Final Report

Accounting for the Impacts of Variable Cement Kiln Emission Rates on Ozone Formation in the Dallas/Fort-Worth Area

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Prepared for

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1. INTRODUCTION

The Dallas/Fort-Worth (DFW) area is currently in violation of the 8-hour ozone standard. On June 15, 2004, EPA designated nine counties in the DFW area (Collin, Dallas, Denton, Tarrant, Ellis, Johnson, Kaufman, Parker and Rockwall) as a moderate 8-hour nonattainment area with an attainment date of 2010. The Texas Commission on Environmental Quality (TCEQ) must develop a State Implementation Plan (SIP) revision demonstrating how and when the region will attain compliance with the ozone standard. The Texas Environmental Research Consortium (TERC) and the DFW roadmap committee have been assisting the TCEQ by improving the tools and data available for SIP development.

Several cement kilns are located in Ellis County just to the south of the DFW urban area and within the DFW 8-hour ozone nonattainment area. The ozone impacts of NOx emissions from cement kilns in Ellis County must be accurately accounted for in SIP ozone modeling and control strategy development. Continuous emissions monitor (CEM) data from some Ellis County kilns show that NOx emission rates are highly variable over time scales as short as hourly. This variability is much larger, in relative terms, than for other comparable size sources (such as electrical utility boilers) due to the nature of the cement making process. Due to the non-linear relationships between ozone and NOx, and the close proximity of the kilns to the DFW area, it is unclear that the worst-case scenario for ozone is simply the maximum NOx emission rate all kilns.

The most technically defensible and cost-effective emissions control approaches for cement kilns are not clear. Updated modeling approaches are required to quantify the ozone impacts of cement kiln emissions under a range of emission scenarios.

ENVIRON analyzed CEM data from the Ellis County cement kilns and performed photochemical modeling analyses designed to evaluate the impact of variability in cement kiln NO_x emissions on ozone formation and resulting implications for the development of control strategies for the DFW area.

2. ANALYSIS OF CEMENT KILN CEM DATA

Hourly continuous emissions monitoring (CEM) data from the Holcim, Ash Grove, and TXI cement kilns were obtained from TCEQ. Statistical summaries of the data were prepared for both the raw data and for a subset of the raw data ("trimmed" data) in which we excluded all hours with zero emissions and the three hours prior to and three hours after the occurrence of either a zero reading or a missing value. Results from analyses of the Holcim and Ash Grove data are presented in **Table 2-1**. Examination of the time series and normal quantile-quantile ("qqnorm") plots (see Appendix A) shows that applying this filter to the data eliminates many but not all of the low readings which, presumably, are associated with the start up or shut down process. We tried various sizes of time windows centered on the zero or missing values and found that nearly all of the very low readings were filtered out by the +/- 3 hour window - the remaining ones don't appear to be associated with zeros or missings and are not filtered out even after going to a +/- 6 hour window. Based on these results, we decided to develop emission levels for the CAMx model sensitivity runs based on the "trimmed" summary statistics developed using the +/- 3 hour window.

These graphical results show that even the trimmed data are not normally distributed (normally distributed data would show up as a straight line on the qqnorm plots) due to extended tails of the distribution at both the low and high ends. There also appear to be high outliers in some cases, most significantly at Holcim Kiln #2. Working with log transformed data doesn't help much due to the presence of very small values. Despite this, it is perfectly acceptable to pick out representative high and low values for purposes of the CAMx sensitivity runs from among the calculated summary statistics.

One very interesting aspect of these results is that the coefficient of variation (COV = standard deviation / mean) in all cases lies between about 21% and 33% with most values very close to 30%. This suggests the possibility of simply assuming that all kilns operate with a COV of 30% and then performing the CAMx sensitivity modeling for all with emissions set at ± 1.645 times the starndard deviation. This will produce values very close to the 5th and 95th percentiles for all kilns.

Table 2-1. Summary statistics of hourly NO_x emissions (lb/hr).

