

## ***Interactive comment on “Characteristics of atmospheric mercury deposition and size-fractionated particulate mercury in urban Nanjing, China” by J. Zhu et al.***

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We thank two referees for the positive comments and suggestions. In our response, we have addressed all of the concerns of the reviewers and revised the paper accordingly.

Reply to Referee #2:

Q: This manuscript presents result from a nine months study on mercury levels in precipitation and size fraction of particulate mercury. This ms is very descriptive and very obscure sometimes. This manuscript is really difficult to read and there are several useless parts. A significant effort of synthesis should be made. The experimental

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section is very weak and lots of very important and basic details are missing. This naturally led to a certain degree of doubt on the quality of the measurements which is re-inforced by the fact that some samples were contaminated due to sample handling. The scientific discussion is not very deep, and I do not see any new or original results in the present study. I also recommend detailed correction by a native English speaker.

Re: To the best of our knowledge this work is the first comprehensive field measurements study of atmospheric mercury deposition and particulate mercury in the Yangtze River Delta (YRD) urban region which is one of most industrialized and urbanized regions in China. Moreover, nine size fractions of particle were analyzed to reveal the size distribution of particulate mercury in detail. The detail methods during experiment have been added in Section 2.1, which all followed EPA standard. Detail information about that could be found in following answers to corresponding questions. Some grammatical and expression problems in our manuscript have been corrected.

Page 28311 Q: Line 1 : “persistent” is not appropriate for Hg which is not degradable per se, because it is an element . Persistent is used for organic molecules. In the case of mercury as for other metal, persistence is obvious.

Re: We have deleted “and persistent”.

Q: “pollutant”: do not forget that Hg is also a compound that is emitted by natural sources.

Re: I think pollutant is chemical compound accumulated in atmosphere which will pose harm to environment or ecosystem no matter it emitted by anthropogenic sources or natural sources.

Q: Line 2: “ecology” is a discipline.

Re: We have changed “ecology” to “ecosystem”.

Q: Negative effect are not provided via the bioaccumulation only but also by biomagnification and toxic and ecotoxic effects.

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Re: We have changed “via bioaccumulation” to “via bioaccumulation and biomagnification”

Q: Line 5-7: I do not agree with your definition of atmospheric mercury. Please revise it. RGM and HgP are not chemical forms but are operationally defined by Tekran users.

Re: I think this is one of classifications for atmospheric mercury. GEM, RGM and HgP are three exist forms in atmosphere and RGM includes kinds of chemical forms such as HgCl<sub>2</sub>, HgBr<sub>2</sub>, HgOBr and so on. A lot of high-impact papers (Lindberg et al., 2002; Jaffe et al., 2005; Landis et al., 2002; Seigneur et al., 2004; Grigal 2002) studying on atmospheric mercury used this classification. There is no doubt other reasonable classifications are acceptable.

Q: Line 11. Fu et al 2010 is self-citation, there are earlier reference dealing with deposition velocity of divalent species.

Re: We don't think Fu et al., 2010 is self-citation. More references about mercury deposition were added there.

Q: Line 11 sentence “atmospheric deposition is (: : :) the main process for scavenging atmospheric mercury”. I do not understand. What could be other processes?

Re: We have changed “main” to “only”.

Q: Line 15: Consider revising this sentence which is not clear

Re: We have changed to “Atmospheric mercury deposition includes both wet and dry processes and each has their own characteristics”.

Q: Line 18: What is the meaning of “human influence”? Are you talking about anthropogenic sources?

Re: Change “human influence” to “anthropogenic sources”

Q: Line 21: The construction of this sentence is awkward.

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Re: Change to “In North America, more than 100 Mercury Deposition Network (MDN) sites are collecting data to examine long-term trends in mercury deposition at regional scales (Vanarsdale et al., 2005; Lai et al., 2007; Hall et al., 2005; Prestbo and Gay, 2009).”

P28312 Q: line15 is there any evidence of HgP association with ice crystal? More generally, the authors suggest that the nature of airborne particles that are likely to sustain Hg adsorption is known. I do not think that is it the case, those are assumptions.

