Response to Reviewer's Comment

(Manuscript No. acp-2014-359)

Reviewer Dr. Cebrunis

1st comment

The paper by Lin et al. is a comprehensive study characterizing size-segregated particulate matter and trace metal emissions in the tunnel. Tunnels are indeed excellent natural laboratories, but I wonder if the authors did a strategic mistake in the sampling set-up greatly diminishing the value of their study. The Equation 2 of the paper can only be applied to a closed system, i.e. applying a box model which implies that an air parcel enters the tunnel at the inlet and exits at the outlet accumulating emissions along the length of the tunnel. The "box" should be "airtight" - no exchange of air is allowed with the clean outside air inside the box. Based on the description of the experimental set-up there was automatically activated air exchange system (triggered by CO exceedances and/or randomly) in-between the inlet and outlet sampling points, thereby invariably diluting accumulated emissions in the air. Considering the dilution effect, Equation 2 can only be used in sections where no active air exchange has happened (not the 8.9 km length of the tunnel) and/or taking into account the dilution effect between those sections which complicates calculations significantly (and only if dilution was constant which was not probably the case). Consequently, I conclude that the emission factors were greatly underestimated in this paper while comparison with other studies reporting similarly low values were only valid providing no mistakes were done in any of the studies. For example, Valiulis et al. (2002 Atmos.Environ.) reported emission factors for Zn, Ba, Mn, Cu and Pb an order of magnitude higher than in this study with similar traffic flow and composition albeit in a much shorter tunnel with only natural ventilation. It fact, Table 6 reports PM emission values in other studies also greatly higher than in this study pointing to the problem above. I argue against any advantage of long tunnels because of mandatory elaborate ventilation systems absent in short tunnels.

Author's response:

Thanks for the reviewer's comment. The ventilation system inside the tunnel is triggered when CO concentration and temperature exceed their threshold values (ex. CO $\geqq$ 75 ppm and temperature $\geqq$ 40°C) . As we check the CO and temperature data monitored by Taiwan Area National Freeway Bureau, it is found that temperature was frequently higher than 40°C at the outlet site, especially, during the July and August sampling periods, suggesting that ventilation system was operated. We also agree that the approach for estimation of EmF used in this work can only be applied in a close system. Since the exchange of inside-air and outside-air was occurred, the EmF

should be much underestimated in this work. Thus, we have followed the reviewer's comment and deleted all the descriptions related to emission factor in the revised manuscript.

2nd comment

In addition, why only PM1 emission value in Hsuehshan tunnel is presented in Table 6 when comparative PM10 and PM1.8 could also be calculated from all three fractions and meaningfully compared to other studies?

Author's response:

Thanks for the reviewer's comment. As the response to 1st comment, all the descriptions related to emission factor have been removed from this manuscript; however, Table 6 has been also deleted in the revised manuscript.

3rd comment

I also wonder why the authors assume that emission factors should be same or similar among different size fractions taking 4.4 - inlet/outlet ratio of PM1 - as a reference? I would argue against the correction of PM1-1.8 emission factor supposedly taking into account dry deposition - a notoriously difficult parameter to estimate, particularly in the tunnel. Different processes (combustion (PM1) versus abrasive wear (PM1-1.8) versus re-suspension (PM1.8-10)) were contributing to different size fractions, so why expect similarity? Dry deposition cannot account for 43% losses of PM1-1.8 particles based on aerosol fundamentals - my estimate is at most 10-15%. However, I agree that the larger the size fraction the larger the underestimation of the emission factors due to deposition. In summary, the experimental set-up clearly suffered from neglecting the dilution effect preventing any meaningful estimation of dry deposition which can be safely neglected by acknowledgement. I believe that the authors will carefully revisit their experimental set-up and calculations of the emission factors and possibly find the way of correcting the emission factors. It is imperative to consider geometry of the tunnel finding unperturbed sections; air exchange rate at all stations estimating a dilution effect; and activation pattern of the ventilation system (and any differences in the pattern between weekdays and weekends) to see which data can be reliably used in Eq.2 (if any). If that is not possible, the sections reporting emission factors should be removed which would be pity because of the otherwise valuable dataset obtained. The remainder of the paper - pollution patterns from air quality point of view, corresponding ratios of metals, size-distributions, etc. - is all fine.

