Response to Anonymous Referee #2

General Comments:

In this paper, Carter's method and local data of Guangzhou were applied to construct new MIR, MOR and EBIR scenarios under observation and emission methods through a box model equipped with MCMv3.3.1 mechanism. At the same time, the MIR-characteristics of VOCs are described and analyzed. The application of recent research results to achieve migration is meaningful and has universality in application. At the same time, the research needs to carry out data processing for each VOC, and the workload is heavy, which is worthy of recognition. After review, it is considered that the article still needs to address the following concerns:

Response: we thank the reviewer for the positive comments and constructive suggestions, which are much helpful for improving the original manuscript. We have carefully considered all of these comments and revised the manuscript accordingly. Below we provide the original reviewer's comments in black italic, with our response and changes in the manuscript in blue and red, respectively.

Specific Comments:

1. For the box model, the observation based method adopted by the author to constrain the concentration of both NO_2 and NO at the same time, which made the O_3 concentration largely fixed by the ratio of NO_2/NO. In this case, could the impact of VOCs on O_3 be reasonably reflected?

Response: thanks for the helpful comment. For the present modelling, at the beginning of each integration step (1 h), the NO and NO_2 inputs into the model were determined by observational data with observation-based inputs, but their evolution over time was determined by the chemistry that was affected by the VOC-involved reactions. For charity, we have added the following descriptions in the revised manuscript.

"While the NO and NO_2 inputs into the model were determined by observational data with observation-based inputs, their evolution over time was determined by the chemistry that was affected by the VOC-involved reactions"

2. The running step of the box model is 1h, is it too sparse for the total integral period of 10h? In the paper, it may be necessary to include the graphs or tables of O_3 concentration changes in the two observation-based and emission models within 10 hours.

Response: we have calculated the RRs with running step of 10 min for comparison. With observation-based inputs, the CO, SO_2, NO, NO_2, HONO, and VOCs concentrations were averaged or interpolated into a 10-min time resolution to constrain the model. With emission-based inputs, the emission rates (unit: molecules cm^{-3} s^{-1}) of NO, NO_2, VOCs (116 compounds), SO_2, and CO were read in with a time resolution with 10 min. Besides, meteorological parameters, including temperature, RH, and pressure were averaged or interpolated into a 10-min time resolution to constrain the model with both inputs.

As Figure R1 shows, the RRs obtained from 10-min inputs exhibited good correlations with those obtained from 1-h inputs (R^2: 0.98-1.00). The discrepancy in RRs magnitudes existed but was relatively small, especially for emission-based inputs (RMA slope: 1.02 under MIR scenarios and 1.03 under MOR scenarios). Considering the heavy computation burden introduced by 10-min integration step, step of 1-h is a good choice for RR calculations.

The graphs of O_3 concentration with 1-h observation-based and emission-based inputs have been included below as well as in the revised SI (Figure S3).

