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Discussions

Interactive comment on "Isotopic composition for source identification of mercury in atmospheric fine particles" *by* Q. Huang et al.

J.ÂăG. Wiederhold (Referee)

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Review of manuscript acp-2016-363 (published in ACP Discussions)

Title: Isotopic composition for source identification of mercury in atmospheric fine particles Authors: Q. Huang, J. B. Chen*, W. L. Huang, P. Q. Fu, B. Guinot, X. B. Feng, L. H. Shang, Z. H. Wang, Z. W. Wang, S. L. Yuan, H. M. Cai, L. F. Wei, and B. Yu

Reviewer: Jan Wiederhold (University of Vienna, Austria)

This manuscript presents Hg isotope data from atmospheric particles (PM2.5) collected over different seasons in Beijing (China). Together with additional geochemical (OC/EC, element concentrations) and meteorological data, the authors try to explain the observed seasonal Hg isotope variations in the particles by varying contribution of

different sources. The Hg isotope compositions of potential source materials (soils, industrial waste materials, coals etc.) were also measured and compared with the values of the collected PM2.5 particles. The topic of the study is very interesting and novel and it lies within the scope of ACP. The manuscript presents an impressive dataset and the quality of the analytical data is high. I congratulate the authors to their interesting study which has the potential to become an important landmark study for Hg isotope signatures in urban PBM. However, I believe that substantial revisions to the manuscript are necessary prior to a possible publication to provide missing information, to correct mistakes, to consider additional relevant publications, and to revise erroneous concepts and interpretations. Overall, I recommend major revisions with additional review. In the following, I will first highlight some general comments before providing a list of line comments referring to individual sections of the manuscript.

My first general comment refers to the important difference between mass-based and volume-based concentration data for atmospheric particles. The authors mostly discuss volume-based concentrations, but I believe that it would be more appropriate to report and consider mass-based concentrations in most parts of the results and discussion section. As further discussed below, some of the discussed correlations seem obvious to me (samples with more PM2.5 will of course also contain higher volume-based element contents) and I am rather surprised that some of these correlations (e.g., Fig 4a) are not better (suggesting significant differences in mass-based concentrations which should be discussed). I suggest starting with a discussion of the seasonal differences in the amount of PM2.5 and then in the following to report and compare only mass-based concentrations values, except when element fluxes are discussed. Please see line comments below for specific examples.

Secondly, I believe that there are still more details needed about some important aspects of the methodological procedures. I acknowledge that the authors have added some more information on the combustion of the filters in response to my previous quick access review. However, I still miss the crucial information how the PM2.5 content was determined (e.g., weighing of filters after drying/conditioning? upper particle size cutoff?) which represents the basis for all mass-based concentrations. In addition, it is not described how the PM2.5 samples were removed from the filters for the performed acid digests or whether a representative aliquot of the filters was cut out prior to combustion and used for the acid digests (which I guess was most likely the chosen approach).

Thirdly, I am very skeptical whether the performed calculations of enrichment factors using Al and the Upper Continental Crust (UCC) as reference points are really applicable to PM2.5 particles and also most of the source materials. The Al concentrations in the PM2.5 particles were very low (max. 15 ppm) suggesting that alumosilicate minerals did not represent a major component of the particles. This doesn′t exclude the presence of other mineral phases (such as carbonates from loess particles, Ca/Al >1 in all PM2.5 samples), but also indicates that organic matter probably constituted a major fraction of the PM2.5 particles. As further detailed below, I suggest re-thinking the performed calculation of enrichment factors.

My next general comment refers to the fact that some recently published studies were not considered by the authors. Most importantly, the study by Das et al. (2016, Elementa, doi:10.12952/journal.elementa.000098) reporting Hg isotope signatures of urban PBM from India should be considered and the data compared with the urban PBM samples reported here. In addition, in the context of Hg isotopes in GEM, the authors should consider the recent papers by Fu et al. (2016, ES&T, doi:10.1021/acs.est.6b00033) and Enrico et al. (2016, ES&T, doi:10.1021/acs.est.5b06058).