Author's response:

In this work, we used a correction factor of 4.4 as a reference ratio to correct the underestimated EmF of different sized PM. Nevertheless, we make a very serious

mistake that different process contributes different sized PM and thereby the correction factor should be overestimated as suggested by the reviewer. Consequently, we have re-organized this part in the revised manuscript. (lines 4-13 on page 10). On the other hand, the approach (Equation 2) for calculation of EmF is unsuitable in a "open system". Thus, we have also deleted the descriptions related to EmF.

Anonymous Reviewer #1

General Comments:

In this manuscript, the authors present results from a field study conducted at the Hsuehshan tunnel in Taiwan. Size resolved particulate matter samples were collected near both the entrance and exit of the tunnel on twelve days in 2013, and subsequently analyzed for total PM mass and metals content through gravimetric and ICP-MS analyses, respectively. Metal size distributions, enrichment factors, element ratios and results from principal component analysis are presented and used to explore sources of metallic aerosol components in the tunnel including tailpipe and wear emissions and resuspended dust. The authors also provide estimates of emission factors for trace elements and PM. In general, the scope of work pursued here is good and the authors have collected a nice data set that contributes to our understanding of vehicle derived trace metal aerosols. With some exceptions (see specific comments below), the manuscript is relatively well written and figures and tables are adequate. This being said, there are some major issues with the manuscript related to emission factor quantification that need to be addressed prior to publication in ACP. Specific comments on the manuscript are included below.

Author's response:

We have followed the reviewer's comments and revised this manuscript. The revised portion will be explained in details of the following response.

1st comment

P. 13966, line 13-24: The authors provide a list of a number of possible sources of vehicle derived metal emissions. I wonder if this information would be clearer to the reader if presented in tabular format.

Author's response:

As suggested, we have added the new "Table S1" in supplementary to list the potential sources of these metallic elements in different sized PM.

2nd comment

P. 13967, lines 2-5: While I agree with the authors that tunnel studies, as compared to near-road sampling, provide a more constrained environment for investigation of vehicle derived PM emissions, I think the authors need to do more here to substantiate the claim that near-road studies are "insufficient". For example, Ning et al. show that

emission factors for several metals can be obtained from near-road sampling. (Ning, Z., A. Polidori, J. J. Schauer, and C. Sioutas (2008), Emission factors of PM species based on freeway measurements and comparison with tunnel and dynamometer studies, Atmos.Environ., 42, 3099–3114, doi:10.1016/j.atmosenv.2007.12.039.)

Author's response:

Thanks for the reviewer's comment. In the revised manuscript, we have cited additional references, such as Jamriska et al. (2004), Ntziachristos et al. (2007) and Ning et al. (2008), to claim the limitations of dynamometer tests and near-road side sampling in characterizing traffic-derived PM. The freeway measurement was done very well by Ning et al. (2008). Such airborne metals, including Cu, Mo, Ba and Pb, showed very good agreement with those measured by tunnel and dynamometer studies, but Mg, Fe and Ca did not. The disagreement was probably because the atmospheric concentrations of Mg, Fe and Ca are contributed by both traffic and non-traffic sources, and the relative abundances of these crustal elements in road dust varies considerably across locations. Moreover, some studies have corroborated that PM concentration near-road side measurements are influenced by local meteorological conditions and traffic activities (Jamriska et al., 2004; Ntziachristos et al., 2007). Thus, tunnel experiment may be an alternative way to characterize the traffic-derived PM. (lines 7-14 on page 4)

3rd comment

P. 13968, lines 16-24: The authors describe the ventilation system utilized in the Hsueushan tunnel here. It is unclear what the status of fans at exchange and inter-change stations was during the aerosol sampling campaign. The authors state that the fans are triggered when temperature or CO concentration thresholds are reached. Were the fans operational during the measurement periods? If so, the additional airflow into and out of the tunnel bore complicates the mass balance used to derive equation2 (see comment on Section 2.4 below).

