Anonymous Referee #1

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This paper analyzes flares using two distinct modeling approaches: small scale combustion modeling of the flare and larger scale dispersion and reaction of the plume on the urban to regional scale. The methods are well described and the results contribute to the understanding of a policy-relevant issue. I recommend publications subject to the following comments.

Major Comments

1) Table 1: I would have expected CO2 to be conserved – or to increase if the plume is reacting. The decrease suggests that something is not quite right. Also, the purpose of showing the slices should be better defined and results presented accordingly, for example, is it to show reactions? Also, the definition of the slices seems a bit strange.
Would it not make more sense to have spacing that increases gradually. There is no colorbar for Fig 2. It would also be interesting to report the maximum temperature of the plume with distance for the different slices.

We agree. Thanks. The method for the mass flow estimation was revised and corrected. We found an error in the code during the mass flow numerical integration. Consequently, we fixed the code and the method was slightly modified to include data within two standard deviations, without losing accuracy on mass conservation. Please see Figures SM2 and SM3 of the supplementary material and reply to point 2 to Referee 2 to complement this point. Colorbar is added to Fig. 2 in the manuscript and a plot of the maximum temperature at each slice location is included as suggested (Fig. SM6 of the supplementary material). The manuscript was modified accordingly.

Regarding the question why to include the slices, they were included mainly for two reasons: to track how the chemical species and physical properties of the combustion process evolve along the flame and the plume, and to depict graphically the method for the mass flow calculation. Taking into account the Referee's suggestion, the manuscript was rewritten to consider only two slices in the discussion: a) S1 at the overfire region and b) S2 at 60 meters away from the flame. For completeness we briefly mention the results of slices at other heights. Table 1 and text in Section 3.1.1 now reads:

Pg15187ln17: "The results of the 2D simulation of the sour gas flare in a cross wind are presented in Figure 2 and Table 1. The table shows mass flow estimates of different species at two slices. These slices are located at different heights with respect to the tip of the simulated flame. S1 corresponds to the overfire region and S2 represents far-field conditions. The slices are included mainly for two reasons 1) to track how the chemical species and physical properties of the combustion process evolve along the flame and the plume, and to depict graphically the method for the mass flow calculation."

Pg15188ln14: "OH levels are estimated to infer about the region in which flaring soot starts to evolve in far-field conditions. Although not shown, slices at 30 and 40 meters above the flame had OH levels slightly higher than soot levels. At 60 meters above the flame, it was considered that the influence of the atmospheric chemistry could start to be important, since the OH levels have decreased about two orders of magnitude. In addition, at this distance

NO2 levels are higher than those of NO. This can support the assumption of far flame conditions, since NO2 concentration increases at lower temperatures (See Figure SM6 of the supplementary material). However, the levels of both SO2 and CO2 are more variable suggesting an increase in the domain height and hence a longer simulation time."

Table 1.

Species	Slice	
	S1 (0m)	S2 (61m)
SO_2	2.64	3.86
NO	2.45E-2	5.58E-2
NO_2	1.84E-2	7.07E-2
Soot	2.24E-4	2.46E-5
CO	1.21E-1	2.81E-1
CO_2	12.61	16.10
OH	8.66E-3	2.17E-5

2) Sec 3.1.2: I may have missed this, but what are the differences between the 3 flares? The paper discusses a single flare modeled by OpenFOAM, and then jumps to comparison with 3 flares in IMPei. Pg18192ln13 then speculates about composition differences between the flares – is there different and more comprehensive information that goes into IMPei? This should be spelled out.

Regarding the differences between the flares, the most remarkable is the process to which each one is related within the Refinery. We included this fact by making the following changes to the manuscript:

First, the paragraph that goes from ln10 to ln16 in pg15189 of Section 3.1.2 is removed. Then, the following paragraph is added in place of the one that goes from ln11 to ln18:

"CO is about 4 times higher than IMPei. With respect to the estimates at S2 slice, CO2 is double than IMPei lower. From the IMPei estimates, practically all the contribution comes from F3. The high variability in the stream composition of each flare as reported by IMPei can be attributed to the Refinery configuration, since the main difference between the flares relies on the process to which they are related within the facilities. This implies different fuel streams, different compositions and variable flow rates. Based on the IMPei emission rates of SO2, soot and CO2 for each flare, it can be inferred that there exists a different amount in mass of carbon and hydrogen sulfide on the feed stream sent to each flare, with the possibility of including hydrogen. Unfortunately, we have no information with this respect to confirm the amount of species other than carbon and sulfur. However, the estimates of this work are comparable to measurements reported by Rivera et al., (2009), and IMP emissions inventory."