AshGrove 2000		minNOx	meanNOx	maxNOx	stdevNOx	No.NonMiss	No.All	5%	10%	50%	90%	95%	COV
Kiln 1	raw	0	233.5629	1000	69.76821	5857	5880	128.04	157.36	227.9	317.74	351.82	0.30
	trimmed	0.2	235.849	1000	66.83998	5767	5767	134.3	161.8	229	318.34	352.2	0.28
Kiln 2	raw	0	222.6073	749.9	84.09018	5857	5880	101.18	143.66	216.1	320.84	364.04	0.38
	trimmed	0.3	230.4369	749.9	75.20648	5561	5561	134.1	155.2	218.8	323.1	367.3	0.33
Kiln 3	raw	0	217.0192	621.7	78.79432	5858	5880	0	132.2	229.5	286.26	316.3	0.36
	trimmed	0.1	235.5408	621.7	49.42693	5296	5296	161.9	186.4	233	289.8	319.625	0.21
AshGrove 2001		minNOx	meanNOx	maxNOx	stdevNOx	No.NonMiss	No.All	5%	10%	50%	90%	95%	COV
Kiln 1	raw	0	199.7853	613.9	97.70559	862400%	876100%	0%	0%	20580%	30717%	347.3	0.49
	trimmed	0.2	225.2017	613.9	71.2359	7545	7545	130.22	151.14	215.8	313.8	354.5	0.32
Kiln 2	raw	0	225.836	604	85.35737	8620	8761	87.685	136.39	226	326.9	361.905	0.38
	trimmed	0.1	236.3948	604	72.12419	8092	8092	132.355	152.51	229.8	329.19	365.735	0.31
Kiln 3	raw	0	254.6169	642	91.06754	8714	8761	111.6	159.53	253.9	361.47	402.87	0.36
	trimmed	1.4	264.8708	642	77.63895	8262	8262	152.105	175.91	257.35	364.1	404.995	0.29
AshGrove 2002		minNOx	meanNOx	maxNOx	stdevNOx	No.NonMiss	No.All	5%	10%	50%	90%	95%	COV
Kiln 1	raw	0	189.7779	591.5	80.82252	8695	8761	0	96.14	194.5	278.5	310.03	0.43
	trimmed	0.3	202.7599	591.5	66.41041	8014	8014	104.795	125.33	199	282.1	312.835	0.33
Kiln 2	raw	0	191.1961	653.1	77.51431	8686	8761	0	109.05	193.4	278.6	306.5	0.41
	trimmed	0.1	204.3998	653.1	61.72889	7947	7947	115.5	135.7	199.5	281.3	309.1	0.30
Kiln 3	raw	0	212.3057	625.8	85.64108	8676	8761	0	112.55	222.1	302.25	328.725	0.40
	trimmed	0.1	232.0668	625.8	59.69473	7730	7730	143.4	163.39	228.4	306.4	333.155	0.26

Holcim		minNOx	meanNOx	maxNOx	stdevNOx	No.NonMiss	No.All	5%	10%	50%	90%	95%	COV
Kiln 1	raw	0	625.7336	1560.085	173.7877	15585	17474	331.0468	442.0064	637.1202	824.1454	862.8268	0.28
	trimmed	59.62534	645.5995	1560.085	143.1393	14540	14540	419.3648	471.9992	646.9618	827.4145	865.0449	0.22
Kiln 2	raw	0	451.5767	2908.433	145.3846	15500	16921	216.7738	295.9416	454.4156	597.3335	641.7638	0.32
	trimmed	15.32213	459.2852	2908.433	137.5007	14532	14532	248.6126	313.6937	457.6204	599.1864	643.5874	0.30