Author's response:

Thanks for the reviewer's comment. In fact, more than 20 monitoring stations record the CO concentrations and temperature inside Huehshan Tunnel. The 1-hour average CO concentrations at these stations never exceeded 50 ppm during the campaigns, indicating that the ventilation system was not triggered due to the high CO conditions. Nevertheless, the temperature inside the tunnel was usually above 40°C at the outlet

site, especially, during July and August sampling period. This reflects that ventilation

system was operated via high temperature. The operation of ventilation system resulted in the exchange between outside-air and inside-air inside Hseuhshan tunnel, leading to underestimated EmF of PM and their metallic elements of this work. Thus, we have deleted all the descriptions which are related to EmF in the revised manuscript.

4th commen

p. 13969, lines 2-3: I'm curious to know why the author's selected Friday-Sunday for their sampling periods. Many vehicle emission studies I am familiar with tend to prioritize weekday sampling, as traffic patterns on weekends and particularly on Sundays may not be representative. This study design is heavily weighted to weekend sampling. Some additional text here may be helpful. What are typical weekly traffic patterns at the tunnel? Is there any change in the overall traffic volume or vehicle mix on weekends relative to weekdays?

Author's response:

Thanks for the reviewer's comment. The traffic volumes inside Hsuehshan Tunnel are very different between workdays and weekends (particularly on Sunday evening). As listed in Table 1, the traffic flow at the northbound on Sunday was usually more than 1800 vehicles per hour, which was 1.3 times higher than that on Friday. The very high traffic volume (>2300 vehicle h^{-1}) was always found after 5 p.m. on Sunday afternnon, causing a traffic jam when lost of people traveled back to Taipei. The traffic jam does influence the characteristics of traffic-related PM metals. That is why we conducted the aerosol measurements inside Hsuehshan Tunnel from Friday to Sunday in each sampling campaign. (lines 16-24 on page 6)

5th comment

P. 13969, line 5: Please include location of sampling inlets within the tunnel bore crosssection (i.e. at what height were the inlets located).

Author's response:

As suggested, we have added the height of sampling intakes of both MOUDIs. (lines 14 and 15 on page 7)

6th comment

P. 13970, line 6: I could not find the method detection limits referred to in this sentence in Table S1.

Author's response:

We have added the method detection limit of each analyzed metal in Table S2 in the revised supplementary.

7th comment

Section 2.4: In regards to the calculation of emission factors using Eq. 2, I share many of the same reservations expressed in the short comment posted by Dr. Ceburnis. As presented, Eq.2 does not account for dilution caused by additional sources of airflow into and out of the tunnel between sampling points and likely results in an underestimate of emission factors. I see this as a major shortcoming of the manuscript and agree with Dr. Ceburnis that the authors need to better justify the appropriateness of Eq.2 as currently applied to evaluating emission factors in the Hsuehshan tunnel. Else, I suggest removing discussion of emission factors from the manuscript. Equation 2: Please include source of wind speed and traffic flow data.

Author's response:

Thanks for the reviewer's comment. We make sure that the ventilation system inside the tunnel was operated during the experiment campaigns, particularly in July and August experimental periods, resulting in air-exchange between polluted (inside the tunnel) and cleaner air (outside of the tunnel) and leading to underestimate significantly the EmF of PM mass and metals. Thus, we have removed all the descriptions related to EmF in the revised manuscript.

8th comment

Page 13972, lines 1-2: The argument that enhancement of carbonaceous material in submicron PM may be caused by absorption of organic gases by Teflon filters is speculative and unconvincing. Unless further support for this claim can be presented, I suggest removing.

Author's response:

As suggested, we have removed the sentence of "Another plausible explanation…..in submicron PM (Cabada et al., 2004)" in the revised manuscript.

9th comment

Page 13972, lines 4-21: In this paragraph, the authors discuss measured outlet to inlet mass concentration ratios of the three PM size fractions considered in this study. The authors assume minimal depositional losses of submicron PM and suggest the measured concentration ratio for this size fraction (4.4) should also apply to larger size fractions if no losses occur. Lower measured concentration ratios for PM1-1.8 (2.3) and PM1.8-10 (1.1) are then used to support quantification of particle losses in the tunnel for these larger PM size fractions. I find this line of reasoning problematic. It is not clear to me why a constant ratio for all size fractions should be assumed. A rearrangement of Eq.2 shows this ratio is dependent on the concentration of a given size fraction at the tunnel inlet and the emission rate within the tunnel: Co/Ci =(EmF×N×L)/(Vair×Ci)+1. Different processes dictate emissions of PM in the three size fractions and a constant emission rate should not be assumed. While the authors are correct that dry deposition will more efficiently remove larger particles, the treatment and quantification of these processes in this paragraph is flawed.