As for information related to IMPei, the following paragraph is inserted into Section 3.1.2, pg15189ln7:

"IMPei emission rates are based on ARPEL methodology (IMP, 2006). The emission rate for SO2, CO2 and CH4 was calculated with a mass balance approach. A combustion efficiency of 98% was considered for CH4 according to the recommendations of British Petroleum. The conversion rate for H2S to SO2 was set to 100% and of 99.5% for CO2 according to recommendations of IPCC. However, in this work we are taking a representative composition based on information provided by trained personnel and estimating the mass rate of pollutants by considering the wind influence on combustion. For this reason, just the total mass flow rate is similar between the combustion model of this work and the reported data by IMPei".

The procedure to assign emissions to flares based on results of the combustion model is inserted as a paragraph in place of the previous paragraph that went from ln10 to ln16 in pg15189 of Section 3.1.2:

"The results of the combustion model represent a high emission scenario for SO2. Since the exact chemical composition is not known at all for each of the three flares in the refinery, the result of the combustion model for each combustion by-product was assigned proportionally to each flare according to the mass fluxes reported by the IMPei. Although IMPei reports soot emission rates for the three flares, the result of the combustion model was set equal for the three flares since the estimated rate is lower than the IMPei value. The same was done with acetylene and ethylene."

3) Pg15184ln22: Could you specify the mass fluxes of the three flares used here? The whole discussion comparing the flare mass fluxes with the IMPei model and RdF is dependent on what estimate is used for the flux in the stack.
Also, in terms of emissions, table 6 has a hint of the different sources from the Tula Industrial Complex. However this is not very clearly spelled out. Are the flares the main sources from the refinery? What other point sources are there, and how do the flares compare with those? Past studies focused on total emissions from the TIC, so providing this information would help make a correct comparison of flare emissions with previous work. It would help to have a brief description of the IMPei model and how much of the input data is the same between IMPei and the present work.

With respect to the mass flow, a value of 5.3 Kg/s is used in the combustion model. Please see reply to point two of Referee 2 to complement this point.

For the description of IMPei model and distinction of common data between IMPei and combustion model, please see the second paragraph in reply to point 2.

Regarding the other emission sources at the Refinery, the following paragraph is added to pg15202ln15 of Section 3.3.2:

"In addition, it is important to note that aside from the elevated flares, Tula Refinery has other important sources, particularly heaters, ground flares, boilers and oxidizers. Based on previous studies conducted by the IMP, elevated flares represent roughly 60% of total SO2

emissions from the Refinery, and about a quarter of the total emissions of the TIC. This implies that in the reported impacts by de Foy et al. (2009), flaring emissions could be comparable to the Popocatepetl volcano emissions. With respect to Table 2 reported in Rivera et al. (2009), an emission rate of about 2.82 Kg/s can be assigned to elevated flares when taking the 1999 emission inventory of SEMARNAT-INE; and of 2.57 Kg/s when taking the emission inventory of PEMEX. However, Fast et al. (2009) report in Table 3 of their paper a slightly higher emission rate for the TIC which would correspond to about 3 Kg/s. These rates are comparable to the result of the combustion model of this work.
As for soot, IMP information suggests that elevated flares represent about 6.5% of total emissions from the Refinery and roughly 1.45% of total emissions coming from TIC. These fractions are based on the assumption of high soot content in the PM2.5 estimate. Taking again Table 3 of Fast et al. (2009), results in an emission rate of about 5.65 g/s, 1.6 times greater than the value of IMPei."

4) Table 5: could you confirm in the caption that the mass flow rates for WRF-Chem are taken from the flare model?

Yes. The mass flow rates were set based on the results obtained with the combustion model. Since the estimation method for the mass flow was updated, Table 5 is changed and reads:

Table 5. Mass flow rates used in WRF-Chem for the three flares at MHR in Tula. Units are in Kg/s.