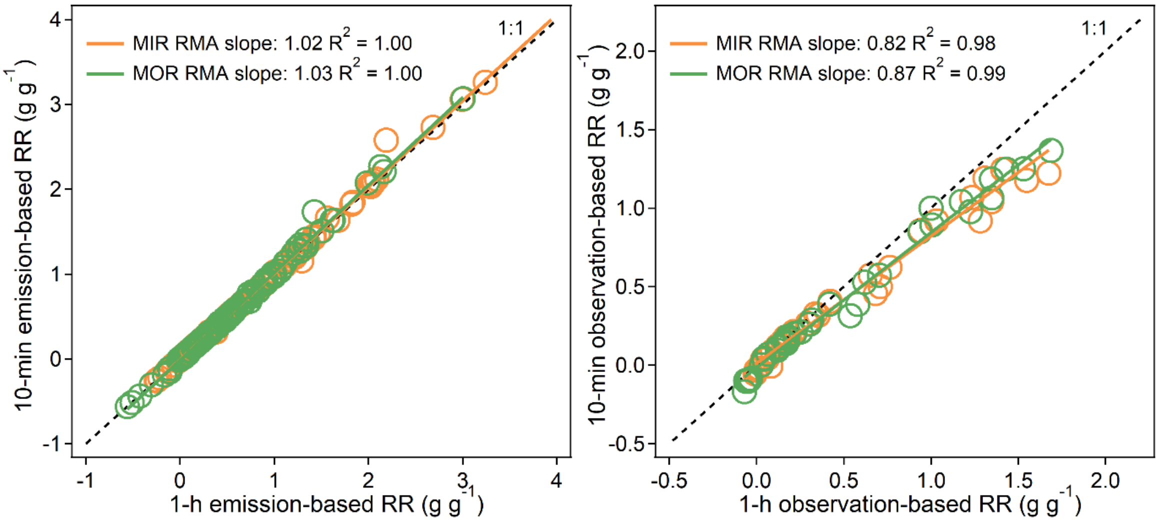


Figure R1. Comparison of RRs for VOCs obtained from 1-h and 10-min inputs. The left panel is for emission-based inputs, and the right panel is for observation-based inputs. The RMA represents reduced major axis. The black dashed line represents the 1:1 line.

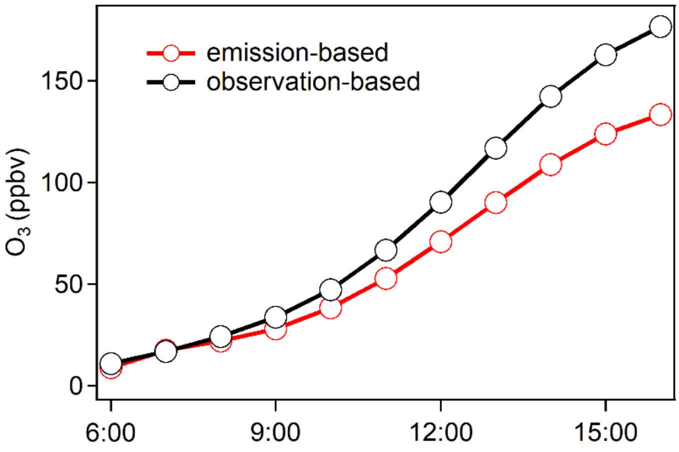


Figure S3. The model-simulated O_3 concentrations with emission-based and observation-based inputs during the 10-h integral period.

3. The MIR table of VOCs species is suggested to refer to the article published by Carter in 2007, which is arranged in the order of commonly used alkanes, olefins and aromatic hydrocarbons.

Response: thanks for the suggestion. We have re-arranged the order of VOC species in IR table as follows.

Revised Table 1. Tabulation of IR (g O_3/g VOC) for VOCs under three specified NOx conditions and base NOx conditions. “EMI” represents emission–based inputs, while “OBS” represents observation–based inputs.

Species	MIR		MOR		EBIR		Base IR	
	EMI	OBS	EMI	OBS	EMI	OBS	EMI	OBS
ethane	0.14	0.19	0.11	0.16	0.08	0.09	0.14	0.19
propane	0.25	0.25	0.15	0.17	0.08	0.07	0.25	0.25
n-butane	0.75	0.83	0.54	0.63	0.35	0.33	0.76	0.83
i-butane	0.83	0.91	0.55	0.71	0.37	0.40	0.85	0.92
n-pentane	0.87	0.94	0.56	0.66	0.30	0.29	0.89	0.93
i-pentane	0.91	0.93	0.64	0.71	0.44	0.38	0.93	0.93
n-hexane	0.62	0.75	0.40	0.48	0.20	0.17	0.62	0.73
2,2-dimethyl butane	0.74	0.67	0.46	0.48	0.27	0.23	0.75	0.67
2,3-dimethyl butane	0.81	0.75	0.54	0.51	0.37	0.26	0.82	0.73
2-methyl pentane	1.12	1.04	0.65	0.67	0.35	0.29	1.13	0.99
3-methyl pentane	1.19	1.18	0.81	0.88	0.52	0.46	1.21	1.18
cyclohexane	1.29	-	0.81	-	0.66	-	1.27	-
n-heptane	0.28	0.34	0.17	0.11	0.03	-0.08	0.28	0.30
n-octane	0.07	-0.0001	-0.03	-0.25	-0.16	-0.35	0.06	-0.07
n-nonane	0.01	-0.02	0.02	-0.23	-0.06	-0.30	0.0003	-0.09
n-decane	0.02	0.06	0.10	-0.14	0.04	-0.22	0.01	-0.003
n-undecane	-0.03	-0.003	0.11	-0.20	0.07	-0.26	-0.04	-0.07
n-dodecane	-0.10	-0.04	0.09	-0.27	0.10	-0.33	-0.12	-0.12
2-methyl hexane	0.73	-	0.52	-	0.32	-	0.74	-
3-methyl hexane	1.06	1.04	0.75	0.69	0.47	0.31	1.07	1.00
ethene	4.71	5.54	2.43	3.98	1.44	2.16	4.75	5.42
propene	6.68	6.83	3.09	4.67	1.78	2.69	6.66	6.66
1-butene	4.77	3.77	1.37	2.14	0.03	0.77	4.68	3.49
i-butene	4.75	-	1.88	-	1.03	-	4.69	-
cis-2-butene	12.64	8.58	4.83	6.09	2.48	3.49	12.52	8.41
trans-2-butene	14.11	9.27	5.17	6.71	2.52	3.87	13.97	9.42
1,3-butadiene	4.73	-	2.12	-	1.36	-	4.66	-
1-pentene	6.18	3.93	2.22	2.31	0.82	1.02	6.09	3.68
3-methyl-1-butene	6.93	-	2.71	-	1.46	-	6.85	-
2-methyl-1-butene	6.08	-	2.38	-	1.24	-	6.02	-
2-methyl-2-butene	10.31	-	3.46	-	1.53	-	10.16	-
cis-2-pentene	9.69	-	3.10	-	0.97	-	9.54	-
trans-2-pentene	9.45	-	3.01	-	0.93	-	9.31	-