Moreover, I have the impression that some of the interpretations and conclusions presented in the manuscript are not sufficiently supported by the presented data and arguments (e.g., isotopic evidence for local anthropogenic sources). The observation that the Hg isotope signatures of PM2.5 samples are “consistent” with signatures of potential anthropogenic sources does not represent sufficient proof as long as it is not

demonstrated that other potential Hg sources (natural or non-local anthropogenic) are isotopically distinct. As further detailed below, I suggest re-wording and carefully toning down some of the interpretations and conclusions.

Furthermore, I believe that the authors should try to clarify and illustrate in a more detailed manner which new conclusions about atmospheric Hg cycling in urban environments can be drawn based on the presented Hg isotope data as opposed to previous studies investigating only elemental concentrations. Obviously, many applications of metal isotope ratios in environmental studies are still in an exploratory stage, but I believe that it is important to demonstrate the added value of isotopic data in comparison to more traditional study approaches.

Finally, there are many problems with tense forms in the manuscript. I tried to list many of them in my line comments below, but I probably missed some. In general, I suggest reporting all study-specific findings in past tense, in contrast to generally-accepted facts which should be reported in present tense. However, statements referring to figures and tables in the manuscript should be in present tense (e.g., “data are shown” instead of “data were shown”). Please check the appropriate use of tense forms throughout the manuscript and/or seek advice from a native English speaker (which I am not).

line comments:

l28: maybe better “more positive” instead of “significant positive”

l36: delete “biological” (is there non-biological toxicity?)

l38: Here and in many other places, please use present tense for generally accepted facts, whereas study-specific findings should be presented in past tense. Here: “has” instead of “had”.

l39: replace “including” with “:”

l42: “is assumed to be” instead of “can be” l51: I suggest citing review papers/chapters on Hg isotopes (Blum et al., Hintelmann et al., Yin et al., …) here instead of only some selected studies which do not give the full picture. You could potentially add a second sentence here referring specifically to previous studies on atmospheric samples, which would cover some of the listed papers but more would need to be added.

l53: The term “mainstream” is not clear in this context. Maybe replace with “primarily”?

l57: I think that there would be better citations for NVE (e.g., Schauble, 2007, GCA, doi:10.1016/j.gca.2007.02.004) and MIE (e.g., Buchachenko, 2009, Russ. Chem. Rev., doi:10.1070/RC2009v078n04ABEH003904 or 2013, J.Phys.Chem. B, doi:10.1021/jp308727w) of Hg isotopes.

l58: I think that more recent studies (both theoretical and experimental) have agreed on a slope for NVE of about 1.6. The statement “>1.5” also includes the higher theoretical values of >2 postulated in earlier papers (e.g., Estrade et al., 2009) which have no experimental support and were based on older compilations of nuclear charge radii which have been updated recently. Please see discussions in Wiederhold et al. (2010, ES&T, doi: 10.1021/es100205t), Ghosh et al. (2013, Chem. Geol., doi:10.1016/j.chemgeo.2012.01.008) or Eiler et al. (2014, Chem. Geol., doi:10.1016/j.chemgeo.2014.02.006) on this topic.

l59: “a” instead of “the”

l59: I suggest writing “mostly between 1.0 and 1.3” as slope for the MIE and, in addition, referring to more recent papers or reviews that discuss these numbers.

l68: This list is not complete anymore due to recent publications (e.g., Das et al., 2016, Fu et al., 2016, Enrico et al., 2016, see details above) and also some older ones are missing here (e.g., Zambardi et al., 2009; Demers et al., 2013).

l70: Check more recent papers for updated isotopic ranges of GEM.

l74: Why “More importantly,”? I suggest replacing this with “In addition,”.

l84: This would be the place to refer to and describe the findings of Das et al. (2016, see above) on Hg isotopes in PBM samples from an urban environment in India.

l89: add “metal” after “non-ferrous” (also in line 280)

l93: “carriers” instead of “carrier”

l93/94: I suggest changing the sentence to “If PM2.5 is emitted…”.

