Response to the Referees' comments

Referee #1

Atmospheric speciated mercury concentrations on an island between China and Korea: sources and transport pathways By Lee et al., 2015

1. **Page 32932 Line 25, suggest to discuss vegetation uptake, e.g. rice (Zhang et al., 2010, EHP)**

   We have added a discussion regarding possible Hg exposure from rice consumption as well as fish consumption in the revised manuscript. While we agree on that rice consumption is a possible exposure pathway of Hg, there has been a lot of research suggesting that fish consumption is the major factor for Hg level in human. We have added the following sentences.

   "Fish consumption has been considered to be the major exposure pathway of Hg for humans (Mergler et al., 2007; UNEP, 2013). In Korea, You et al. (2012) showed that MeHg concentrations in blood were affected by fish consumption as well as by gender difference. However, rice consumption was also found to be the predominant pathway of MeHg exposure for the inhabitants residing in a highly contaminated area of China (Zhang et al., 2010)."

2. **Page 32933 Line 5, this might not be true in various regions especially at coastal sites due to the Br reactions.**

   We are uncertain what this comment is referring to.

3. **Line 15, suggest to read and cite Gustin et al., 2015 ACP overview paper**

   We mentioned the uncertainty associated with the KCl denuder method for GOM and PBM measurements in section of 2.2 (Sampling and analysis) in the original manuscript, but in response to the reviewer's opinion, we have added the following sentences in the Introduction in the revised manuscript.

   "It is typically assumed that GOM comprises $HgCl_2$, $HgBr_2$, HgO, $Hg(NO_3)_2$, and $HgSO_4$. However, the sampling method including the use of a KCl denuder has been shown to be subject to interferences from ozone, water vapor and possibly other compounds (Lyman et al. 2010; Talbot et al., 2011; Jeff et al., 2014; Finley et al., 2013; Gustin et al., 2013; Huang et al., 2013; McClure et al., 2014), and it also should be noted that the different Hg(II) compounds have different collection efficiencies by the KCl coated denuder (Gustin et al., 2015)."

4. Line 21, there are some preliminary conclusions in Subir et al., 2011 AE

In Subir et al. (2011), they mentioned that there are several factors that lead to uncertainties in the mercury reaction rate constants and atmospheric concentrations of reacting chemicals. Given the relatively high abundance of ozone in the atmosphere, it is plausible that it plays an important role in Hg^0(g) oxidation. Oxidation reactions with atomic halogens are often significant in the marine boundary layer, but it may be insignificant in urban and remote areas due to the low concentration of atomic halogens. It is also apparent that various natural surfaces and atmospheric heterogeneity play an important role in the oxidation of gaseous mercury. We are going to slightly change the sentences, as follows.

"In the atmosphere, Hg species can be interconverted through various redox reactions. It is known that GOM can be produced by homogeneous and heterogeneous reactions of GEM with O_3, OH, and Br/BrO (Hedgecock and Pirrone, 2004; Obrist et al., 2011; Subir et al., 2011), but there is no consensus on which oxidants are most important under which environmental conditions."

5. Line 25, Rutter and Schuaer,. 2007 AE and ES&T

We have added the reference. Thank you.

6. Page 32934 Line 2, reference needed.

We have added a reference.

7. Line 5, west of China?

We have revised to "east of China"

8. Line 6-11, please reword, Hg blood concentrations are mainly from fish consumption, and where the fish was caught in Korea? Sea of Japan? East China Sea? If so, why we concern the ambient air Hg concentrations in Seoul area?

In Korea the self-sufficiency rate of fishery products was 76.8% in 2013 according to the Ministry of Oceans and Fisheries of Korea (www.mof.go.kr/statPortal); therefore, it is reasonable to be concerned with atmospheric Hg concentrations in Korea as the first step in decreases the Hg concentration in blood of Koreans. In addition, atmospheric mercury is transported over a large scale, which connects the boundary layers of the Sea of Japan, East China Sea, and inland Korea. To be clear in this study, atmospheric Hg concentrations were measured on an island located between China and inland Korea, not in the Seoul area.

9. Section 2.1, what is the major wind direction at this site?

The major wind direction is from south to west as indicated in wind rose below.