isoprene	7.89	7.09	3.26	4.88	1.78	2.51	7.82	6.87
1-hexene	5.69	-	2.44	-	1.37	-	5.61	-
cis-2-hexene	9.83	-	3.25	-	1.20	-	9.68	-
trans-2-hexene	5.44	-	1.77	-	0.66	-	5.36	-
β-pinene	2.46	-	1.08	-	0.84	-	2.37	-
limonene	7.36	-	2.91	-	1.87	-	7.18	-
benzene	0.38	0.49	0.08	0.27	-0.06	0.02	0.38	0.46
toluene	2.12	2.33	0.96	1.67	0.41	0.84	2.14	2.3
ethyl benzene	2.02	1.95	0.72	1.21	0.09	0.48	2.02	1.87
m-xylene	6.41	5.72	2.63	4.00	1.27	2.38	6.38	5.47
o-xylene	5.41	5.20	2.31	3.72	1.11	2.14	5.41	5.06
p-xylene	4.17	-	1.82	-	0.87	-	4.17	-
styrene	1.45	0.46	-0.04	-0.17	-0.43	-0.48	1.41	0.30
n-propyl benzene	1.79	1.61	0.71	1.01	0.21	0.42	1.79	1.56
i-propyl benzene	2.41	1.87	1.09	1.26	0.5	0.62	2.43	1.82
m-ethyl toluene	5.83	4.23	2.15	2.80	0.70	1.47	5.8	3.98
o-ethyl toluene	4.47	3.61	1.69	2.46	0.48	1.26	4.46	3.49
p-ethyl toluene	3.87	-	1.43	-	0.36	-	3.87	-
1,2,3-trimethyl benzene	8.57	7.25	3.65	5.35	1.91	3.24	8.54	7.20
1,2,4-trimethyl benzene	9.54	7.81	3.95	5.69	2.07	3.43	9.48	7.69
1,3,5-trimethyl benzene	9.64	7.47	3.91	5.36	2.10	3.29	9.54	7.26
1,3-dimethyl-5-ethyl benzene	8.64	-	3.22	-	1.42	-	8.55	-
formaldehyde	6.71	-	2.21	-	0.97	-	6.61	-
methanol	0.38	-	0.23	-	0.14	-	0.39	-
formic acid	0.06	-	0.05	-	0.04	-	0.06	-
ethylene oxide	0.04	-	0.03	-	0.03	-	0.04	-
acetaldehyde	4.10	-	1.88	-	1.15	-	4.06	-
ethanol	0.66	-	0.45	-	0.29	-	0.67	-
dimethyl ether	0.57	-	0.47	-	0.38	-	0.58	-
glyoxal	3.11	-	1.02	-	0.42	-	3.06	-
acetic acid	0.35	-	0.24	-	0.17	-	0.35	-
acrolein	3.01	-	1.31	-	0.84	-	2.97	-
propionaldehyde	2.60	-	0.21	-	-0.55	-	2.49	-
acetone	0.22	-	0.10	-	0.05	-	0.22	-
i-propyl alcohol	0.49	-	0.33	-	0.23	-	0.50	-
n-propyl alcohol	1.86	-	0.85	-	0.29	-	1.87	-
methyl glyoxal	15.27	-	5.25	-	2.31	-	15.1	-
methyl acetate	0.18	-	0.12	-	0.08	-	0.19	-
propylene glycol	2.45	-	1.28	-	0.74	-	2.48	-
dimethoxy methane	0.41	-	0.33	-	0.25	-	0.42	-
crotonaldehyde	3.97	-	1.85	-	1.19	-	3.92	-
methacrolein	5.23	-	2.21	-	1.28	-	5.17	-
2-methyl propanal	6.29	-	2.14	-	1.11	-	6.16	-
butanal	4.54	-	1.38	-	0.33	-	4.43	-
methyl ethyl ketone	1.18	-	0.51	-	0.27	-	1.17	-
i-butyl alcohol	2.28	-	1.18	-	0.74	-	2.29	-
n-butyl alcohol	1.27	-	0.57	-	0.19	-	1.27	-
sec-butyl alcohol	1.40		0.90	-	0.60	-	1.43	-
diethyl ether	2.42	-	1.36	-	0.92	-	2.43	-