l99: “coupled” instead of “coupling”

l113: Here and in the following: In contrast to the names of months, the names of seasons are usually not capitalized (e.g., “summer” instead of “Summer”).

l115: delete the second “the”

l122: “is” instead of “was”

l125: I suggest stating here the air volume in m3 which is represented by one sample (24 h x flow rate). Did you weigh the filters before and after use to quantify the PM fraction? If yes, did you have to dry/condition them to correct for humidity differences? What is the upper cutoff of the collected particle fraction, i.e. did you had a pre-filter to exclude larger particles? You used very high flow rates, so bigger particles may well have entered the sampling system. In conclusion, please provide more details about the PM2.5 sampling procedure.

l126: Please specify what negligible means in this context (e.g., <1% of Hg in samples?).

l138: Please add “samples” after “topsoil”. Moreover, I would be interested to learn more about these “topsoil samples”. Are these “organic surface layers” (e.g., litter, O-horizons) or “mineral soil horizons” (e.g., Ah horizons). In simplified terms, are these samples dominantly organic or mineral material?

l140: How did you collect the “total suspended particle” sample and which size fraction does it represent?

l143: delete “the”

l148: delete “the”

l151: Why did you use 20% $SnCl_2$ for concentration measurements?

l56: “J. Wiederhold” did not provide any of these two standards. Joel Blum provides the UM-Almaden standard and NIST-3133 is available from NIST. I (Jan Wiederhold) only provide the “ETH Fluka” secondary standard which is mentioned in line 160, but which was not used in this study.

l162: add “a” after “via”

l165: “quartz” instead of “quarts” (also in line 168)

l169: I suggest adding “precleaned” before “at 500°C”. I assume that you didn′t do the capping at 500°C. . .

l170: I suggest clarifying this to “The sample tube was then placed into the large quartz tube of the furnace”.

l171: Do you mean “routine” instead of “route”?

l173: This doesn′t make sense. If there was indeed Hg(0) in the trap solutions which was not oxidized by the HNO_3, it would have been purged out during the combustion procedure. Thus, if you added BrCl afterwards, it could only serve the purpose of stabilizing the Hg(II) in solution, rather than oxidizing it.

l174: add “of” before “about”

l185: Didn′t you also use Tl for mass-bias correction in addition to standard-bracketing?

l189: Did you also measure 204Hg? The previous method paper (Huang et al., 2015, JAAS) included data for 204 and if you have these data, please add them to the manuscript. As you certainly know, data for 204 in parallel to 200 might be helpful

to better understand even-mass MIF.

l195: Please make sure to add permil signs to all values and their errors (here after “0.13”).

l196: How did you calculate the precision of the NIST data (bracketed against itself? with samples in between or not?).

l197: Here and in the following (e.g., l202): Please add permil signs to all isotope results. The permil sign is not a unit (such as mg/L) but a factor and the delta value is not correctly reported if you don′t add the permil sign.

l211: How do you know that the recoveries for the samples were in the acceptable range? As far as I can tell, you didn′t know the Hg concentrations of your PM2.5 samples prior to the combustion. If you saved a part of the filter and performed an acid digest on it, then please provide the necessary details. Otherwise, I don′t think that you can make a statement on recovery of your PM2.5 samples during the combustion step.

l212: On which sample material did you conduct the OC/EC analysis? Did you have to remove the particles from the filter prior to analysis? If yes, how was this achieved? If there was inorganic carbon in the samples (e.g., carbonate from loess particles), would this interfere with the OC/EC analysis?

l217: Please explain how you digested the PM2.5 samples. Did you cut out a part of the filter prior to combustion and digested it? If yes, did the HF dissolve the whole quartz fiber filter?

l218: I suggest replacing “run out” with “exhausted”.

l224: “are” instead of “were”.

l225: I don′t think that you explained in the methods section how you quantified the PM2.5 contents of your samples.