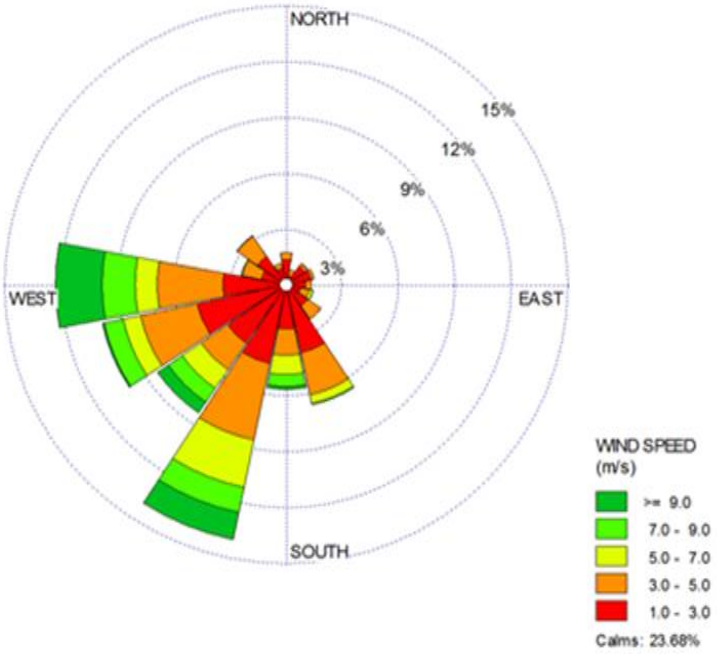

Fig. R1. Wind rose for the whole sampling period.

10. Page 32935, how that is possible using Tekran 2537B to measure TGM? GOM will loss in the line upstream of the gold traps.

A Tekran 2537 will collect and measure TGM if GOM is able to pass through the inlet to the instrument and the gold traps are not passivated. The sampling line and inlet were maintained at 50^{o}C to prevent the GOM sorption, but we agree on that there is a possibility that some of GOM may be sorbed in the line upstream of the gold traps. However, it is typically assumed that Tekran 2537 can collect and analyze TGM in most of studies (Temme et al., 2002; Gustin et al., 2013; Han et al., 2014, Zhang et al., 2015). In any case since GOM concentrations are low relative to GEM, any loss of GOM will not impact the reported TGM concentration. This statement is contained in the revised manuscript.

11. Line 20-29, this is not a way to write scientific article, the authors cited Edgerton 2015 conference presentation. I cannot find this manuscript or any detail information of this study online. Therefore, I do not think this study can support the statement here. I understand the uncertainties of GOM and PBM measurements using KCl denuder and filter

are huge; however, the core of this study is to discuss the species measured by this high uncertain technology. The authors should discuss these uncertainties in detail and investigate or explain how these uncertainties will impact their results and conclusions. I do not see anything like this in the entire manuscript.

Edgerton presented his results in ICMGP, 2015 and if this reference is not appropriate we will change it to "personal communication".

We acknowledge that there are uncertainties associated with the measurement technique used in this study. As we mentioned in the manuscript, it has been shown that the KCl denuder method is subject to interferences from ozone and water vapor. Gustin's group proposed an alternative method of ion exchange surrogate surface and nylon filter and found the huge discrepancy between the measurement of the KCl method and the filter method. However, we believe that approach can also be biased because GEM sorption, capture of PBM particles, and dew that may collect on the surrogate surface. The nylon filter pack and ion exchange filter pack methods used by Huang et al. (2013) also have potential interferences due to PBM collection and potential chemical reactions occurring on the filter surface due to the long sampling days (14 days). Gustin's group used a manifold to assess GOM and PBM accuracy in RAMIX using a GOM permeation source, which was calibrated by the same equipment being evaluated (Gustin et al., 2013). Also, we are skeptical that the permeation tube can maintain a constant emission rate due to the adsorption on the chamber or tubing wall and conversion to GEM on surfaces.

While we agree on that the current Tekran speciation system likely has a problem with GOM measurements, we also believe that no universally accepted better method has been developed yet. Historically, many measurements of GOM made with the KCl denuder method have been successfully interpreted, at least qualitatively. The Tekran speciation system has been proven to produce reliable and physically meaningful results including the fact that high GOM and PBM concentrations were observed where reactive halogen chemistry was favorable (Chand et al., 2008) and that elevated PBM/GOM was measured from biomass fires (Wang et al., 2010). Rutter et al. (2009) estimated the local source contribution to each Hg species based on RM:GEM ratio even at plume event maxima.