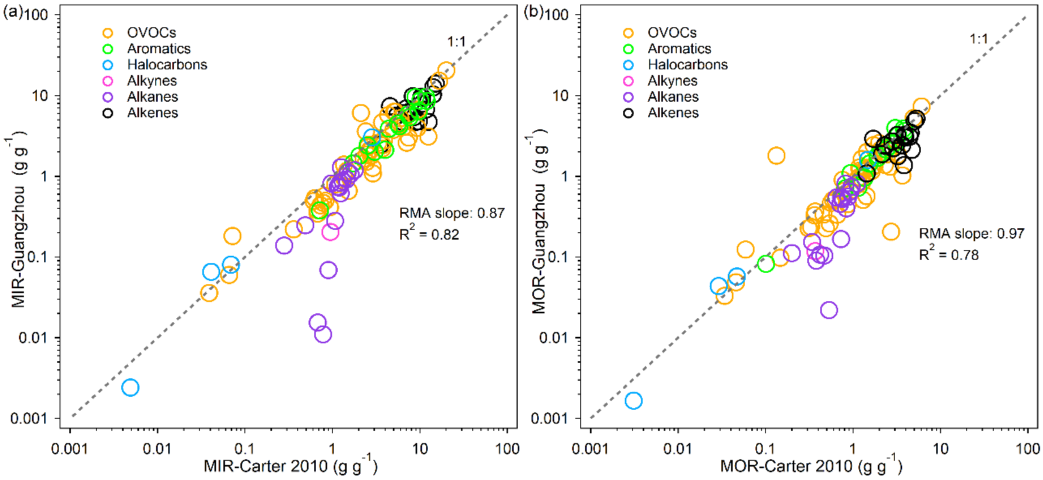
biacetyl	20.42	-	7.30	-	3.42	-	20.25	-
ethyl acetate	0.54	-	0.37	-	0.24	-	0.55	-
1-methoxy-2-propanol	1.51	-	0.95	-	0.66	-	1.53	-
2-ethoxy-ethanol	2.20	-	1.16	-	0.79	-	2.19	-
diethylene glycol	2.6	-	1.22	-	0.69	-	2.61	-
3-methylbutanal	3.75	-	1.67	-	1.09	-	3.70	-
pentanal	6.27	-	2.57	-	1.49	-	6.15	-
methyl tert-butyl ether	0.44	-	0.33	-	0.24	-	0.45	-
i-propyl acetate	0.80	-	0.51	-	0.34	-	0.81	-
propyl acetate	0.47	-	0.23	-	0.07	-	0.47	-
phenol	1.80	-	-0.26	-	-1.37	-	1.82	-
2-hexanone	2.71	-	1.05	-	0.41	-	2.67	-
cyclohexanone	0.97	-	0.66	-	0.52	-	0.97	-
hexanal	5.72	-	2.42	-	1.53	-	5.61	-
4-methyl-2-pentanone	2.78	-	1.32	-	0.78	-	2.77	-
4-methyl-2-pentanol	2.03	-	1.27	-	0.83	-	2.07	-
hexanol	2.13	-	1.17	-	0.77	-	2.12	-
n-butyl acetate	0.50	-	0.26	-	0.1	-	0.50	-
2-butoxy-ethanol	1.08	-	0.51	-	0.25	-	1.07	-
benzaldehyde	-1.02	-	-1.04	-	-1.17	-	-1.04	-
acetophenone	0.35	-	-0.27	-	-0.56	-	0.33	-
benzyl alcohol	-0.33	-	-0.74	-	-0.97	-	-0.36	-
2-Methylbenzaldehyde	-1.19	-	-1.36	-	-1.65	-	-1.22	-
3-Methylbenzaldehyde	-1.16	-	-1.24	-	-1.50	-	-1.18	-
4-methylbenzaldehyde	-0.65	-	-0.41	-	-0.51	-	-0.66	-
heptanal	4.63	-	2.01	-	1.28	-	4.54	-
5-methyl-2-hexanone	3.60	-	1.64	-	1.03	-	3.56	-
2,3-dimethyl phenol	6.08	-	1.80	-	0.19	-	6.05	-
3-octanol	1.65	-	0.97	-	0.62	-	1.66	-
dichloromethane	0.07	-	0.04	-	0.03	-	0.07	-
acetylene	0.20	0.22	0.12	0.17	0.07	0.09	0.21	0.22
vinyl chloride	3.03	-	1.60	-	0.94	-	3.06	-
1,1-dichloroethane	0.08	-	0.06	-	0.04	-	0.08	-
1,1,1-trichloroethane	0.002	-	0.002	-	0.001	-	0.002	-