Author's response:

In this work, we used a factor of 4.4 as a reference ratio to correct the O/I ratios of $PM_{1\text{-}1.8}$ and $PM_{1.8\text{-}10}$. We agree that it is problematic since different process contributes different sized aerosols in real ambient conditions. Thus, we have re-organized this part in the revised manuscript. (lines 4-13 on 10)

10th comment

P. 13976, beginning line 19: I found the discussion of PCA results a bit confusing and difficult to follow. I suggest revision of this paragraph to more clearly explain interpretation of PCA results and relation between statistically determined principal components and potential sources. Some specific comments: -One main question I have is in regard to treatment of gasoline and diesel tailpipe emissions. In the fine PM group, PC1 is associated wear debris, dust, and gasoline emissions. PC2 is associated with "tailpipe emissions" which seem to refer to emissions from diesel engines based on the text of this paragraph. First, I think the "tailpipe emission" potential source entries in Table 3 should be reworded to clarify whether the authors link the corresponding principal component to gasoline tailpipe emissions, diesel tailpipe emissions, or both. Also, the authors do not present enough evidence in the

manuscript as to why different metals emission profiles should be expected for these two sources. Are different metal associated with these two fuels? Are lubrication oil formulations and additives different for gasoline and diesel engines? I think some additional text/references here would be helpful for the reader. -What was the fraction of diesel vehicles in the tunnel during sampling? In the site description section the authors explain that only passenger vehicles, light-duty trucks, and shuttle buses are allowed in the tunnel, with heavy-duty trucks (typically a major source of diesel emissions) presumably prohibited. A better documentation of the fraction of gasoline and diesel vehicles in the tunnel during sampling periods may improve the identification of potential sources for principal components. I am confused by PC4 in the submicron fraction which is attributed to "fuel oil". Are the authors referring to diesel fuel here or are they referring to heavier fuel oils typically burned in larger diesel engines (e.g. marine engines). If the former, how is this a distinct source from the "tailpipe emission" component? If the latter, are the authors suggesting a contribution to PM in the tunnel from a diesel source other than on-road vehicles? Some clarification of what is meant by fuel oil here would be helpful.

Author's response:

As suggested, we have re-written this paragraph in the revised manuscript. We have separately identified potential sources of "gasoline" and "diesel" engines to three sized PM by PCA results based on their fingerprinting elements. (lines 5-25 on page 15, lines 1-14 on page 16 and Table 3 on page 35). In submicron PM, high loadings were found for Ni and V in PC 4. Previous study suggested that Ni and V were attributed to fuel oil combustion from both gasoline and diesel engines (Wang et al., 2003; Shafer et al., 2008), but higher emission rates were for gasoline engines (Cheng et al., 2010), thus this factor is considered as fuel foil combustion from gasoline engines. On the other hand, we agree the reviewer's comment that better explanations will be given for PCA results if we know the fraction for each traveling traffic type inside the tunnel. Unfortunately, the traffic types in the tunnel provided by Taiwan Area National Freeway Bureau were only divided into LDV and HDV (Table 1); thus we could not know how many fraction of diesel vehicle is.

11th comment

Section 3.5: See my comments above on concerns with the calculation of emission factors in this study. In particular, the use of correction factors of 1.43 and 1.75 for the

PM1-1.8 and PM1.8-10 size fractions, respectively, appears to be erroneous. Unless the authors can justify the appropriateness of Eq. 2 for the calculation of emission factors, this section should be removed from the manuscript.

Author's response:

As suggested, we have removed the section 3.5 in the revised manuscript.

12th comment

Figure 1: In the top and middle panels, I found the similarity of colors used made the figures difficult to read. I suggest changing the color scheme in these panels to one with a greater degree of contrast.

Author's response:

As suggested, the top and middle panels in Figure 1 have been re-plotted.