In response to this comment, we re-calculated GOM concentration using the empirical equation developed by McClure et al. (2014), and re-analyzed one of the important findings of this study, gas-particle partitioning. We re-calculated K_p (please look at the response to the comment 15) with re-calculated GOM concentrations. Since McClure et al. (2014) suggested the equation

(RH=0.63 GOM loss % + 18.1) at RH of 21 to 62%, we re-calculated GOM concentration measured only when RH was from 20 to 65%. Then, we compared the multi-linear relationship between re-calculated K_p and original K_p. As shown below, the re-calculated K_p is not different from the original K_p (Fig. R1). Therefore, we believe that the GOM concentrations reported in this study do not cause significant problems on data analysis, interpretation, and subsequent findings although they might be underestimated at high RH and high ozone concentration.

We already included a paragraph on possible uncertainties caused by the denuder system in the original manuscript. In response to this comment, we have included the results using re-calculated GOM concentration generated by the equation derived by McClure et al. (2014), and have provided the relevant figures (Fig. R2 shown below) in a supplementary file as Fig. 2S.

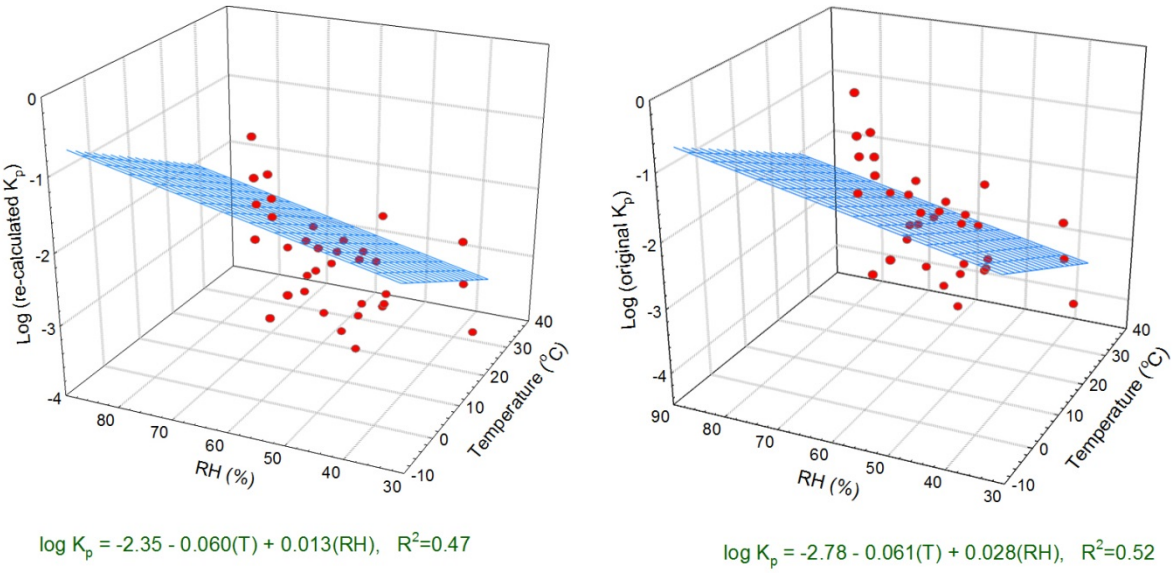

Fig. R2. Comparison of K_p using re-calculated GOM concentration (left) with K_p using uncorrected GOM concentration (right). Data collected when RH was out of 20~65% were excluded.

12. Page 32937 Line 15 can 200/500 m height separate regional and local transport? How? Any references to support this hypothesis? What is average PBL at this site?

Mixing depth ranged from 500 to 1000 m at the sampling site during the whole sampling period. The starting height should be representative of the mixing height of the boundary layer, and most studies computed back trajectories at a single start height of 500 m to depict regional transport

(Han et al., 2007; Zhang et al., 2015). For depicting the local transport, an arrival height of 100 ~200 m can be used (Han et al., 2005). In order to describe the long-range transport in continental or greater scale, a higher starting height such as 1000 m has been chosen (Han et al., 2004; Fu et al., 2011, 2012a, b). Weiss-Penzias et al. (2011) used three altitudes including 100, 300, and 500 m to identify the potential local, regional, and/or global sources of GOM in the Southeast US. However, there is always an error by choosing a starting point since there are differences between the model topography and the real topography, making the selection of a starting height difficult. Even though the initial trajectory position error may be small the final position error can be amplified (for backward trajectory) (Stohl, 1998). This type of resolution error can be estimated by starting several trajectories about the initial point (Seibert, 1993; Baumann and Stohl, 1997), and the divergence of these trajectories will give an estimate of the uncertainty due to divergence in the flow field. In most cases, the ensembles stayed close together (Han, 2003).