l227: If you discuss carbon concentrations of the PM2.5 samples, I would discuss primarily the mass-based values. In my view (although I am certainly not an expert in this field), I suggest that you first discuss the variations in the amount of PM2.5 (i.e. total mass of particles on the filter after 24 h sampling) and its seasonal variations. In the following, I would then primarily discuss mass-based concentrations to describe qualitative differences between the PM2.5 samples and only come back to volumetric values if you want to discuss total fluxes of Hg or other constituents.

l228-232: Based on these values, I can′t tell whether the described variations were due to the fact that the OC/EC contents of the particles varied or only the amount of particles (or both).

l234: This value means that the winter samples consisted of about 17 mass-% OC which probably means that about one third of the PM2.5 sample mass consisted of organic matter (using the crude approximation OM $\sim$ 2xOC). Some samples maybe consisted of up to 50% of organic matter. This needs to be considered in the interpretation of Hg content and other elemental concentrations and strongly questions the normalization to "upper continental crust" values for rocks (see further comments below).

l236: "discuss" instead of "discussed"

l236: Why did you choose EC values for the further discussion? In my (probably rather ignorant) view, the elemental carbon fraction of the total carbon is not necessarily important for the interaction with Hg or other metals which will bind to functional groups of organic matter, but much less to unreactive elemental carbon. In any case, you should present a better introduction into the different carbon fractions (total carbon, organic carbon, elemental carbon, black carbon, inorganic carbon, . . .) and what they represent.

l239: "are" instead of "were"

l244: "those" instead of "the" and add "a" after "From"

l250: In my view, if you discuss "Hg contents in atmospheric particles", then these should be mass-based values and not volumetric values. I don′t know the convention in atmospheric chemistry, but maybe "Hg load in atmospheric particles" could be used to compare volumetric concentrations from different sites?

l264: Please also consider the new data by Das et al. (reference see above) in this context. In general, I would keep the comparison to other studies rather short in the results section and save this for the discussion sections.

l266: "are shown" instead of "were showed"

l272: I suggest discussing the mass-based Hg contents in more detail and for instance comparing them with the OC contents. I wouldn′t be surprised if you find a correlation as if often observed in natural samples (e.g., Hg/C ratios in soils or sediments).

l289: "effects are" instead of "effect were"

l292: "is" instead of "was"

l295: Al is not an "insoluble" element but only somewhat less reactive compared with other elements during some mineral weathering reactions. As discussed above, I suggest removing the questionable normalization of the PM2.5 samples to the rock composition of the upper continental crust because these particles are very different and contain multiple constituents (e.g., organic matter, secondary minerals) which cannot be simply compared with primary minerals in igneous rocks. I acknowledge that discussing element concentration ratios relative to Al (or other "lithogenic" elements) might make sense in some cases to estimate mineral matter vs. non-mineral matter, but you need to state and consider the assumptions of this approach (Al as a potential tracer for mineral material in PM2.5). Al concentration varied by more than an order of magnitude for the PM2.5 samples (Table S3) and even several magnitudes for the source materials. Moreover, the maximum Al contents were only 16 ppm in the PM2.5 samples and 63 ppm in the source materials, questioning whether this element can serve as a good reference base for the normalization of dilution effects.

l296: This approach might have some usefulness in interpreting element contents in relatively coarse grained and mineral-matter dominated river sediments (e.g., Chen et al., 2014, G3), but I am not convinced that it can be easily adapted to atmospheric PM2.5 samples.

l300: “is” instead of “was”. In addition, the “UCC” is generally not a good reference point for “natural terrestrial reservoirs” when discussing mercury cycling in the environment which is often dominated by organic-matter-bound Hg. Moreover, I believe that the 50 ppb average value for “lithogenic” Hg (UCC) from the Rudnick&Gao compilation is actually very poorly-constrained and might be too high considering newer data (see e.g., discussion in Canil et al., 2015, Chem. Geol., doi: 10.1016/j.chemgeo.2014.12.029 or data on various rock reference materials from Marie et al., 2015, GGR, doi: 10.1111/j.1751-908X.2013.00254.x).