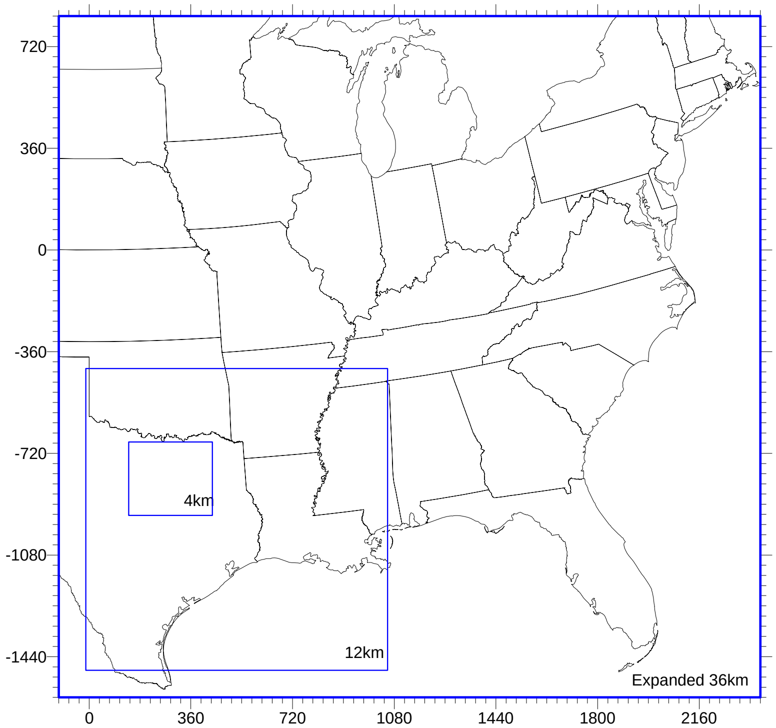
3. CAMx SENSITIVITY ANALYSIS

MODELING INPUTS

CAMx Inputs

Modeling was performed for the August 13-22, 1999 episode period of the "Run 40 FY2010" model case described by Tai et al. (2005a). This is the future year 2010 case developed from the base year Run 40. The Run 40 configuration may be summarized as follows:

- Meteorology from MM5 Run 6 using the Eta PBL scheme and Noah Land Surface Model.
- MM5 meteorology processed for CAMx using MM5CAMx with vertical diffusivity (Kv) based on MM5 turbulent kinetic energy (TKE).
- Expanded CAMx regional 36-km model domain, as shown in Figure 3-1.
- CAMx model top extended to 16 km with 20 layers and a surface layer depth of 20 m.
- Modified version of CAMx 4.03 with 17 extra inorganic reactions (Tai et al., 2005b).
- The core episode period (August 13-22, 1999) was extended to September 1, 1999, although only the core period was used in this modeling.



CAMx Grid Definitions for DFW

	nx x ny	SW to NE Corners
CAMx 36km expanded	69 x 67	(-108, -1584) to (2376, 828)
CAMx 12km	89 x 89*	(-12, -1488) to (1056, -420)
CAMx 04km	74 x 65*	(140, -940) to (436, -680)

* includes buffer cells

Figure 3-1. CAMx 36/12/4-km nested grids for the DFW expanded domain.

Emissions Inputs

The 2010 future year emissions for the core period (August 13-22) were based on the TCEQ 2010 inventory inside the standard domain, and a projected ODEQ 2002 inventory for areas outside the standard domain. Emissions for 2010 in the expanded region were estimated by scaling the ODEQ emissions to 2010 using ratios of the 2010 and 2001 base case annual average emission rates from each state and source group, as used in the draft CAIR guidelines (EPA, 2004). Scaling factors for each state and each source group – area, off-road mobile, on-road mobile, and point sources are described by Tai et al. (2005a).

Tables 3-1 and 3-2 show the 2010 future year base case NOx and VOC emissions, respectively, from four emission categories (biogenics, on-road mobile, area and off-road mobile, and point sources) and 28 source regions, as defined in Tai et al. (2005b), on Tuesday, August 17, 1999 - the date with the highest observed ozone. These tables also show the total 2010 anthropogenic emissions and the percent change from the 1999 base case anthropogenic emissions. The 2010 emissions include reductions due to EPA's Clean Air Interstate Rule (CAIR) estimated as described in Tai et al. (2005).

Table 3-1. 2010 NOx emissions by source region and emission category on August 17.

August 17, 1999 for FY2010 NOx Emissions (Tons per day)						
	Biogenics	**Mobile**	**Area + Off-road**	**Points**	**Anthro**	**% Change in anthro from 1999**
Collin Co	10	12	15	3	29	-49
Dallas Co	4	65	76	18	159	-53
Denton Co	8	15	19	3	37	-40
Tarrant Co	3	38	45	12	95	-53
Parker Co	1	5	5	2	12	-63
Johnson Co	5	4	7	4	15	-38
Ellis Co	15	7	9	45	61	5
Kaufman Co	5	5	4	7	16	-24
Rockwall Co	2	3	1	0	4	-43
DFW 9-County	**52**	**154**	**180**	**95**	**429**	**-47**
DFW 16-County	**83**	**176**	**222**	**151**	**548**	**-45**
NE Texas	16	80	128	217	425	-36
Central TX	113	64	144	197	405	-36
Houston	21	139	175	293	607	-55
South TX	229	159	213	325	697	-36
West Texas	524	130	310	187	626	-36
Gulf + Mexico	79	14	381	600	995	970
Oklahoma	227	175	244	690	1109	-22
Louisiana	106	179	962	918	2058	-19
Arkansas	125	119	303	305	727	-28
Mississippi	121	169	323	403	895	-16
Alabama	75	243	343	513	1099	-41
Tennessee	118	290	460	383	1133	-48
Kentucky	145	221	462	430	1113	-64
Georgia	110	416	300	356	1073	-54
Florida	56	746	460	310	1515	-61
Mid Atlantic States	293	1164	902	1268	3334	-51
Northeast US	314	2052	3231	1256	6539	-40
Northern Plains	5238	3064	4465	4375	11905	-43
Total	**7992**	**9601**	**14027**	**13177**	**36804**	**-43**

