Response to Reviewer's Comment

(Manuscript No. acp-2014-359)

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.