l302: This statement doesn′t make sense to me. Table S4 does not contain Hg concentrations. If you are referring to the Hg concentrations of topsoil samples in Table S2, then these are very variable and certainly dominated by Hg sources other than “lithogenic” alumosilicates. Thus, although higher Hg contents (or EFs) might indeed imply that the Hg is not originating from crustal rocks, this doesn′t prove a “strong anthropogenic contribution” because Hg in PM2.5 might have many “natural” (or at least “non-local industrial”) Hg sources other than the UCC. Normalizing metal concentrations in industrial waste materials such as sintering dust to UCC values is also not really useful in my view. If enrichment factors should be calculated, I would rather suggest to normalize element contents in urban atmospheric PM2.5 samples to contents in “pristine” atmospheric PM2.5 samples collected far away from local pollution sources. However, even this is probably difficult (if technically feasible at all) because of the different dominant constituents of the particles (e.g., mineral-matter vs. organic matter).

l306: Don′t get me wrong, I am totally convinced that the collected PM2.5 samples are strongly influenced by anthropogenic contributions, I am just not convinced by the presented argumentation.

l308: Maybe I am getting confused now, but isn′t it rather obvious that volumetric-based element concentrations correlate with the volumetric PM2.5 content or other elemental contents (more particles = higher volumetric element contents)? It seems actually surprising that you only get an r2 of 0.4 for the correlation of volumetric Hg and PM2.5. This implies that the mass-based Hg concentrations are varying over the seasons (see Table S1) which should be further explored and discussed in my view (and maybe also Hg/OC ratios etc.).

l310: “results” instead of “resulted”

l311/312: Again, I suggest discussing only element correlations on a mass basis.

l312: “show” instead of “showed”

l318: Again, I don′t doubt the anthropogenic contribution in PM2.5 but I believe that the calculation of EFs using Al and relative to the UCC is not meaningful and generates values which are not a realistic quantitative estimate of the true anthropogenic enrichment relative to “natural PM2.5”. These extremely high numbers seem to imply extreme anthropogenic enrichment effects whereas some of it can be simply explained with higher metal contents in natural organic matter compared with crustal rocks.

l319: What do you mean by “largely enriched”? Do you mean “strongly enriched”?

l320: What do you mean by “centralized human activities”? This term is not clear to me.

l323: add “a” before “large”

l323-335: This section illustrates a problematic tendency in the interpretation of the data. The finding that Hg isotope ratios are “consistent” with those of potential source materials is not sufficient to make strong statements about Hg sources. In order to establish a robust link between the Hg isotope data of the PM2.5 samples and specific anthropogenic Hg sources, you first need to show that other potential Hg sources (natural Hg and non-local anthropogenic Hg) exhibit contrasting signatures. Being “consistent” is not the same as identifying source materials based on isotopic differences. The wording here develops from “consistent” and “likely indicated” to “confirming these anthropogenic emission(s) as the major sources..” which is not appropriate in my view. Please carefully check your arguments and tone down interpretations where necessary.

l338: Please consider my critical comments about the Al normalization written above.

l350: Does “As a result” refer to the previously discussed PCA analysis? As far as I can tell, Hg isotope data were not included in the PCA analysis. How can you state with certainty that “the Hg isotope compositions suggested. . .” if you don′t know whether the measured Hg isotope signatures of the local anthropogenic sources are distinct from other potential sources?

l353: “are” instead of “were”

l355: Would you expect a linear relationship between delta-values and EFs based on stable isotope mixing theory? As you are certainly aware, mixing lines of delta values vs. concentrations are only linear if plotted with the inverse concentration (1/Hg).

l360: Please explain what the “EC/Al” ratio is supposed to show. Is this maybe a measure for the relative content of organic matter (or rather only certain C fractions) and mineral matter in the PM2.5 samples?

l369: “considerably” instead of “considerately”

l370: It appears that this “winter effect” on carbon contents is mainly apparent in OC and less in EC.

l373: Again, being “consistent” is not a strong support but only shows that it could be possible to explain the data in this way, without demonstrating that other explanations are not possible.

l375: What do you mean by “rapid” in this context?

l376: What is the relevance of the Zn/Al ratio for Hg cycling? Please add more explanations.