Table 3-2. 2010 VOC emissions by source region and emission category on August 17.

August 17, 1999 for FY2010 VOC Emissions (Tons per day)						
	Biogenics	**Mobile**	**Area + Off-road**	**Points**	**Anthro**	**% Change in anthro from 1999**
Collin Co	27	7	19	1	27	-29
Dallas Co	50	37	115	12	165	-23
Denton Co	65	8	25	2	35	-13
Tarrant Co	64	21	80	9	110	-16
Parker Co	121	2	13	1	15	-4
Johnson Co	111	2	13	0	15	9
Ellis Co	89	2	15	7	24	16
Kaufman Co	112	2	16	2	20	17
Rockwall Co	3	1	5	0	5	-8
DFW 9-County	**642**	**82**	**300**	**35**	**417**	**-16**
DFW 16-County	**1538**	**92**	**388**	**39**	**519**	**-13**
NE Texas	4917	34	210	21	265	-12
Central TX	6098	26	239	27	293	5
Houston	1683	74	281	107	462	-35
South TX	2069	75	458	24	558	-15
West Texas	6198	56	638	16	710	-4
Gulf + Mexico	658	11	339	48	398	268
Oklahoma	7940	101	302	168	570	-25
Louisiana	9941	95	381	235	712	-31
Arkansas	13925	61	364	131	556	-23
Mississippi	14818	80	381	163	623	-29
Alabama	13954	146	421	340	907	-20
Tennessee	8678	160	668	341	1169	-21
Kentucky	3753	123	420	221	764	-30
Georgia	12198	231	630	78	938	-24
Florida	9793	652	981	70	1703	-29
Mid Atlantic States	31294	951	1659	478	3088	-21
Northeast US	20472	1243	4737	186	6166	-30
Northern Plains	40144	2180	5428	1281	8890	-29
Total	**210073**	**6389**	**18926**	**3975**	**29290**	**-25**

RESULTS

Figures 3-2 to 3-5 show spatial plots of contributions to the episode max 8-hour ozone from each kiln (Holcim, Ash Grove, TXI, and the 3 combined) at 5 constant emission rates (0.538x, 0.72x, 1.00x, 1.28x, and 1.462x). The plots represent the difference from the zero-out run from the appropriate kiln(s). Key results are:

- Ash Grove showed the lowest impact.
- Holcim was in the middle, with peak contributions in the same grid cell as Ash Grove.
- TXI had the highest contributions with the peak further west (in eastern Parker Co.).

- The combination of the 3 kilns produced large contributions to the episode peak in Parker Co, and near Fort Worth, but had little impact near Frisco (too VOC limited).

We examined the 8-hr ozone impact from the kilns by tallying contributions from each grid cell hour in the 4 km modeling domain into several bins, based on the base case (zero-out) ozone level and change in ozone. Results are presented in Appendix B for both running 8-hour averages and daily maximums. Grid cells from 8 days are used (Aug 13 and 14 were excluded). This was performed for the 3 kilns individually and combined at 6 constant emission rates (0, 0.538, 0.72, 1.00, 1.28, and 1.462x mean rate), and then for 6 more runs using the combined kilns at the mean rate for 22 hours/day and then spiking the emissions by 1.462x mean rate for 2 hours per day(at 2 and 3am, 6 and 7am, 10 and 11am, 2 and 3pm, 6 and 7pm, 10 and 11pm).

Summaries of the number of grid hours >= 84 ppb and the ppb-hours >= 84 ppb (summation of max(O3 - 84, 0.0)) for each run show that:

- Ash Grove had the least impact
- Holcim generally added more grid hours >= 84 ppb than TXI, but the sum of ppb-hours was lower than TXI.
- The 3 kilns combined produced more ppb-hours >= 84 ppb than the three kilns individually.
- The 6-7am and 10-11am spikes in emissions had the greatest impact on the number of grid hours and ppb hours >= 84 ppb.
- Spikes in the evening (hr 18 and 19 and hours 22 and 23) had little impact. Actually, the spike at hours 18 and 19 made a small improvement to the stats.