Specie	Flare emission rate		
	F1	F2	F3
SO_2	1.71	0.80	0.13
NO_2	1.04E-2	1.04E-2	3.50E-2
NO	1.32E-2	1.32E-2	4.43E-2
NO_x	2.36E-2	2.36E-2	7.93E-2
CO	0.52E-2	0.52E-2	1.79E-1
C_2H_2	9.67E-3	9.67E-3	9.67E-3
C_2H_4	2.0E-2	2.0E-2	2.0E-2
Soot	2.46E-5	2.46E-5	2.46E-5

5) Pg15189ln17: What is the conversion rate of H2S? Is all the sulfur in the plume converted to SO2? It would be interesting to have a plot of concentration for a species that is being diluted in the plume and one that is being formed in the plume (eg. Fig 2 with 2 extra panels, zooming on the plume).

Based on the combustion model results, we calculated a combustion efficiency of about 84% for SO2. This implies that not all the H2S in the fuel stream is converted to SO2.

Wind-flame interaction can contribute to a reduced efficiency. A plot showing the evolution of H2S and SO2 has been included as suggested (Fig SM7 of the supplementary material).

6) I'm not sure I could see the point of discussing the E1 and E2 methods for mass flow estimation. E1 is clearly better; I would recommend removing the discussion of E2. If the estimate from E2 gives a better fit with prior work, it seems that it is more likely because the emissions are overestimated than because E2 is a better way to estimate the fluxes.

Thank you, we agree. As the mass flux calculation method was modified, the E1 and E2 methods are not included in the discussion anymore and those were removed from the manuscript. See as a reference the third paragraph in point 1.

7) Pg15192ln25: How does the amount of HONO predicted by the method compare to the concentrations in Li et al.? Maybe a rough box model calculation can be used to obtain a sense of the magnitudes involved. Likewise for HCHO. This section should be enhances if it is to be retained.

The purpose of including the emission rates of HONO and HCHO was to show the applicability of the combustion model, since to the authors knowledge there are not reported estimates of HONO for flaring activities in Mexico with a CFD combustion model. However, the objective of this work is to focus on the contribution of SO2 and soot to the MILAGRO supersites. Since Li et al. (2010) study the influence of HONO in the MCMA, an accurate comparison of the rates obtained in this work with respect to those reported by Li et al would require the use of the MCMA Emission Inventory. Following your suggestion, this section was removed. Nevertheless, a brief paragraph mentioning the applicability of the combustion model in the estimation of these species is retained in Section 3.1.2 as follows: "It is important to mention that the applicability of the combustion model could be extended to estimate other important species for atmospheric, in particular nitrous acid (HONO) and formaldehyde, even though they are not related with the purpose of this work. Previous research reports the importance of HONO in the morning photochemistry of the MCMA (Li et al., 2010), and current research has reported measurements of primary emissions of formaldehyde at Mont Belvieu, in the Houston Galveston Bay facilities (Parrish et al. 2011)."

8) Sec 3.3.1 and 3.3.2 are very long – could they be shortened somewhat? Is there any reaction of SO2 on the timescales considered? Does it make a difference using WRFChem versus just a transport model with no reactions? Fig. 6 shows the EC and SO2 plumes, but it seems that because both of these are basically just transported with limited reaction in the basin they both look the same.

The purpose of running WRF-Chem with chemistry, is to test the performance of this model with the inputs of the combustion model in order to further study secondary pollutants by the elevated flares of Tula Refinery. We expect no significant differences in SO2 levels if running WRF-Chem in tracer mode.

Sections 3.3.1 and 3.3.2 have been shortened by focusing the discussion on the plume impact at supersites on 23 March. Fig. 6 shows EC only.

9) Table 6: Expand the caption to remind the reader that FPRPP is the power plant and MHR the refinery. Also, use S0 and S5 and refer to Fig 2 for the cross sections. How was the percentage contribution calculated? (This also applies for Fig 7) Could you add this in the text with a brief reminder in the caption?

The following paragraph is inserted into pg15198ln16 in section 3.3.1:

"The percentage contribution to the supersites was estimated following de Foy et al (2009), by taking the model´s to observations mean values ratio for the entire simulation period of this work. Although not shown, the contribution was also estimated by taking the area under the curve for both observations and model results for the entire simulation period and comparing them. In this case, there were variations up to 5% with respect to taking the mean values. For simplicity we retained the contribution obtained with the mean values."

As for the plot shown in Fig 7, the following paragraph is inserted in pg15202ln19. "It was obtained by tracking the points on which the plume exceeded a threshold value within a region encompassing Tula and MCMA. Basically it shows how much time the plume spent in this region in all the simulation period. The threshold value is based on the detection limits of measuring instruments. A value of 0.01ug/m3 is used for soot whilst 1 ppb is set for SO2. Please refer to Fig. 1 in the supplementary material for the procedure."