In this study, we used two starting heights together to describe the local and the regional transport meteorological pattern, and believe that the arrival heights of 200 and 500 m are appropriate. We did not separately use 200 m for local and 500 m for regional transport, but used both starting heights together. In order to clear up any confusion, we have rephrased the sentence as follows.

"...and the arrival heights of both 200 and 500 m were used to describe the local and the regional transport meteorological pattern."

13. PSCF section, how did you select weighted number? Did you evaluate these numbers in Asia?

We used the same weighting method as in many other studies (Fu et al., 2011; Han et al., 2007; Polissar et al., 2001a,b) to adjust for a small number of trajectory endpoints in grid cell. This arbitrary weight function does not depend on the location of study.

14. Page 32939 line 15, you only have couple weeks data for a month or even less, how can they represent seasonal variation?

In response to this comment, we have deleted the seasonal terms including spring, summer, fall, and winter. Instead, we are going to replace them with the corresponding month in the revised manuscript.

"When the data were grouped into three categories including the first (Apr., 2013, May, 2013, Mar., 2014, May, 2014), the second (Aug, 2013, Aug., 2014.), and the third (Jan., 2013, Feb., 2013) periods, both TGM (ANOVA/Tukey test, p-value<0.001) and PBM (p-value=0.024, Kruska-

Wallis test) had the highest concentrations in cold period ((Jan., 2013, Feb., 2013) while there was no statistical difference in GOM concentrations among different categories (p-value= 0.288, Kruskal-Wallis test).”

15. Page 32941 line 13 Eq 5, instead of using GOM/PBM ratio, why not using Kp to do the linear regression? In this way, I cannot compare with previous studies and PM2.5 impacts are ignored. In some places the authors use R, and in other places they use R2, in some places they only show P without R, why?

We did not directly use K_p because the total ambient aerosol mass concentration (μg m^{-3}) was not measured; however, we obtained PM_{10} concentration measured at the nearest national air quality monitoring station. If we assume that PM_{10} concentration can be representative of the total ambient aerosol mass, K_p can be used. When we used K_p instead of PBM/GOM ratio the coefficient of determination, R^2 increased to 0.29 (R=0.54) (Fig. R3 shown below). We think that this increase was due to the use of PM_{10} concentration, and this result more strongly suggests the significance of gas-particle partitioning.

The correlation coefficient, R is used to identify whether there is statistical correlation and dependence between X and Y or not while the coefficient of determination, R^2 indicates how well data fit a statistical model, identifying whether the dependent variable, Y is statistically explained by the independent variable, X. Therefore, we believe that both R and R^2 are appropriate and have added “R^2” in the revised manuscript.

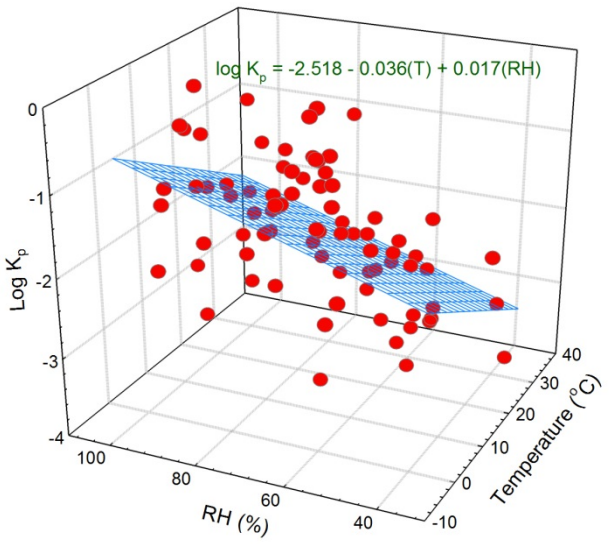

Fig. R3. The gas-particle partitioning coefficient, K_p, related to atmospheric temperature and relative humidity (RH) (n=81).