Also shown in Appendix B are changes from associated zero-out runs. Each grid cell in the zero-out run is classified into 5 groups (<70ppb, 70-80, 80-84, 84-90, 90+) and each group is then tallied into 11 categories as to how the 8hr ozone contributions differed when the kiln used different emissions. These results show that:

- Ash Grove tended to reduce lower concentrations of ozone when higher rates were used.
- In the 80-84 ppb zero-out group, Ash grove needed a constant rate of 1.462x to have a contribution > 3 ppb.
- TXI had low-O3 reductions, but not as much as Ash Grove. TXI contributed at least 3 ppb to 71 grid cells when the zero-out run was between 80 and 84 ppb , when using the running 8-hr averages (In comparison, Ash Grove had only 2).
- Holcim was in between, but closer to TXI.
- The combination of all 3 resulted in a lot more grid cells in the 80-84 ppb range with high contributions, even at low emission rates.

Similar tables were generated showing the difference in grid-hours from the mean (1.00x) to show the impacts from the spikes:

- Like the grid-hours sheet showed, the 6-7am and 10-11am spike in emissions yielded more higher ozone contributions.

- The hour 14-15 spike raised lower-level ozone, but the number of higher contributions at high concentrations dropped sharply compared to the 10-11am spike.
- The hour 18-19 and 22-23 spikes had a lot more grid cells showing a reduction in ozone in the <70 ppb group, and had little impact on high ozone concentrations.