13th comment

Figure 5: This figure does not seem to add much to the manuscript beyond what is already presented in Tables 2 and 5. Suggest removing or moving to Supplemental Information.

Author's response:

Thanks for the reviewer's comment. In the revised manuscript, we have re-organized the second paragraph of section 3.4 (lines 19-25 on page 18 and line 1 on page 19) and all the information of this description are shown in Figure 5. Thus, we have retained Figure 5 in the revised manuscript.

14th comment

Figure 6: See above comments on concerns with emission factor calculations.

Author's response:

The response of this comment is as the same as the 7th comment. In the revised manuscript, we have also removed Figures 6 and 7 which show the results of EmFs for PM metals.

15th comment

P. 13965, line 5: change "impactor" to "impactors"

Author's response:

We have changed "…deposited impactor (MOUDI)" to "….deposited impactors

(MOUDI). (line 6 on page 2)

16th comment

P. 13966, lines 2, 11: change “particulate matters” to “particulate matter”

Author’s response:

As suggested, we have changed “particulate matters” to “particulate matter” in the revised manuscript. (lines 4 and 13 on page 3)

17th comment

P. 13966, lines 12, 17: suggest changing “coarser” to “larger diameter” here, or provide specific ranges of particle diameters

Author’s response:

In the revised manuscript, “coarser particle” has been replaced by “larger particle”. (lines 15 and 19 on page 3)

18th comment

P. 13966 line 24: begin new paragraph with “A number of: : :”

Author’s response:

As suggested, we have created a new paragraph with “A number of …..” on page 4.

19th comment

P. 13967, line 7-8: suggest deleting “..and their associated compositions” as this has already been stated previously in the sentence.

Author’s response:

As suggested, we have deleted “and their associated compositions” in this sentence.

20th comment

P. 13972, line 9: change “peak” to “pick”

Author’s response:

We have corrected “peak” to “pick”. (line 11 on page 10)

21th comment

P. 13981, line 23: change “affect” to “effect”

Author's response:

Thanks the reviewer's comment. In the revised, we have deleted the descriptions related EmF and of course, the word of "affect" has also been removed.

Anonymous Reviewer #2

General comment

In this paper, MOUDI was used to get the size-fractionated aerosol samples at the inlet and outlet sites of Hsuehshan Tunnel in northern Taiwan. 36 metals in aerosols were analyzed by ICP-MS. The concentrations, size distributions, and major sources of those metals are presented based on the ErF, correlation matrix and PCA analysis. Moreover, the authors give the information about fingerprinting ratios of traffic-derived metals and EmF of PM10, especially of PM1 metals. The data set in this paper is valuable, and the results and most of the discussions are reasonable. The description is precise and the tables and most of the figures are good. Overall, the paper is deserved to be published in ACP after the authors revise the following concerns.

Author's response:

We have followed the reviewer's comments and revised this manuscript. The revised portion will be explained in details of the following response.

1st comment

P13968 Line 8-10: Many experiments related to the traffic emissions were conducted in Hsuehshan Tunnel (See Reference). Is there any difference between this experiment and before? It seems that the authors ignore the previous works in Hsuehshan Tunnel in introduction.

Author's response:

As suggested, we have added the description of previous works in Hsuehshan Tunnel in the section of "Introduction".(lines 10-23 on page 5)

2nd comment

P13968 Line 16-23: According to the description in paper, both sites are near the exchange and/or interchange station. Did the ventilation system work during the sampling period and how long? Did the activities of the ventilation system affect the sampling result? Please provide the relative illustration.

Author's response:

Thanks for the reviewer's comment. The ventilation system was operated during the aerosol campaigns, especially, during the July and August campaigns. Cheng et al. (2010) suggested that ultra PM levels was diluted approximately 10-50% with fresh air from tunnel air shafts. For submicron, fine and coarse PM, we have no idea how

many fractions were diluted; however, the dilution of PM could result in underestimated EmF of this work since the equation (2) could be used in a close system only. This might be true since our EmF is much lower than other studies. Thus, we have removed the section of EmF in the revised manuscript.

3rd comment

2.3 P13971 Line 20-23 and P13972 Line 1-2: The authors mentioned that the abundance of PM1 may be the result of the absorption of organic gases by Teflon filter. The blank filter was sampled according to the description in P13969 Line 24-25. Did the results of those blank weights support this possibility?