Re: We have deleted “and ice crystal”

P28314 Q: line 7: precipitation sampler brand? Did you use MDN standard samplers? How does this sampler complies hg sampling requirements? Where blanks made? How? Results? There is a lack of analytical details Also some samples were contaminated during handling. What do you mean? How are sample generally handled? What kind of bottle? How is it cleaned? How is the sample preserved? Is the system refrigerated? Sampling frequency? Overflow handling? How was total Hg determined in details? Standard, reagents, blanks, replicates and all the basic information that is needed.

Re: Our precipitation sampler is Qingdao Xuanhui SCJ-300 which is made in China but its design and sampling method are almost same with Aerochemetrics rain collection devices. Blank was determined by ultrapure water which went through whole totally cleaned system. The blank was obviously under the detection limits (0.08 ng l<sup>-1</sup>) in all cases. Samples in spring were contaminated because CVAFS was broken then. Acid-cleaned Teflon bottles (volume: 100 mL) were used to collect precipitation for THg analysis. Bottles were stored at around 4°C in a refrigerator after sampling until analysis. As we mentioned in Section 2.1, we collected and changed to new bottles every five days if rained during those five days. Total mercury was determined by CVAFS followed US EPA Method 1631 (US EPA 2002). We will add more detail as mentioned above to Section 2.1 of our manuscript.

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Q: I understand that major ions were analyzed in the same sample? How can it be since most of the procedure for Hg collection use acid-cleaned bottles? How can Hg be preserved in your samples during collection without using acid (HCl or equivalent)? In that case, IC analysis is impossible using the same sample. How does a Wan Tang professional IC work?

Re: We collected two bottles simultaneously. One was for mercury analysis and the other was for major water-soluble ions analysis. The samples for mercury analysis were preserved by adding trace-metal grade HCl. However, there is no any other added in the samples for ions analysis. The work method of Professional IC Ion Chromatography can refer to Wang et al., *Journal of Environmental Sciences*, 2012, 24(8); Shon et al., *Atmospheric Environment*, 2012, 50. We will add these details to Section 2.1 of our manuscript.

Q: Why particle were sampled on random days? Is there any sampling strategy behind?

Re: As sampling days are limited, we regard random days as the averaged condition for that half a month.

Q: Same question that for Total Hg. How was Hg measured in those filters? Were blank available?

Re: Prior to analysis, the sampled filters were soaked in 10ml doubling diluted aqua regia solution separately and extracted using ultrasonication for 30 min, followed by digestion with a microwave digestion system for 2 hr to ensure that total mercury was dissolved. Then the extracted samples were analyzed using cold vapor atomic fluorescence spectrometer (CVAFS) followed EPA method 1631E (U.S. EPA, 2002) after cooled aside for 1 hr and added with ultrapure water to constant volume of 25ml. Blank filters went through the same handling process. We will add these details to Section 2.1 of our manuscript.

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Page 28315 Q: Line 19. You say that your estimate should be more accurate than the previous colleagues. Did you compare it ? is it based on a comparison of both approaches?

Re: We use the parameterization considering particle dry deposition velocity as a function of particle size and meteorological variables which are measured at our site. Particle size and meteorological condition affect deposition velocity a lot. However most of previous publication like Fang et al. (2012), Wang et al. (2006) and Lombard et al. (2011) use a constant deposition velocity for all HgP in different particle sizes and in any meteorological condition. We think our method is more scientific and accurate.

Page 28316 Q: line 4: should I understand that Hg in precipitation is only measured in 5 days samples? Please clarify because it is very confusing.

Re: No. We collected precipitation samples every 5 days if it rained during nine months. So the total mercury concentration we got was volume weighted mean concentration during every 5 days.

Q: Line 22-28: I do not understand your point

Re: We want to say that the correlation coefficient between THg concentration in precipitation and flux was lower than that between precipitation amount and flux. So the seasonal variability of mercury wet deposition flux was more strongly linked to precipitation amounts.

Page 28317 Q: line 9 and subsequents: I am not convinced that the relationship between precipitation and deposition flux suggest a continuous source of mercury during a precipitation event. This study does not show enough data during a precipitation event itself to prove it. The authors hypothesize GEM oxidation as a permanent source, but GEM oxidation rate are really slow (except with high bromine radicals concentrations). What about anthropogenic and natural sources of divalent Hg compounds?

