Responses to referee #1:

Measurements of NOx and VOCs were made in a very polluted region between two mega cities, Beijing and Tianjin. Ozone sensitivity to NOx and VOC changes was calculated with a box model, constrained by observations. Photochemistry reminds me of what was found in Houston, Texas in several field campaigns starting in 2000. Ozone levels were extremely high: "Highest 1-hour ozone was nearly 200 ppb." VOC to NOx ratios were very high with the consequence that "Ozone production is typically limited by NOx under current precursor conditions." This is supported by the data but is it very unusual that ozone production is NOx limited under such highly polluted conditions.

I would like to see better documentation of modeling methods and results. Questions about the calculations are given below. More important are the results contained in Fig. 16 of Chameides et al (1992). That graph shows that conditions from this field campaign (200 ppbc Propy-Equiv and 20 ppbv NOx) give rise to an ozone production rate greater than 100 ppb per hour. Clearly that rate can't be sustained for a long time period without ozone concentrations becoming much larger than indicated in Fig. 7 or in the observations. Measurements are evidently dominated by fresh emissions as indicated by very high concentrations of short lived butenes. If this were Houston, the mix of high NOx and extremely high VOC reactivity would be caused by emissions of light olefins from petrochemical facilities. Here the mixture of VOCs is different. I don't know enough about differences in emissions sources in China and the US to comment.

The authors have made measurements under interesting conditions. I'm not familiar with most of the work done around Beijing so I can't say that conditions were unique. Hundreds of scientists participated in the Houston studies. This is a much smaller effort and it would be unfair to expect results that are anywhere near as comprehensive.

I believe this article should be published with some significant modifications. Some are listed below. The list contains a mix of items that are important and some simple typos. What I would really like to see is an appraisal of how these measurements fit into a broader context – and what to make of the extremely high ozone production rates suggested by Chamedies et al. Perhaps the answer is simple and has to do with how the box model calculations in this paper are carried out. Then the question becomes whether methods are appropriate and what are calculations really saying.

We appreciate the referee for valuable comments and instructive suggestions.

The 2009 HaChi (Haze in China) project was conducted to handle air quality issues involving aerosol and ozone pollution in the North China Plain (NCP). Although many extensive field campaigns have been carried out in areas like Houston, Texas with combined efforts of institutions and universities, the field study between two megacities in the polluted NCP was conducted for the first time here in China. As a starting point, the HaChi project has provided us with important information regarding atmospheric

photochemistry in this region. Undoubtedly, future efforts could be expected to reach more thorough and comprehensive understanding.

High ozone episodes were frequently encountered during the observational period. Typical NOx-limitation has been confirmed by analyzing ambient NOx and VOCs data, as well as model simulations. It is interesting to find that ozone photochemical production is NOx-sensitive in the polluted NCP, also mentioned by the referee. As far as our information goes, the high concentrations of reactive VOCs should be responsible for the NOx-sensitive chemical regime.

Following the referee's suggestions listed below, we have revised the manuscript accordingly to give a more elaborate interpretation of the modeling work. Particularly, the referee mentioned that a net ozone production rate of more than 100 ppbv per hour should be reached in our case following Fig. 16 in Chameides et al. (1992). However, neither the observations of ozone nor the modeling results in our study have shown any support in such high net ozone production rates. At first sight, the discrepancy in the two studies seems to be confusing. Then, we noticed that model settings of the two studies were quite different. The equivalent propene concentrations were used to calculate the net ozone production rates in Chameides et al. (1992), while model inputs were constrained by measurements of speciated VOCs in our sensitivity study. As a matter of fact, the respective chemical pathways and oxidation products after initial OH-oxidation differ greatly among various species (Atkinson, 2000). Therefore, the use of equivalent propene concentrations or speciated VOCs alone could give rise to discrepancies in model results, not to mention the use of different box models. A test has been made using total equivalent propene concentrations and speciated VOCs in our model. An overestimate in ozone peak concentration has been found when using total equivalent propene concentrations. Thus, it is hard to expect that net ozone production rates obtained in Chameides et al. (1992) would be definitely reached in our case. Besides, Chameides et al. (1992) stated that the trends of net ozone production rates were qualitatively consistent with their analysis of the ambient data. Accordingly, the modeled changes of ozone in responses to precursor changes also qualitatively agree well with what has been revealed by the ambient data, as well as Chameides et al. (1992).

Last but not the least, we thank the referee for proposing a broader view of our work. We have added related content in the introduction and conclusion section.

Specifically, we have addressed each concern as below and corresponding revisions have been made in the manuscript.

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmos. Environ., 34, 2063-2101, 2000.

Comments in order of appearance in text: Abstract, line 24-25. “Total VOC reactivity is dominated by anthropogenic VOCs, including aromatics, alkanes, and most alkenes.” I don’t know what information this sentence is trying to convey.

We have rephrased this vague sentence: “On average, total VOC reactivity is dominated by anthropogenic VOCs.”