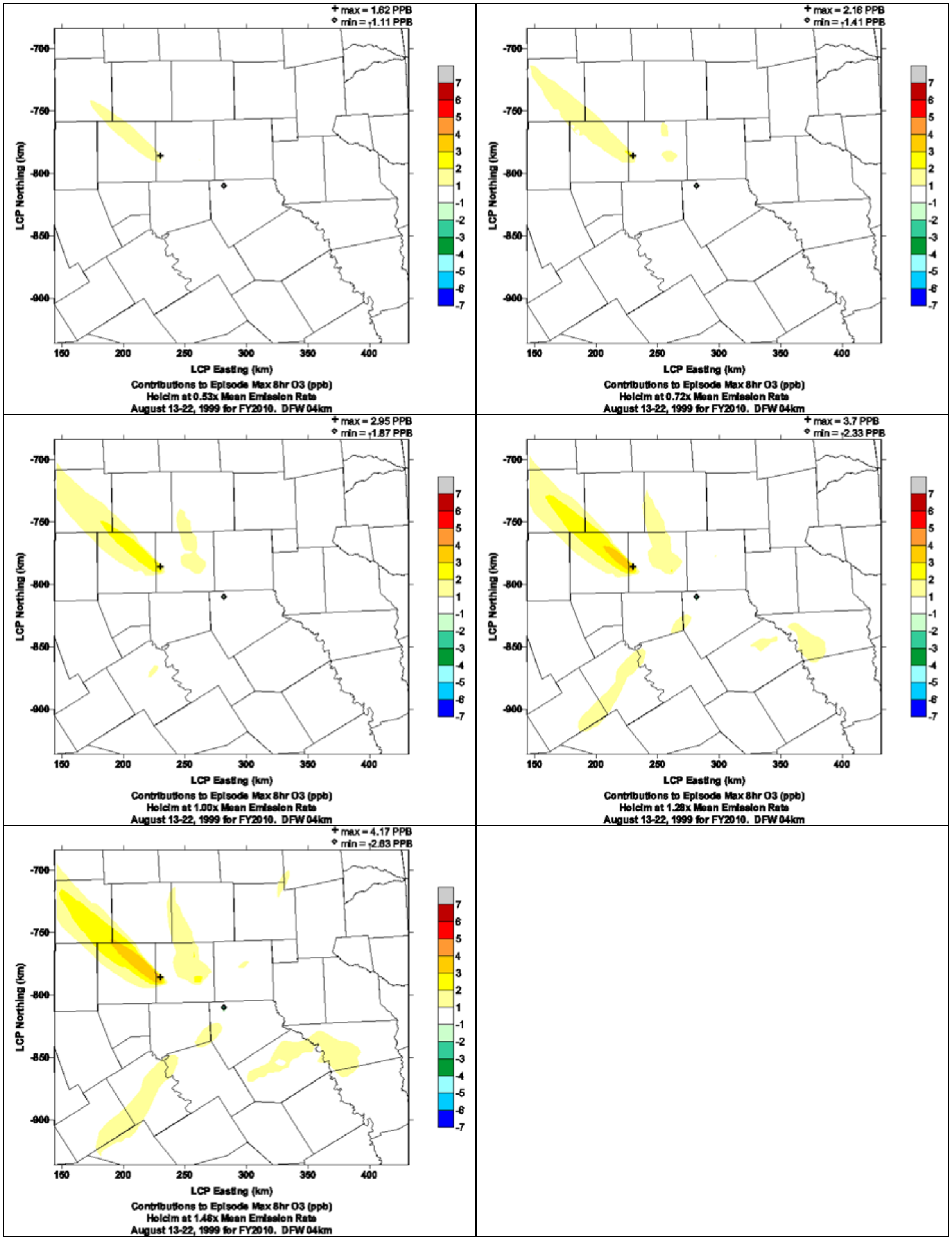


Figure 3-2. Contributions to episode maximum 8-hour ozone concentrations from the Holcim facility relative to the zero emissions run.