Author's response:

Thanks for the reviewer's comment. We do not have any support for this argument. Thus, we have deleted this sentence in the revised manuscript.

4th comment

P13972 Line 11-21: The authors suggest that the ratio of 4.4 might be regarded as a reference ratio of difference in PM mass between two sites caused by traffic emissions. I can't agree with this suggestion. Except for the direct traffic emission, the secondary formation from trace gases is an important factor for the concentration of PM1. However, the contribution of secondary formation is little in coarse particles. It's not reasonable to use the same ratio in different size particles. In my opinion, the O/I ratio of elements may be taken as a reference ratio. My suggestion is to provide the O/I ratios of elements in three size bins.

Author's response:

Thanks for the reviewer's comment. In this study, we used a correction factor of 4.4 as a reference ratio to correct the underestimated EmF of different sized PM. The potential sources of PM inside the tunnel are included wear abrasion, pipe emissions, re-suspended road dust and secondary formation. However, different processes emit distinct sized PM into ambient air inside the tunnel, indicating that we could not use the same O/I ratio for different sized particles; thus, we have re-organized this part as seen on lines 4-13 on page 10 in the revised manuscript.

5th comment

P13974 Line 4-6 and Fig1c: Most of the O/I ratio for traffic-derived elements is about 2-3. Why are the O/I ratios for Zn and Mn so high?

Author's response:

Thanks for the reviewer's comment. The high O/I ratios for Zn and Mn were caused by the high Zn and Mn concentrations at the outlet site on July 19. If we remove the outliers, the O/I ratios for Mn and Zn will be 2.4±1.1 and 2.7±1.1, respectively, which are very similar to most of the traffic-derived elements. We don't think this case is caused by the errors from the chemical analyses as we have double checked by ICP-MS. Until now, we don't have any idea for the answer and just show the results in Figure 1c.

6th comment

P13975 Line 25-26: The R Cu-Zn (0.63 in coarse mode) is less than 0.67.

Author's response:

Thanks for the reviewer's comment. We have corrected the sentence of "….Cu, Ba, Sb (r>0.67) in $PM_{1.8-10}$…" to "….Cu, Ba, Sb (r>0.63) in $PM_{1.8-10}$…". (line 8 on page 14).

7th comment

P13976 Line 5-7: The authors point out that Pb only correlated moderately with Cu, Sb and Ba and Zn had a good correlation with Cu, Ba and Sb in PM>1(P13975 Line 25-26). However, Zn and Pb show the similar correlation with Cu, Ba and Sb in Table 2 (See the following table). So that it's hard to get the conclusion "Pb was contributed preferentially by combustion process".

Author's response:

We agreed the reviewer's comment. Both wear abrasion and tailpipe emissions are important sources for airborne Pb particles. According our data, Pb correlated well with Cu, Ba, Sb and Zn with r > 0.6 in both coarse and fine sizes, indicating mixed sources of wear abrasion and pipe emissions. In submicron PM, good correlation is found for Pb-Zn (0.77), but not for Pb-Cu (0.35), Pb-Ba (0.38) and Pb-Sb (0.45), indicating that Pb was contributed preferentially by combustion process in the small particles. (lines 16-20 on page 14)

8th comment

2.8 P13976 Line 22: “Ti” can’t be found in PC2 of coarse particles in Table 3. It should be “Pb”

Author’s response:

In the revised manuscript, we have deleted “Ti” in the sentence of “road dust (associated with Na….)”. (lines 8-9 on page 15)

9th comment

2.9 P13976 Line 20-25: Zn and Pb had similar loadings in PC1 of coarse and fine particles (See Table 3). Why isn’t gasoline emission a possible source in coarse particles?

Author’s response:

Thanks for the reviewer’s comment. As shown in Table 3, Zn and Pb exhibit moderate loading in PC2. Previously study suggested that Zn and Pb were detected together and they constituted up to 0.2 % of the total fresh diesel PM, which is consistent with that reported by Sharma et al. (2005); therefore PC1 was also likely contributed by diesel emissions. (lines 6-12 on page 15 and in Table 3)

10th comment

P13976 and P13977: What’s the reason for the assignment of gasoline emissions or/and diesel emissions in PCA results? It seems that the assignment is based on the loading of Pb and Zn. If so, please provide relative references.