l382: “potentially” instead of “eventually”

l383: Again, does “lower contents of Hg” refer to mass-based on volume-based concentrations? I think that the mass-based Hg concentration were actually highest in winter.

l388: I think that the “higher EC content” in autumn is mainly seen in volume-based but not so much in mass-based contents.

l397-399: I don′t know the regulations for ACP, but in my opinion references to manuscripts “in preparation” should be removed.

l401: Another potential reference for light ïĄĎ199Hg of litter could be Jiskra et al. (EST, 2015, doi: 10.1021/acs.est.5b00742).

l404: Again, please try to explain the relevance of the Zn/Al ratio in the context of the studied samples.

l407: “occurring” instead of “occurred”

l408: “EC enrichment in Autumn particles” implies in my understanding that you talk about mass-based concentrations. However, this effect is only seen for volume-based concentrations and the average mass-based EC value for autumn is lower than for winter.

l412: add “which” before “displayed”

l418: “Much higher” than which other samples or reference points?

l421: Maybe add “or fractionation during atmospheric processing” after “contribution”

l428: Did these previous studies also report data on the PBM fraction which is relevant here?

l445: Can you add more information on these “background particles” and their assumed composition?

l445: “matter” instead of “matters”

l448: “process effects” instead of “processes effect”

l457: I suggest replacing “not induce significant” by “only induce very small” because the discussed processes have been in fact shown to cause small MIF by the NVE (see Smith et al., 2015 for precipitation and Wiederhold et al., 2010 for Hg(II)-thiol complexation)

l459: I think that this statement is only correct for MIF but not for MDF.

l462: add “a” before “possible”

l463: “Potentially” instead of “Eventually”

l467: “ratios” instead of “ratio”

l472: Maybe better “contrasting even-mass” instead of “even contrast”

l474: “lack” instead of “lank”

l476: I suggest adding “currently” after “is”

l481-482: Please consider my critical comments about enrichment factors and try to identify and explain better which additional new information can be deduced based on the Hg isotope data.

l483: I am not sure whether you can really rule out an influence of atmospheric processing on the measured Hg isotope data in PM2.5 particles.

l487-488: “predominant contributions” instead of “predominated contribution”

l489: Delete “the” and maybe add “probably” after “was”

l495: This link to “species-specific Hg” is an interesting point but it hasn′t be discussed before in the manuscript and would require more explanations in my view.

l496: “at” instead of “in a”

l707-709: I suggest removing the reference “in preparation”.

Figure 1: I suggest adding the information “n = 6” or “n = 5” into the 4 columns of the figure (in the caption or maybe below the words of the seasons?). Alternatively, you could also consider plotting all individual data points together with the mean and SD. I am not sure how meaningful 25th and 75th percentiles are in a dataset with n = 5 or 6. In addition, as mentioned above, I suggest using mass-based concentrations for EC and THg.

Figure 2: “analytical” instead of “analytic”

l756: I suggest adding “MIF during” after “or”

Figure 4: Please consider my comments above on mass-based vs. volume-based concentrations.

Figure 5: Please add more information about the relevance of “Co/Al” and “EC/Al” ratios in the context of Hg in PM2.5 particles.

Figure 6: Please consider my comment above on potential non-linearity in this plot when assuming a conservative two end-member mixing model.

Figure 7: What are the units for the Zn/Al ratios on the y-axis (maybe Zn in ng/g and Al in mg/kg?). Again, I suggest using mass-based EC concentrations for the x-axis.

SI, l34: “component” instead of “composition”. However, as written above I am not sure whether this approach should be transferred from river sediments to PM2.5 particles and industrial sources materials considering their large variations in Al concentrations.

SI, l37: Did you use the same units for all elements and Al (e.g., ng/g) or did you use different units such as given in Table S3?

SI, l64: Please explain what you mean by “petrological source contribution”? Maybe better “lithogenic”?

SI, l85: “were” instead of “are”

SI, Table S3: I suggest adding Hg and C into the table and check for (mass-based) elemental correlations. —end of review—

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