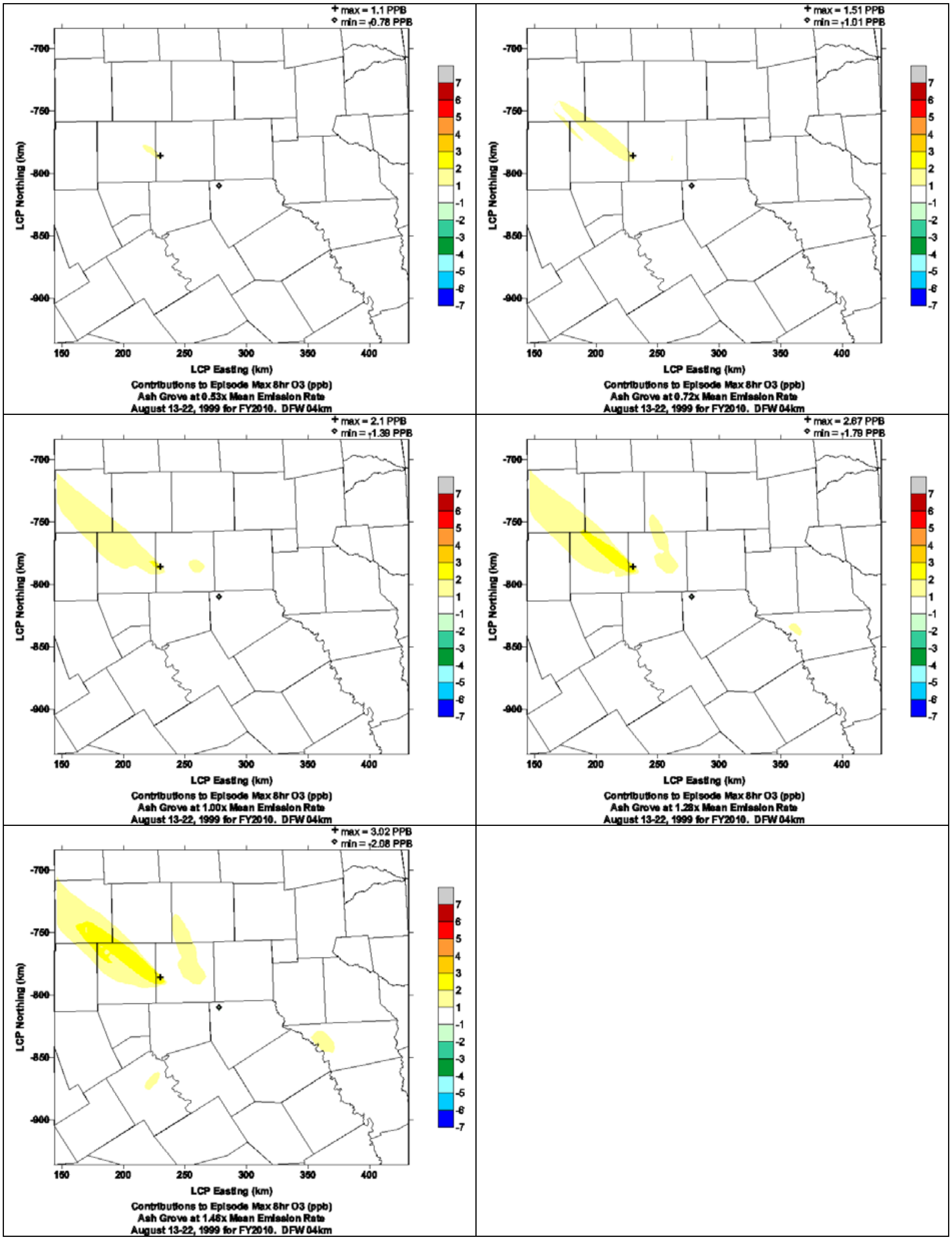


Figure 3-3. Contributions to episode maximum 8-hour ozone concentrations from the Ash Grove facility relative to the zero emissions run.

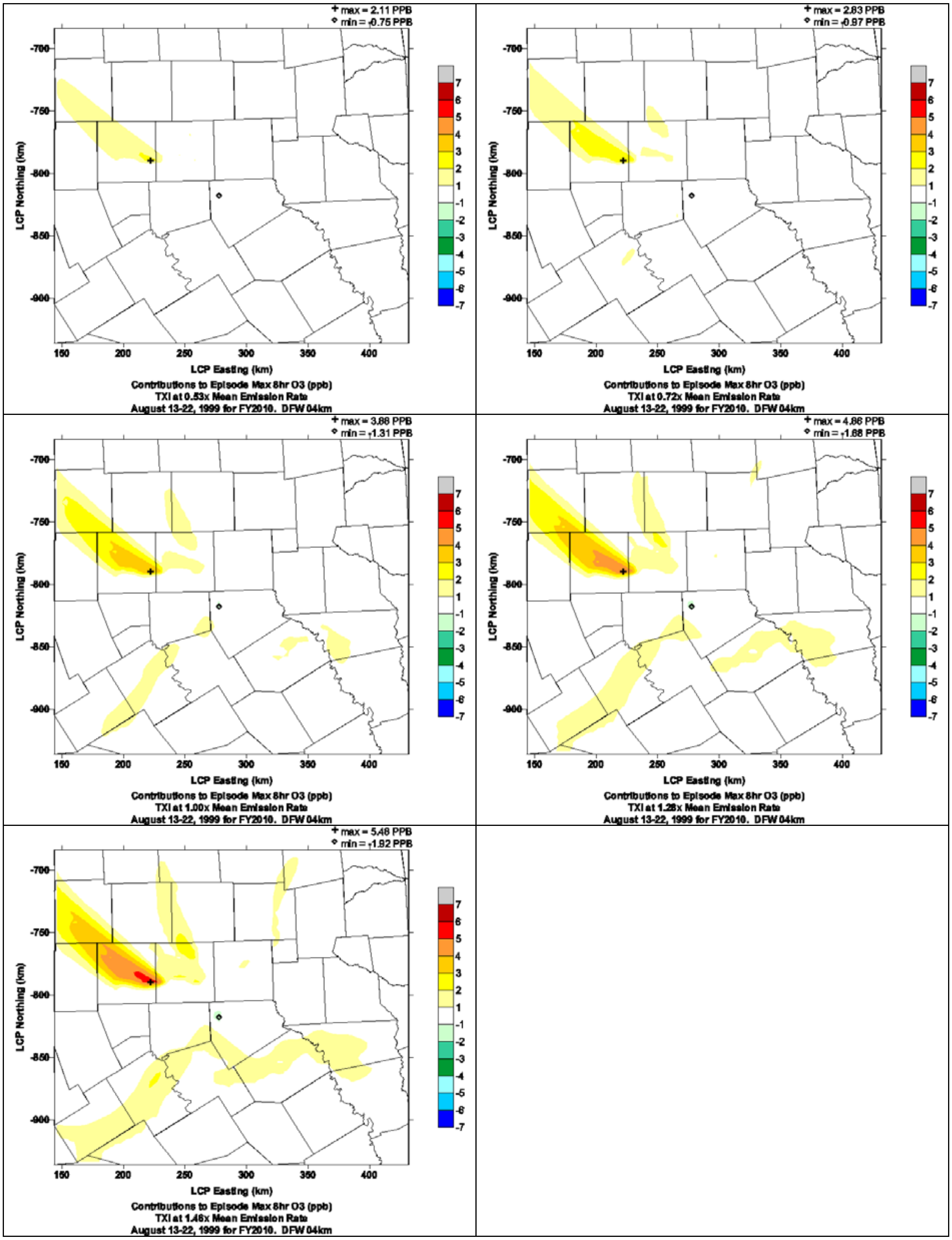


Figure 3-4. Contributions to episode maximum 8-hour ozone concentrations from the TXI facility relative to the zero emissions run.