4. Fig. 5a is one of the most important conclusions of the whole paper, which is used to compare the MIR-values of the article and the MIR-values in the literature. Compared with the logarithmic axis, the comparison results of the conventional axis are more convincing. At the same time, scatter plots similar to the size order in Fig. 5b should be reduced, because the deviation of MIR order in a considerable number of VOCs species is large, and R^2 is of little significance. This paper needs to further prove the validity of the calculated MIR in Guangzhou, so it can be used to replace the MIR from US (mainly Carter’s publication) for Guangzhou.

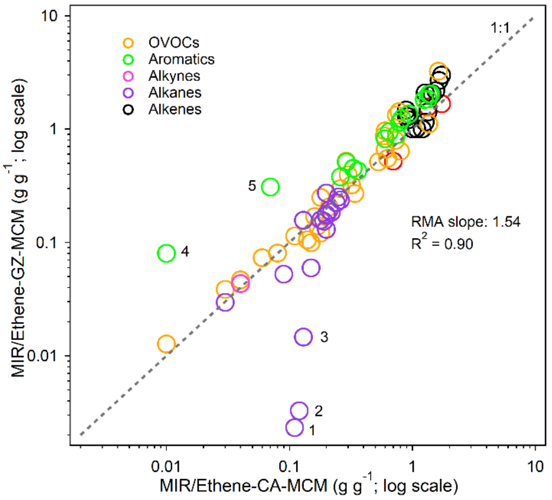
Response: thanks for the suggestion, but the logarithmic scale may actually be more useful for displaying differences in reactivity results, so the readers can see the data reasonably well at any magnitude range. In addition, the results of ranks have been removed in the revised

Figures 5 and 6.

We adopted and improved Carter's method for MCMv3.3.1 to calculate IRs under MIR, MOR and EBIR scenarios in Guangzhou, and the IR-Guangzhou were compared with those provided in Carter (2007). A nonnegligible discrepancy was found between IR-Guangzhou and IR-Carter, and our results revealed the significant impact of environmental conditions on IR/RR magnitudes. Rough application of U.S.'s IR scales in China may ambiguously identify the reactivity of VOCs, especially those relied heavily on chemical conditions such as styrene and long-chain alkanes. Besides, the discrepancy in IR magnitudes would introduce uncertainty to the OFP quantification. Take the above factors into account, it would be better to use localized IRs to provide scientific support for VOCs control in Guangzhou.