Section 2.2 NOx measurements, Sec 3.3 line 26-28, and Fig. 2. Measurement should be described here, not later on in Sec. 3.3. Evidently this is a 2 channel machine, measuring NO and NOy. I don’t know the details of this instrument, but a Mo converter heated to 350 will quantitatively reduce HNO3, organic nitrates, nitrate aerosol, and PAN to NO. In anything but fresh emissions, NOx oxidation products will be greater than NO2. The ratio, NO2/NO appearing in Fig. 2c should by replaced by, for example NO/NOy, or NO/NOy* is there is indeed the converter does not quantitatively reduce NOx oxidation products. An explanation of NOy* would be needed.

We thank the referee for this comment. We agree with the referee that the details of NOx measurements better to be described in Sec. 2.2 instead of Sec. 3.3. We also agree with the referee that NOx measurements using a molybdenum converter would suffer from interferences of NOx oxidation products. The instrument we used to measure NO and NOx concentrations during the field campaign is a chemiluminescence analyzer (TE 42CTL, USA) with a Mo converter. NO_2 is converted to NO on the heated Mo converter surface (325℃) and it is therefore NOx that can be directly measured by this technique. However, other reactive nitrogen compounds such as PAN and HNO_3 might be partly converted to NO and affect measured NOx concentrations. Therefore, measured NOx concentration is always an upper limit of the real NOx level in the ambient atmosphere. According to the comments, the description of NOx measurements has been given in Sec. 2.2, with an explanation for NOx*. In Fig. 2c, we have replaced NOx with NOx*, and NO_2/NOx with 1-NO/NOx*. Corresponding modifications regarding interpretation of NOx have also been made in the manuscript, with NOx replaced by NOx* where measured concentrations are described and NOx remained NOx for the rest.

Page 4, line 16-18. Why were 4 bags filled for a VOC analysis. Are results always averaged?

Each VOC sample was collected by drawing the ambient air into an 8L Teflon bag four times during the 2-hour sampling period at a 30-minute interval. We have rephrased the description of VOC samplings to be more precise: “An 8L Teflon bag was used to collect the ambient air at a 30-minute interval during each sampling period. Thus, each VOC sample represented an average condition of the 2-hour sampling period.”

Page 5, line 4. It is good to see the factor Cj in the Propy-Equiv(J) formula, because that is how it was defined in Chameides et al. Many people leave it out.

Thank you.

Page 5, line 21 “Six scenarios were arranged.” I don’t think that scenario is the best description. The 6 cases represent calculations based on real data from 6 different days. I think of scenario as made-up, as in the variation of NOx concentration.

We agree with the referee and have replaced all “scenarios” with “cases” in the manuscript.

Page 5, Sec. 2.4 Observation based modeling approach. More information is needed to describe the calculations. Some of my questions:
Were VOCs and NOx held constant at observed or prescribed values during 5 day calculation?
Do initial VOCs represent measured concentrations at some particular time of day?
How was NOx partitioned between NO, NO2, and perhaps other compounds?
Did this partitioning change to follow a diurnal cycle?
Were oxidation products allowed to accumulate? The steady state concentrations of short lived products such as HCHO and CH3CHO will become large and effect O3 production. Less reactive ketones will also build up to large values over 5 days.

We have described the modeling approach in Sec 2.4 in a more elaborate way following the referee’s questions. VOCs were constrained by measured concentrations during each five sampling periods on each day (daily averaged parameters listed in Table 1). NOx was maintained constant with adjusted NO_2 concentrations at prescribed values. The partition between NO and NO_2 followed a diurnal cycle with NO completely consumed at night and generated by photolysis of NO_2 in the daytime. Other nitrogen compounds such as HNO_3 and PAN were unconstrained. There were totally 42 model runs. In each model run, concentrations of constrained species were always reset to prescribed values and repeated on each day, while concentrations of unconstrained species were allowed to accumulate until stabilized. Aldehydes and ketones were allowed to accumulate by each time step, but soon arrived at a stable state on the second modeling day.

Page 6, line 14 “remain averagely” replace with averaged.

We have revised it accordingly.

Page 9, line 4 “far away from the petrochemical facilities near the coastal area” Are these the facilities in the yellow area in Fig. 1? Text implies that they are to the east, which might put them off the right side of map – east of 118 longitude.

Yes, the petrochemical facilities near the coastal area locate in the yellow area in Fig. 1. We have rephrased related sentences in Sec. 2.1: “The campaign site is surrounded by a number of small factories within a distance of 10 km. Most of the neighboring industrial sources are clustered to the east of the site… Moreover, an active petrochemical complex is situated in the heavily industrialized zone near the coastal area.”

Page 10, line 14 1 to 14 ppbv isoprene 14 ppb is a very high concentration, probably close to the maximum reported from biogenic sources. Is there any chance that the high isoprene is from petrochemical facilities? Isoprene is a feedstock.