Re: There is no doubt that anthropogenic sources of mercury compounds and particu-

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late mercury make a continuous contribution to the THg concentration in precipitation. However, these anthropogenic sources keep almost constant around the year. GEM oxidation is much higher in summer which can be used to explain a little higher THg concentration in precipitation in summer. Although GEM oxidation rate is really slow, GEM concentration in Nanjing is high to 9.9 ng/m<sup>3</sup>. We consider GEM oxidation as a part of contribution to the THg concentration in precipitation in summer.

Q: How can photochemistry enhance GEM oxidation? Please, give details.

Re: GEM oxidation by O<sub>3</sub> and OH are both photochemistry processes. Also photochemical activities of O<sub>3</sub> and OH production will enhance in summer and then GEM oxidation increases.

Q: By the way, high TGM peak provide more GEM which is not effectively scavenged. Where are provided those correlation coeff? How are they calculated?

Re: Those correlation coefficients are calculated among the THg concentration, precipitation amount and mercury wet deposition flux we measured. These correlation coefficients were provided in Paragraph 2 of Section 3.1.

Q: Line 18: "on the other hand (: : :)" the fact that a portion of atmospheric water-soluble Hg is not present in your THg wet deposited samples may be due to several reasons including sample collection and preservation: an important loss of THg will happen in your sample over a 5 days period; the vertical distribution of Hg(II) compounds may be heterogeneous; some divalent compounds might not be easily soluble if attached to some organics. I do not understand what is the continuous emission source.

Re: Continuous emission source is probably RGM and HgP from anthropogenic sources and GEM oxidation also makes a little contribution.

Page 28318 Q: line 2. I think that the fact that urban Japan is closed to urban china is not a major criterion explaining different Hg fluxes. Anthropogenic sources are likely

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the main driver.

Re: Yes, the wet deposition flux in urban Japan and urban China are quite different though they are close because of quite different anthropogenic sources.

Q: Line 7: more coal burning occur in Guiyang. Is there a scientific report/study about it? Is there any estimate of anthropogenic sources in those 3 cities? What is space heating? You state that Hg content in coal decreased through the last year? Is it a scientific fact? Are there any studies?

Re: Based on the estimate of anthropogenic sources from Streets et al., Atmos. Environ., 2005, 39 and the area of each province these three cities located, mercury emissions are 0.34kgkm<sup>-2</sup>yr<sup>-1</sup>, 0.22 kgkm<sup>-2</sup>yr<sup>-1</sup> and 0.19 kgkm<sup>-2</sup>yr<sup>-1</sup> in Changchun, Guiyang and Nanjing separately. It's obviously anthropogenic mercury emission is larger in Guiyang and Changchun than that in Nanjing. Space heating means coal burning for heating in cold season. This always occur in Northern China like Changchun and mountain areas like Guiyang due to terribly cold in winter. However, heating isn't needed in Nanjing and other Eastern and Southern China. Streets et al., Atmos. Environ., 2005, 39 and Zhang et al., Environ. Sci. Technol., 2012, 46 showed mercury content in coal measured in China in 1999 and 2008 separately. By comparison, mercury content in coal was lower in 2008 in most of provinces in China.

Q: In London, wet depositions are not comparable but largely higher than at Nanjing (0.7- 18.1 vs 15-45).

Re: No, the deposition in London was 15.–45.3 μg/year and 0.7-18.1 μg/month. Their units are different.

Q: Your conclusion (line 19-21) is very trivial and should be removed. You should also precise that depollution of power plant exhaust , pollutant dispersion are also important factors.

Re: Remove "This indicates that high population density and industrialization with large

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energy consumption may be important factors for environmental contamination at urban areas.”

Q: Line 23: I doubt that H<sup>+</sup> was measured.

Re: H<sup>+</sup> was calculated by pH of precipitation we measured.

Q: Line 25: among the ionic constituent: Author suggest that sulfate contribute the most? How is it calculated? Is it an average of all samples?

Re: It's calculated by the concentration of each ion in each precipitation sample. The average of sulfate concentration in all samples shows sulfate contributes the most.

Q: Line 27: this is not a trend really. How is it calculated? Is it an average, or do individual samples show the same pattern?

Re: It is an average condition of all precipitation samples.

Q: Page 28319: I do not understand how the total anions contribution is calculated.

Re: The contribution of anions and cations are calculated by the ratio of averaged concentration of anions and cations to total anions concentration.