Author’s response:

Thanks for the reviewer’s comment. The assignment for gasoline and diesel emissions is based on Pb and Zn loadings in PCA. If high/moderate loading was found for Pb only; thus we would say gasoline emission. However, high/moderate loadings were found for both Pb and Zn, indicating diesel emissions (Agarwal et al., 2014) (lines 9-18 on page 15)

11th comment

P13976 Line26-27: There is a high loading of Na in PC3 of fine particles. Is it possible that some particles are from sea salt?

Author’s response:

Thanks for the reviewer’s comment. We did agree the reviewer’s comment that Na is an abundant species in sea-salt aerosols, but in soluble form. In this study, most of Na

in fine PM had a low enrichment factor (<3.0), which is one order lower than that (20-70) of sea-salt aerosol measured over East China Sea (Hsu et al., 2010, Marine Chemistry). This indicates that Na in the tunnel seems to originate mainly from soil, but not from sea-salt.

12th comment

P13977 Line 10-13 and P13978 Line 15-24: In this paper, V catches my attention. The authors claim that V is mainly from combustion. However, O/I ratio and ErF of V are both low in this study. So, I'm doubt about the source of V and the use of V/Ni ratio as a fingerprinting ratio in Hsuehshan Tunnel.

Author's response:

It is well known that V and Ni are both indicators for heavy oil combustion with a V/Ni ratio of 3-4 (Hedberg et al., 2005; Mazzei et al., 2008). Moreover, combustion process from vehicle engines is an important source for particulate V and Ni, leading to declined V/Ni ratio of <2 (Qin et al., 1997; Watson et al., 2001). Natural source such as soil may be another source of V and Ni of V/Ni ~1.5 (Hsu et al., unpublished data). In this study, V/Ni ratio of <2 plus high EF (>10) for V and Ni in fine and submicron PM, indicating that they were both contributed by anthropogenic emissions. In coarse PM, V/Ni ratio (<2) was found; however, a low EF value (~2) for V and a high EF for Ni (>10) indicate that they were from different sources. V in coarse mode might be contributed by soil and Ni might be attributed to combustion sources. (lines 1-10 on page 18)

13th comment

P13979 Line 14-19: The authors mention that "In contrast to the La/Ce ratio: : :..soil and crustal materials". I can't get the same information from Table 5 because the values of La/Ce and La/Nd are both lower than that in soil and crustal materials. My suggestion is to delete Table 5 and relevant content.

Author's response:

As suggested, we have deleted Table 5 in the revised manuscript. Nevertheless, we just showed the La/Ce ratios to highlight Ce in Hsuehshan Tunnel might be contributed from vehicle fleets. (lines 19-25 on page 18 and lines 1-5 on page 19)

14th comment

the section of 3.5: for the same reason mentioned above, I suggest that it's better to delete the relevant content of EmF of PM and only present the EmF of elements.

Author's response:

The approach for estimating EmF of PM metals in this study could only be used in a closed system. Unfortunately, Hsuehshan Tunnel is not an ideal laboratory to study EmF because the exchange between outside-air and inside-air occurred during the sampling periods, especially, in July and August, resulting in underestimated EmF of airborne PM. Thus, we have omitted all the descriptions related EmF in the revised manuscript.

15th comment

P13982 Line 23-26: The description of elemental classification in summary is different from that in P13972 Line 24-29 and some elements, such as Mo and Pb, are difficult to be divided into different groups. My suggestion is to delete the classification in summary.

Author's response:

Thanks for the reviewer's comment. We have deleted the elemental classification in summary in the revised manuscript.

16th comment

3.1 Fig1.b: It's hard to get useful information from Fig1b. my suggestion is to redraw it.

Author's response:

Thanks for the reviewer's comment. Figure 1b shows the fractions of each metal in three different sized PM. The original Figure 1b used similarity of colors in the three size bins and made difficult to read. Thus, we have re-plotted Fig.1b in the revised manuscript.