We thank the referee for this helpful comment. Isoprene has been known as one of the most important biogenic VOCs. The emission rate of isoprene is determined by leaf temperature and light intensity according to Guenther et al. (1993). Hence, the highest isoprene concentrations are often found in the afternoon when biogenic emissions tend to be the strongest. Nevertheless, isoprene could also be of anthropogenic origin. The traffic emission of isoprene has been reported at both urban and rural locations (e.g. McLaren et al., 1996; Reimann et al., 2000; Borbon et al., 2001). Besides, isoprene is largely used in the manufacture of synthetic rubber, thus a feedstock as mentioned by the referee. During the field campaign, high concentrations of isoprene were observed with the highest value of nearly 14 ppbv. Interestingly, daily peak of isoprene appeared in late evening in period 2 instead of in the afternoon in period 1. We have performed analysis of correlations between isoprene and MTBE, a reliable tracer for vehicular emissions, to indicate negligible traffic origin of isoprene in this region. We did not include in the manuscript discussions on that isoprene could by any chance be released from petrochemical facilities, since it has been stated that the landscape is generally well vegetated to the west of the site. Therefore, no industrial origins of isoprene have been expected under dominant westerly winds during period 2. After considering the referee's suggestion, we have further examined vinyl chloride, also a feedstock in petrochemical industries (Na et al., 2001), and found the temporal variation of vinyl chloride almost opposite to that of isoprene through the whole sampling period. Actually, vinyl chloride was hardly detected in period 2 when very high concentrations of isoprene were observed, in supportive of previous analysis. However, we should still be very cautious to rule out any possibilities, as suggested by the referee. Thus, we have supplemented in the manuscript aforementioned analysis. Moreover, further studies are much needed and we have thereby added: "To support this hypothesis, further efforts involving the development of VOC emission inventories, and direct measurements of free radicals and major isoprene degradation products along the transport pathway would be highly appreciated."

Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J. C., and Guillermo, R.: An investigation into the traffic-related fraction of isoprene at an urban location, Atmos. Environ., 35, 3749-3760, 2001.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K. and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, J. Geophys. Res., 98, 12609-12617, 1993.

McLaren, R., Singleton, D. L., Lai, J. Y. K., Khouw, B., Singer, E., Wu, Z., and Niki, H.: Analysis of motor vehicle sources and their contribution to ambient hydrocarbon distributions at urban sites in Toronto during the Southern Oxidants Study, Atmos.

Environ., 30, 2219-2232, 1996.

Na, K., Kim, Y. P., Moon, K. C., Moon, I. and Fung, K.: Concentrations of volatile organic compounds in an industrial area of Korea, Atmos. Environ., 35, 2747-2756, 2001.

Reimann, S., Calanca, P., and Hofer, P.: The anthropogenic contribution to isoprene concentrations in a rural atmosphere, Atmos. Environ., 34, 109-115, 2000.

Page 10, line 29 Measured n-hexane ... Better to say n-hexane is the most abundant species measured ...

We have revised it accordingly.

Page 12, line 13 -14 underestimate of the overall VOC reactivity .. where only a subset of speciated VOCs are capable of being specified as model inputs My concern is that the direction of error is not known because of the secondary VOCs produced in the calculations vs. what is actually in the atmosphere.

Thank you. We agree with the referee that uncertainties caused by differences in modeled secondary VOCs and actual VOC oxidation products in the atmosphere should be considered in addition to an underestimate of input VOCs. We have revised it in the manuscript.

Figure 5 and text. Is the third category of compounds, all those not in category 1 or 2? Compounds whose average is within a factor of two for periods 1 and 2?

We thank the referee for raising these questions, which remind us of some information that has been left out in the manuscript. We did not include all VOCs in Fig. 5, because 21 VOC species were not detected during both periods. Except for those 21 VOCs, all other species were grouped in 3 categories as shown in Fig. 5. To categorize the VOC species, a criterion has been put forward on the basis of the mathematical relationship between the average concentrations of period 1 (denoted as C1) and that of period 2 (denoted as C2). The first category involves species with C2>2*C1, while species with C1>2*C2 fall into the second category. The third category contains all those species not in category 1 and 2, except for 21 species that were detected neither in period 1 nor in period 2. Species in the third category have comparable concentrations for both periods. We have made revisions both in Sec. 3.2 and the legend of Fig. 5 to make the descriptions more clearly. For reference, species not included in Fig. 5 are listed here: 2-Methylheptane, 3-Methylheptane, 2,2-Dimethylbutane, 2,3,4-Trimethylpentane, n-Undecane, 1,3-Butadiene, 1-Hexene, 1,4-Dioxane, Hexachloro-1,3-Butadiene, Vinyl Bromide, trans-1,2-Dichloroethylene, Tetrachloroethylene, Chloroethane, 1,1,1-Tricholoethane, 1,1,2,2-Tetrachloroethane, 1,2-Dibromoethane, Bromoform, Bromomethane, Bromodichloromethane, 1,2-Dichlorobenzene, 1,2,4-Trichlorobenzene.