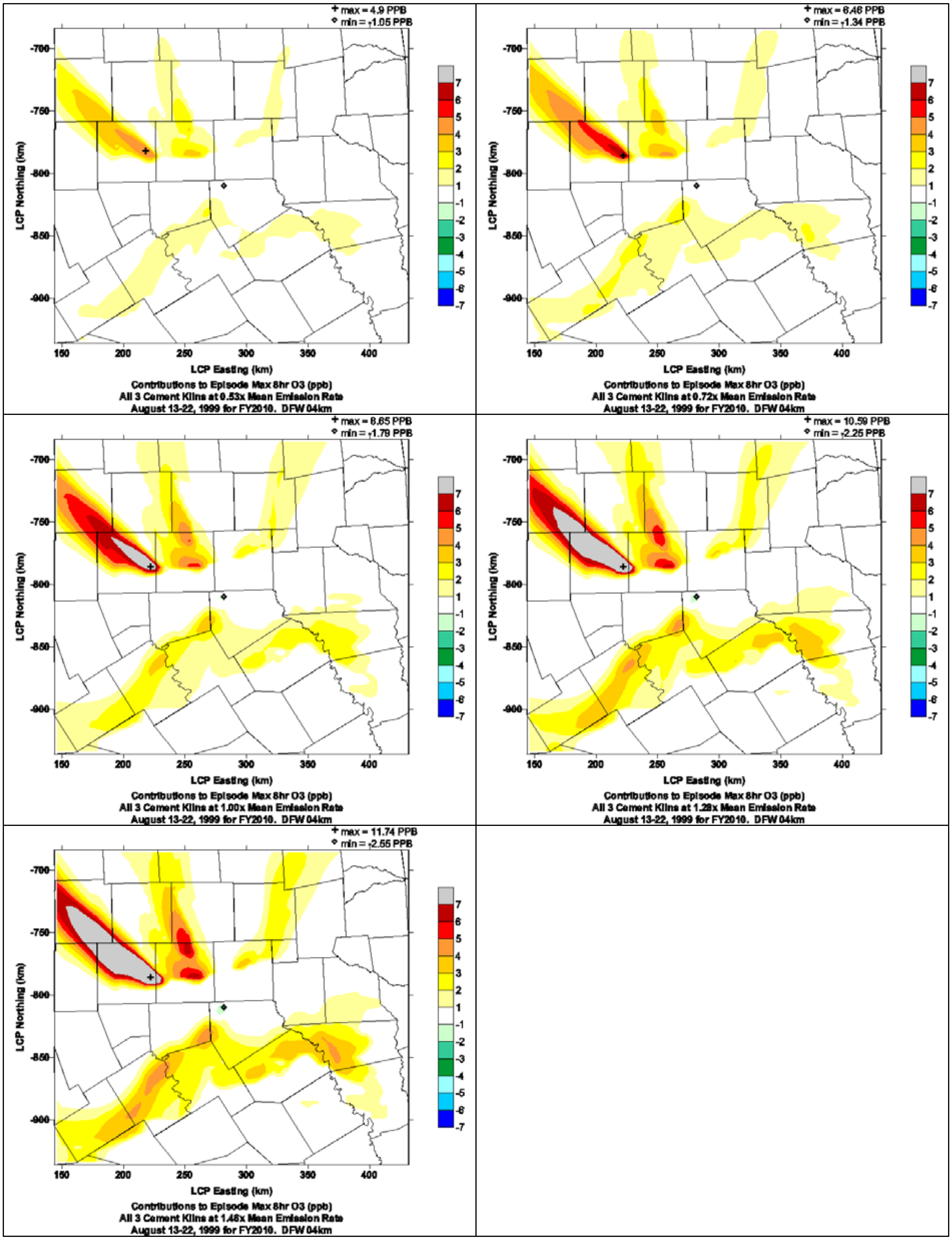


Figure 3-5. Contributions to episode maximum 8-hour ozone concentrations from all three cement plants relative to the zero emissions run.

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