −0.490 |
| Min Δ | −0.784 | −1.350 | −1.825 | −1.912 | −1.243 |
| Mean | −0.001 | −0.343 | −0.641 | −0.717 | −0.842 |
| Median | −0.099 | −0.398 | −0.563 | −0.683 | −0.830 |
| SD | 0.365 | 0.305 | 0.335 | 0.287 | 0.196 |
| Cells > 0 | 71 | 83 | 38 | 20 | 0 |
| Percent > 0 | 40.8 | 12.0 | 1.3 | 0.3 | |

**Table 9.** Statistical information relevant to Figure 13 that shows the ozone changes (in ppb) in the 4-km fine-grid region for episode day 9 (July 15), comparing a $NO_x$ (10% of the total base VOC) weight addition to the base $NO_x$ plotted against the base ozone in those cells.

| Base Ozone | 75–85 | 85–95 | 95–105 | 105–115 | 115–125 | 125–135 | 135–145 | 145–155 | 155–165 | 165–175 |
|---|---|---|---|---|---|---|---|---|---|---|
| Cells | 12,430 | 9,245 | 6,858 | 3,692 | 1,188 | 409 | 207 | 148 | 83 | 5 |
| Max Δ | 2.69 | 2.96 | 3.34 | 3.38 | 3.17 | 3.41 | 3.46 | 3.40 | 3.27 | 1.15 |
| Min Δ | −6.21 | −6.37 | −6.91 | −5.43 | −4.48 | −4.19 | −3.74 | −2.90 | −1.37 | −0.63 |
| Mean | 0.93 | 1.14 | 1.18 | 1.00 | 0.88 | 0.87 | 0.52 | 0.91 | 1.34 | 0.53 |
| Median | 0.96 | 1.23 | 1.38 | 1.34 | 1.21 | 1.21 | 0.48 | 1.13 | 1.59 | 0.70 |
| SD | 0.78 | 0.96 | 1.12 | 1.29 | 1.33 | 1.43 | 1.59 | 1.54 | 1.14 | 0.68 |
| Cells > 0 | 749 | 693 | 699 | 648 | 276 | 95 | 70 | 39 | 13 | 1 |
| Percent > 0 | 6.0 | 7.5 | 10.2 | 17.6 | 23.2 | 23.2 | 33.8 | 26.4 | 15.7 | 20.0 |

the lowest ozone levels (i.e., but still greater than 75 ppb). Moreover, for the case presented here, NPB additions were seen to always reduce ozone compared with even the base case for the very highest ozone levels. However, a similar result was seen in the first paper[1] for the South Coast Air Basin for both base-case emissions and future emissions, with the tendency of NPB to show negative reactivity at the higher ozone-containing grid cells actually increasing (i.e., more negative) for the future. That is, even though the very highest future predicted ozone values were less because of the controls on overall emissions, the impacts of NPB were still more negative.

The box-model-derived MIR reactivity factors predict that NPB should form more ozone than ethane,[14] in contrast to the negative ozone reactivity and generally "less reactive than ethane" results found using a grid-model for both the central to eastern U.S. episode studied here and the previous South Coast episode studied earlier.[1] There were a small minority of grid cells seen in this eastern U.S. episode where NPB did form more ozone than ethane, and the negative ozone response to $NO_x$ additions in these grid cells confirmed that they were more similar to the conditions of the MIR box-model. However, these MIR-like grid cells were very few in number, occurred early in the episode before the highest ozone levels were reached, and did not include any of the highest ozone grid cells on each of the days studied. These new findings on this eastern U.S. episode and even the less-analyzed earlier study of the South Coast area[1] suggest that the high-$NO_x$, single-box, single-day conditions used to generate the MIR factors may not be appropriate to episodic ozone formation when ozone formation tends to rarely have strongly negative ozone responses to $NO_x$ additions.

## ACKNOWLEDGMENTS

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