Q: Line 2: how was the pH measured or calculated?

Re: pH was measured by pH meter.

Q: How is obtained the reference level provided by China Met Administration ? Is it consistent to compare both values?

Re: The reference level of acid rain was widely used in Chinese Meteorological Administration. It is defined as the acidity only considering the solution of CO<sub>2</sub> in atmosphere. We have deleted this reference level because it's not international standard.

Q: Your average pH is more alkaline, but I do not mean anything since a mean pH is a non-sense. Sulfate and nitrate should provide more acidity since there are associated with strong acids. Re: pH showed a basic characteristic of precipitation.

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Q: Line 6: better correlation between ions do not necessarily mean that there are associated. This approach is not scientifically sounded. Please check the corresponding literature.

Re: Better correlation between ions indicates similar variation of these two ions and these two ions probably came from the same air mass and source area. This method was also used in Caffrey et al., Atmos. Chem. Phys. 2010,10; Gratz et al., Sci. Total Environ., 2013, 448 which can be referred.

Q: Line 14-18. I do not follow this discussion about marine sources of Hg. This is really unclear. From what I know, oceans are not thought to be an important source of divalent Hg.

Re: Yes, our analysis here indicated little contribution to mercury deposition in Nanjing from sea salt aerosols. However, other studies like Engle et al., Appl. Geochem., 2008, 23 and affrey et al., Atmos. Chem. Phys. 2010,10 showed significantly correlation between sea salt aerosol deposition and mercury deposition in coastal area.

Page 28320 Q: Line 2 Sources of carboxylic acids of low molecular weight are the direct emissions from burned biomass, automotive vehicles, ants, vegetation and formation through secondary chemical transformations in the atmosphere from biogenic and/or anthropogenic precursors.

Re: Yes, formate comes from typical biogenic source as well as anthropogenic sources include vehicle emissions and the combustion of wood and agricultural debris. However many studies (Keene and Galloway, 1988; Galloway and Keene, 1989; Pena et al., 2002; Avery et al., 2001, 2006) indicated that commonly the concentrations of organic acids emitted directly from vegetation and formed secondarily in the atmosphere increase during the spring and summer plant growing seasons. Most of our precipitation samples were collected in summer, so we regard vegetation as the most important source for formate.

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Q: Line 10-14: this is out of scope and it is not relevant with the present results.

Re: These indicate natural sources like soil surface and vegetation are important source for atmospheric mercury in Nanjing and local re-volatilized mercury from natural sources are probably very large.

Q: Line 27 and fig 2: how many samples were used to calculate the monthly value?

Re: Totally 17 samples were used to calculate the characteristic of HgP.

Page 28321: Q: line 4-14: Should I understand that TGM was measured? Where does it come from? Please remove all this paragraph or change your ms by presenting TGM values.

Re: Yes, TGM was measured in our site simultaneously. The data and sample method was published in Zhu et al. (2012). I will add some explanation in Section 2.1 Sampling site and methods.

Q: Figure 2: what does the percentage on the horizontal axis mean?

Re: Do you mean the percentage in Figure 3? That indicates the percentage of mass in each size stage to total mass

Q: Line 23: what do you mean with "a small peak"?

Re: We have changed "a small peak" to "a lower peak".

Page 28322 Q: line 6-11: The detailed explanation is not needed here.

Re: We think this explanation is needed to prove that gas-particle partitioning of atmospheric mercury actively occurred on fine particles during the cold season.

Page 28323 Q: line 10: What is "morey"?

Re: We have changed "Morey" to "More"

Q: Line 16: I do not understand why the concentration of HgP was estimated since you

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measured it.

Re: We measured HgP for three days semimonthly. However, we need hourly HgP concentration to estimate dry deposition combined with hourly deposition velocity calculated by meteorological condition. So we estimated HgP concentration in those days without measurement with hypothesis that the size distribution of HgP and mercury content in PM10 remained constant during the time period following the sample collection time window.

Q: type Table 1 : precipitation amount.

Re: We have changed "precipiation" to "precipitation"

Q: Page 28321 Line 24, "regarded" Page 28325 line 1: "mercury" Landis et al 2002 : page numbers are not correct

Re: We have changed "4524" to "4517"

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 28309, 2013.

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