17th comment

3.2 P13973 line10: suggest modifying "at the entrance" to "at the inlet site"

Author's response:

As suggested, "..at the entrance" has been changed to " at the inlet site". (line 7 on page 11)

18th comment

Table 2 is not a complete Table for losing PM<1. My suggestion is to remove Table2 to supplement.

Author's response:

Thanks for the reviewer's comment. We retain Table 2 in the revised manuscript to show correlation matrices of selected elements in coarse and fine PM. As for submicron PM, the correlation matrix of selected metals is shown in Table S3.

19th comment

Figure 5 is better to be removed to supplement.

Author's response:

Thanks for the reviewer's comment. In the revised manuscript, we still keep Figure 5 to illustrate the correlation and fingerprinting ratio of La/Ce as written on lines 17-25 on page 18 and lines 1-5 on page 19.

Anonymous Refree#3

General comment:

This manuscript entitled “Characteristics of Trace metals in Traffic-Derived Particles in Hsuehshan Tunnel, Taiwan: Size Distribution, Fingerprinting Metal Ratio, and Emission Factor” by Lin et al. mainly describes the PM metals in the 2nd longest tunnel in Asia. It is well reported and discussed what the authors found. In general, the paper is well organized and easy to follow. It is suitable for inclusion in Atmospheric Chemistry and Physics. The manuscript is scientifically sound and should be accepted for publication after moderate revision and address. The comments are in the following:

Author’s response:

We have followed the reviewer’s comments and revised this manuscript. The revised portion will be explained in details of the following response.

1st comment

P. 13971 Line 21-24. The abundance of submicron PM at the outlet site was due to enhancing carbonaceous PM. Do the authors have experimental data to support this hypothesis? If no, it should be removed.

Author’s response:

Thanks for the reviewer’s comment. We do not have any support for this possibility. Thus, we have removed this sentence in the revised manuscript.

2nd comment

P. 13980 line 1: The emission factor of PM was significantly lower than other studies. Is the ventilation system triggered during the sampling period? If so, how about the influence of ventilation on the estimated emission factor?

Author’s response:

Thanks for the reviewer’s comment. The ventilation system was operated during the four experimental periods, resulting in underestimated EmF values for both PM mass and metals. As suggested by other reviewers, we have omitted the section of “3.5 Emission factors of trace elements” in the revised manuscript.

3th comment

P. 13996. Please correct “Petrolium refining” to “petroleum refining”

Author's response:

Thanks for the reviewer's comment. We have deleted Table 5 in the revised manuscript and "Petroleum refining" has been also removed.

4th comment

Sb/Cu is an important ratio to trace the traffic-produced PM. However, the Sb/Cu ratio in this study is lower especially when compared with those in US. The authors should clarify this reason.

Author's response:

The reason for the lower Cu/Sb ratios in Hsuehshan Tunnel is written in the text (lines 9-17 on page 17). The previous study indicated that Japanese car had Sb/Cu ratios ranging from 0.05-0.11 which were lower than those of American vehicles. Nevertheless, we import lots of cars (almost half of the total vehicles in Taiwan) from Japan, and the abundance of Japanese car in Taiwan may result in the lower ratio of Sb/Cu.

5th comment

P 13998. The resolution of Figure 1(b) is very poor. Please replot this figure.

Author's response:

Thanks for the reviewer's comment. In the revised manuscript, we have re-plotted the new Figure 1(b) and improved its quality and resolution.

6th comment

6. Please describe the temperature and CO concentration during the sampling period. It is very important information, whether the ventilation system is triggered or not.

Author's response:

According to the monitoring data provided by Taiwan Area National Freeway Bureau, the 1-hour average CO concentrations at these stations never exceeded 50 ppm, but temperature frequently exceeded 40°C, especially, in July and August. This suggests that the ventilation system was triggered due to high temperature, resulting in underestimation of EmF. As suggested by other two reviewers, we have deleted all the descriptions of EmF in the revised manuscript.

7th comment

Is this the only one paper for estimated emission factor on Hsuehshan Tunnel? If not, please cite all the related paper in this manuscript.

Author's response:

In fact, this study is not only one work for estimating EmF of PM inside Hsuehshan, but is the first one for PM metals. Because underestimated EmF is due to the exchange between inside-air and outside-air, all the descriptions of EmF have been removed as suggested by other reviewers.