16. **Page 32942 Line 17-24, CPF can only explain local sources not regional transport. Be care here ! I understand that the authors use back trajectories to support their conclusions based on CPF, but I suggest to delete these regional transport statements in this section.**

We agree with the Referee. We have deleted the regional transport statement in the revised manuscript.

"CPF plot shows that the top 25% TGM concentrations were associated with winds from the NNW and eastern direction, pointing towards northeastern China and inland Korean sources; however, when the criterion was set to the top 10% the winds from NNW became less important and the sources located in southern and eastern areas from the sampling site were identified as an important source direction (Fig. 5)."

17. **Page 32944 line 5, again CPF has its limitation**

We have revised this as follows.

"According to the CPF results, the winds from NW and NE of the sampling site were responsible for the elevated PBM concentrations while easterly winds pointing words inland Korea were associated with increased GOM concentrations."

18. Page 20, I do not think using GOM/PBM ratio to check long range transport is a good method. If wet deposition occurs during transport, the ratio will be dramatically changed

We did not use a certain criterion of GOM/PBM ratio to identify the local vs. long-range transport. Instead, we are looking at the decreasing or increasing trend of the GOM/PBM ratio. Because GOM has a shorter atmospheric residence time than PBM due to the higher dry and wet deposition velocities than PBM, the ratio of GOM/PBM can be used as an indicator to identify the relative importance of local sources relative to long-range transport. Therefore, if wet deposition occurs during transport, it would cause a decreased ratio of GOM/PBM, and if the pollutants transport is longer range the ratio of GOM/PBM would decrease due to the possible wet and dry deposition during long transport. To conclude, the ratio of GOM/PBM changes due to transformation mechanisms and removal which is likely to decrease if the pollutant transport distance increases. As the referee indicated, if wet deposition occurs during transport the ratio of GOM/PBM will decrease, which is a key point of using the GOM/PBM ratio to indicate long-range transport. Lynam and Keeler (2005) also found that high GOM/PBM was observed with influences from local sources and low GOM/PBM ratio appeared with influence from regional sources in Detroit. In Korea, Kim et al. (2009) also found the significant increase of the PBM/GOM ratio during the high PM2.5 concentration events caused by regional transport from China.

In response to this comment, we have added more discussion about the result, and compare our result with other studies including Lynam and Keeler (2005) and Kim et al. (2009).

References

Baumann, K. and Stohl, A.: Validation of a long-range trajectory model using gas balloon tracks from the Gordon Bennet Cup 95, J. of Appl. Meteo., 36, 711-720, 1997.

Chand, D., Jaffe, D., Prestbo, E., Swartzendruber, P.C., Hafnenr, W., Weiss-Penzias, P.., Kato, S., Takami, A., Hatakeyama, S., and Kajii, Y.: Reactive and particulate mercury in the Asian marine boundary layer, Atmos. Environ., 42, 7988-7996, 2008.

Fu, X., Feng, X., Qiu, G., Shang, L., and Zhang, h.: Speciated atmospheric mercury and its potential source in Guiyang, China, Atmos. Environ, 45, 4205-4212, 2011.

Fu, X.W., Feng, X., Liang, P., Deliger, Zhang, H., Ji, J., and Liu, P.: Temporal trend and sources of speciated atmospheric mercury at Waliguan GAW station, Northwestern China, Atmos. Chem. Phys., 12, 1951-1964, 2012a.

Fu, X.W., Feng, X., Shang, L.H., Wang, S.F., and Zhang, H.: Two years of measurements of atmospheric total gaseous mercury (TGM) at a remote site in Mt. Changbai area, Northeastern China, Atmos. Chem. Phys., 12, 4215-4226, 2012b

Gustin, M.S., Huang, J., Miller, M.B., Peterson, C., Jaffe, D.A., Ambrose, J., Finley, B.D., Lyman, S.N., Call, K., Talbot, R., Feddersen, D.,, Mao, H. and Lindberg, S.E.: Do we understand what the mercury speciation instruments are actually measuring? Results of RAMIX. Environ. Sci. Technol. 47(13), 7295-7306, 2013.

Gustin, M.S., Amos, H.M., Huang, J., Miller, M.B., and Heidecorn, K.; Measuring and modeling mercury in the atmosphere: a critical review, Atmos. Chem. Phys., 15, 5697-5713, 2015.

Han, Y.J.: Mercury in New York State: Concentrations and source identification using hybrid receptor modeling, Ph.D. Dissertation, Clarkson University, Potsdam, NY, USA, 2003.