Revised Figure 5. Comparison of emission-based (a) MIR and (b) MOR scales for 111 common VOC species between Guangzhou and the U.S. The panels are in log scale, and only positively reactive VOCs are shown. The grey dashed line represents the 1:1 line. The MIR-Carter 2010 and MOR-Carter 2010 data are taken from Carter et al. (2010).



1: *n*-nonane 2: *n*-decane 3: *n*-octane 4: benzene 5: styrene

Revised Figure 6: Comparison of the MIR/Ethene (the MIR value of a given VOC divided by the MIR value of ethene) values for 79 common VOC species between Guangzhou and California. Only positively reactive VOCs are shown, and the top five VOC species with a relatively large reactivity value change (shown below the panel) are marked with numbers. The grey dashed line represents the 1:1 line. The MIR-Ethene-CA-MCM data are taken from Derwent et al. (2010).

5. In Table 2a, why change the simulation time to 3 days? 10 h can describe the period of time during which VOCs receive light and undergo photolysis reaction cycle in real day, and the situation of 3 days lacks practical significance.

Response: the 3-day simulation was used to characterize a regional scenario which extended the IR evaluation from urban scale to regional scale, as the O_3 pollution is a regional environmental problem and the relative importance of VOCs and NOx as well as of different VOC species to O_3 formation may be different between urban and regional scales.

For clarity, the following modifications have been made in the revised manuscript.

"A regional scenario (the model integration time lasted for 3 days, whereas the other factors were kept unchanged; indicated as "3 days" in Table 2) was designed to evaluate the relative importance of VOCs and NOx as well as of different VOC species to O_3 formation in regional scales."

However, for the MIR scenario and MOR scenario, there were differences in RMA slope changes in the 3-day simulation, and some R^2 were too small. It needs to be clarified.

Response: Because NOx is consumed and removed rapidly, the NOx emissions rather than VOC emissions from upwind urban sources would play more important roles in O_3 concentrations over large regional scales. This is confirmed by the overall lower MIRs and MORs in the 3-day scenarios than in the 10-hour scenarios. The NOx conditions under MIR scenarios are higher than under MOR scenarios, therefore, the MORs dropped much faster than MIRs in 3-day scenarios.

The reactive compounds (such as alkenes) typically react near its source and contribute to the photochemical production of O_3 in the area in which it is emitted, but the fast consumption made their IRs show large downward trends in 3-day regional scenarios. In contrast, the unreactive compounds (such as alkanes) have a longer residence time in the atmosphere, and they would build up and undergo extensive photochemical reactions in 3-day regional scenarios. Besides, the unreactive compounds and their oxidation products would indirectly impact the IRs of other compounds by exerting effects on radical recycling. Taken together, the unreactive compounds played relatively more important roles in 3-day regional scenarios and their IRs showed slowly downward or even upward trends compared to those calculated based on 10-hour scenarios. The opposite trends explained why R^2 were relatively small for alkanes and alkenes between 3-day and 10-hour scenarios. This also explained the poor correlations in IRs for aldehydes between 3-day and 10-hour scenarios, as aldehydes' IRs showed a wide distribution and showed varying sensitivity to the changes of NOx availability.

For clarity, the following modifications have been made in the revised manuscript.

"The overall MIR and MOR values for the 116 VOCs changed by -5 % ($p = 0.07$) and -61 % ($p < 0.01$), respectively, implying that the NOx emissions rather than VOC emissions from upwind urban sources would play more important roles in O_3 concentrations over large regional scales. The NOx conditions under MIR scenarios are higher than under MOR scenarios, therefore, the MORs dropped much faster than MIRs in 3-day regional scenarios."

"Along the 3-day scale, the reactive VOC groups (such as alkenes) with a short lifetime were rapidly consumed in urban scales, but their IRs showed fast downward trends in 3-day regional scales (e.g., the median rank of alkenes dropped by -11 and -27 under the MIR and MOR scenarios, respectively). In contrast, the role of unreactive VOC groups became more important, which would build up and undergo extensive photochemical reactions along the 3-day scale (Stockwell et al., 2001). Besides, the unreactive VOC groups (such as alkanes) and their oxidation products would indirectly impact the IRs of other compounds by exerting effects on radical recycling. Taken together, the IRs for unreactive VOC groups showed slowly downward or even upward trends in 3-day scenarios than 10-hour scenarios. The opposite trends explained why R^2 were relatively small for some VOC groups between 3-day and 10-hour scenarios."