Caption of Table 6 is changed to: "Estimated contribution of flaring activities from TIC to SO2 and soot levels at MILAGRO supersites. SO2 units are in ppb and soot units are in ug/m3. FPRPP refers to Francisco Perez Rios Power Plant and MHR refers to Miguel Hidalgo Refinery. Far flame estimate and overfire scenarios correspond to slices S1 and S2 (Fig. 2)".

19) Could you say something about the impact on air quality in the MCMA of replacing the refinery, as is currently being planned?

As a note, there is an ongoing project to build a new refinery in the area, which it will imply doubling the amount of produced fuels, but reducing the total amount of emission to the atmosphere by improving efficiency on the processes and switching from gasoil to natural gas as a fuel. Based on previous studies and on the results of these work there could be an improvement in the air quality of the MCMA, particularly on the north region. In this scenario, the impact would be perceived mostly on SO2 levels, since the emissions from TIC can contribute more than local sources, whereas for soot urban sources prevail. Nevertheless, the emissions from the Power Plant would be exerting influence on SO2 levels of the MCMA. However, further research needs to be performed. For this reason, we are extending the results of this work to include the national Emission Inventory in order to assess the contribution of flaring emissions in the air quality of MCMA, particularly on

secondary pollutants. In addition, the combustion model would help in assessing technological improvements in flares. This will require further research as well.

Minor Comments:

20) Pg15181ln1: could you provide a reference for the estimate?

The respective reference has been included. Thank you. Now it reads "... of VOCs (SEMARNAT, 2006)

21) "transient code" – shouldn't this be "unsteady" or "time-varying"?

This term was used to account for the OpenFOAM solver used in this work, in the sense that it solves the time-dependent solution of the combustion process. For clarity, pg15183ln15 was changed to: "It is a combustion code that solves the Navier-Stokes equation in unsteady state"

22) Pg15185ln20: the discussion about the other paper is vague. Is there a clear split between the two? Does the other one contain information pertinent to this paper? You might one to remove this or clarify the difference.

Please see the reply to point 1 to Referee 2-

23) Tables 3 and 4 could be merged. Also, please include units.

Table 4 was merged with Table 3. Units were included as suggested. Thank you. The mean bias was added to the Table.

24) The labels for Fig 6 is illegible.

Fig 6. now includes EC only. Labels were augmented for readability. Thank you

25) The captions for the tables and figures could be expanded to make it easier to understand
what is going on.

Brief text is added to the captions as suggested.

Caption in Table 2 is changed to: " Summary of the mass flow rates of combustion air pollutants. Units are in kilograms per second (Kg/s). F1, F2, and F3 stands for Flare number 1, 2 and 3 respectively. RdF represents the combined reference of Rivera et al., (2009) and de Foy et al., (2009a). * SOx emissions". In addition, the name of the performance statistics is changed to:

Table 3 and Table 4 are merged as suggested by Referee 2. Please see reply to point 23

Caption in Fig. 4 is changed to: “Time series of EC obtained with the soot mass rate of the far field slice (S5) from the combustion model (dashed blue) and measurements (red) at T1 site.”

Caption in Fig. 5 is changed to: “Model (blue) and measurements (red) time series of EC concentration for the simulation period. Results correspond to total TIC emissions (Power plant plus Refinery). T0 (upper panel); T1 (middle panel) and T2 (bottom panel).”

Caption in Fig. 6 is changed to: “Modeled plume of SO2 and wind fields at the surface for 23 March at 12:00 LST.”

Caption in Fig. 7 is changed to: “Suggested spatial contribution of SO2 and EC in the period from 22 March to 27 March of 2006.”

References

IMP: Estudio de las emisiones de la zona industrial de Tula y su impacto en la calidad del aire regional, IMP, PS-MA-IF-F21393-1, Anexo C, 2006.

de Foy, B., Krotkov, N. A., Bei, N., Herndon, S. C., Huey, L. G., Martínez, A.-P., Ruiz-Suárez, L. G., Wood, E. C., Zavala, M., and Molina, L. T.: Hit from both sides: tracking industrial and volcanic plumes in Mexico City with surface measurements and OMI SO2 retrievals during the MILAGRO field campaign, Atmos. Chem. Phys., 9, 9599-9617, 2009.