Han, Y.J., Kim, J.E., Kim, P.R., Kim, W.J., Yi, S.M., Seo, Y.S., and Kim, S.H.: General trends of atmospheric mercury concentrations in urban and rural areas in Korea and characteristics of high-concentration events, Atmos. Environ., 94, 754-764, 2014.

Huang, J., Miller, M.B., Weiss-Penzias, P. and Gustin, M.S.: Comparison of gaseous oxidized Hg measured by KCl-coated denuders, and nylon and cation exchange membranes. Environ. Sci. Technol., 47(13), 7307-7316, 2013.

Kim, S.H., Han, Y.J., Holsen, T.M., and Yi, S.M.: Characteristics of atmospheric speciated mercury concentrations (TGM, Hg(II) and Hg(p) in Seoul, Korea, Atmos. Environ., 43(20), 3267-3274, 2009.

Lynam, M. M. and Keeler, G. J.: Automated speciated mercury measurements in Michigan, Environ. Sci. Technol., 39, 9253-9562, 2005.

McClure, C.D., Jaffe, D.A. and Edgerton, E.S.: Evaluation of the KCl denuder method for gaseous oxidized mercury using $HgBr_2$ at an In-Service AMNet site, Environ. Sci. Technol., 48, 11437-11444, 2014.

Polissar, A.V., Hopke, P.K. and Harris, J.M.: Source regions for atmospheric aerosol measured at

Barrow, Alaska, Environ. Sci. Technol., 35, 4214–4226, 2001.

Polissar, A.V., Hopke, P.K. and Poirot, R.L.: Atmospheric aerosol over Vermont: Chemical composition and sources, Environ. Sci. Technol., 35, 4604–4621, 2001.

Rutter, A.P. and Schauer, J.J.: The effect of temperature on the gas-particle partitioning of reactive mercury in atmospheric aerosols, Atmos. Environ., 41, 8647-8657, 2007a

Rutter, A.P. and Schauer, J.J.: The impact of aerosol composition on the particle to gas partitioning of reactive mercury, Environ. Sci. Technol., 41(11), 3934-3939, 2007b

Rutter, A.P., Snyder, D.C., Stone, E.A., Schauer, J.J., Gonzalez-Abraham, R., Molina, L.T., Márquez, C., Cárdenas, B, and de Foy, B.: In situ measurements of speciated atmospheric mercury and the identification of source regions in the Mexico City metropolitan area, Atmos. Chem. Phys., 9, 207-220, 2009.

Stohl, A.: Computation, accuracy and applications of trajectories- A review and bibliography, Atmos. Environ., 32(6), 947-966, 1998.

Subir, M., Ariya, P. A., and Dastoor, A. P.: A review of uncertainties in atmospheric modeling of mercury chemistry I. Uncertainties in existing kinetic parameters–Fundamental limitations and the importance of heterogeneous chemistry, Atmos. Environ., 45(32), 5664-5676, 2011.

Temme, C., Einax, Jr.., W., Ebinghaus, R., and Schroeder, W.H.: Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the South Atlantic Ocean during polar summer, Environ. Sci. Technol., 37, 22-31, 2002

Wang, Y., Hunag, J., Zananski, T.J., Hopke, P.K., and Holsen, T.M.: Impacts of the Canadian forest fires on atmospheric mercury and carbonaceous particles in Northern New York, Environ. Sci. Technol., 2010, 44, 8435-8440, 2010.

Wang, S., Holsen, T.M., Huang, J. and Han, Y.J.: Evaluation of various methods to measure particulate bound mercury and associated artifacts, Atmos. Chem. Phys. Discuss. 13, 8585-8614, 2013.

Weiss-Penzias, P.S., Gustin, M.S., Lyman, S.N.: Sources of gaseous oxidized mercury and mercury dry deposition at two southeastern U.S. sites, Atmos. Environ., 45(27), 4569-4579, 2011.

Zhang, H., Feng, X., Larssen, T., Qiu, G., and Vogt, R.D.: In inland China, rice, rather than fish, is the

major pathway for methylmercury exposure, Environmental Health Perspectives, 118, 1183-1188, 2010.

Zhang, H., Fu, X.W., Lin, C.-J., Wang, X., and Feng, X.B.: Observation and analysis of speciated atmospheric mercury in Shangri-La, Tibetan Plateau, China, Atmos. Chem. Phys., 15, 653-665, 2015.