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Atmospheric Chemistry and Physics Discussions

Interactive comment on "4D dispersion of total gaseous mercury derived from a mining source: identification of criteria to assess risks related with high concentrations of atmospheric mercury" *by* José M. Esbrí et al.

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Dear Editor(s), thanks very much for driving this interesting (although somehow too long, true?) process of revision of our manuscript, which has received very interesting and important inputs aimed to improve its final quality. These are the responses to the last questions raised by reviewers. Some of them are comments, maybe not needed any response, but please tell us to provide responses to them if you consider it necessary. We think that we have properly answered the important concerns of this reviewer, which are also sincerely acknowledged by us; we particularly thanks his/hers

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positive comments on the quality of our work, and we are sure that the proposal of deriving the manuscript to another Journal can be interesting, but please consider the question of this work being a contribution to the Special Issue of this Journal devoted to the 2019 International Conference of Mercury as a Global Pollutant. This was our initial aim, and we got the go ahead of Prof. Ashu Dastoor, invited editor of this SI, for this idea. We have written our responses in red bellow the reviewer's comments, and we have indicated in blue the new texts added to the manuscript in the context of this revision. We have upload a supplement file with these colours differentation. This manuscript presents an experimental design using atmospheric Hg monitoring instruments to improve the characterization of a Hg point source over time and space. There is indeed some interesting data and discussion in the manuscript. Nonetheless, I do not recommend the manuscript for publication for several reasons: 1. I feel it is not ideally suited to ACP. It is written as a methods paper based on its experimental design to improve the source characterization across four dimensions. Thus, I would recommend it's submission for Atmospheric Monitoring Techniques, or another similar journal. I do not feel it has the necessary impact or scope for ACP. 2. Given the direction of the paper (such that it is delivered as a methods style paper). I also see some short-comings here. The authors are validly critiquing the need for more time representative studies rather than short "snap-shots" in time that are typically made when taking mercury measurements (especially mobile ones) at source sites using active monitoring instruments. Yet their own work does exactly this. 4 snapshots spread across the 4 seasons (I assume there is only one profile in each season). Are the days they did their horizontal transects truly representative of the whole season? Why is this approach any better than taking a single snap-shot and describing the meteorological conditions present during said snap-shot? This is particularly so because the sampling along the profiles was by changing location for each new sample, thus time can play a role in the observed concentration differences and not only spatial variation. Indeed, the authors even mention and discuss this, but it means changes in the measured concentrations can be related to both space and

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time. This exact point was raised in a study by McLagan et al., (2018). This study used passive samplers concurrently deployed in high numbers across the source area and the time integrated samples (over week long or seasonal deployments) give much more relevant data to assess chronic exposure risk and longer-term trends. The concurrent deployments mean concentration variability is limited to spatial differences. This study is highly relevant to this manuscript and should be discussed in detail (not referenced at all). 3. There is a lot of discussion of mixing layer or boundary layer characteristics based on only the TGM data measured at 3 different heights in the vertical profiles to a maximum of 3 m. Can these large scale phenomena (generally hundreds of metres be described with any certainty based of TGM measurements at three heights extending to only 3 m? I am highly skeptical of this. This applies to this whole section 3.1. 4. The methods section is lacking details. There is nothing describing when the horizontal profiles where made (time of day, date) and there is also nothing on the number of profiles made in each season. Thus, I have to assume each profile was only driven once per season? Thus, 4 “snap-shots-in-time”. Details of the sampling instrumentation are also severely lacking. We need more details on the specific setup of the Tekran 2537B and the Lumex RA-915M to define the exact species being sampled. Heated lines, filters, sampling duration? At least reference another paper whose setup was followed. Were there any external injections to test the quality of the internal calibration source? 5. Some of the writing is also very heavy and needs to be made more concise. Whole paragraphs are used at times to make a point that could be summarised in a sentence and many sentences are very long and convoluted. The authors think that the manuscript cover the main aims and scopes of the journal. The subject of this work is centered in field measurements, as one of the main subjects stablish by the journal in the webpage (https://www.atmospheric-chemistry-and-physics.net/about/aims_and_scope.html). Also, this work has general relevance and must be taken in account to further studies to avoid the obtaining of conclusions based on brief or not sufficiently representative data. For all these reasons and for the quality of the manuscript, as it can be deduced from the other

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three complete reviews received, and other three short comments; on these bases, we think that the manuscript is suitable to be published on this journal. In fact, the authors must say that they have selected the special issue from the ICGMP 2019, not specially the journal, thinking that the manuscript has novelty enough to be selected by the guest editor, Prof. Ashu Dastoor, for this special issue. In the point 2, the reviewer suggest that our work criticize and make a short snap-shots, but we think that there are a misunderstood on this suggestion, because this point is not sufficiently explained in the materials and methods section. As it can be seen in figure 5, the number of monitoring of each season appears as N in each graph, corresponding to a range of 4 to 10 monitoring in different days. We have added a brief text in the method section to explain this point: “Data acquisition was carried out during 24 different days for profile 1, 29 for profile 2 and 27 for profile 3 during the period between May 2014 and June 2015. Monitoring days tried to include two meteorological conditions: days of wind calms and days with regional winds”. But the reviewer suggestion that these short number of monitoring days remains to be snap-shots seems right to us. In fact, this is the main difficult of geochemistry works, for instance, to make a geochemical atlas of our region, we take 908 soil samples from an area of some 80,000 km2, and we make a geochemistry map of elements distribution. We must assume that there is a distance between our representation of reality and reality itself and the objective of this study is to try to make that distance the minimum acceptable, based on real data. To reduce this distance there are two main approaches: randomizing the sampling or doing a sampling that takes into account the main factors of heterogeneity. In the proposed example of the atlas, we have dealt with it by choosing the samples based on the lithologies since these are the main source of heterogeneity in the soils of the region. In the research work corresponding to this manuscript, we have identified wind as the main source of heterogeneity, and it has been this parameter that has been used to choose the different monitoring days. It is mandatory to carry out these monitoring that look for spatial patterns of dispersion in similar time periods between them so that they can be comparable. In this sense, it is essential to take snap-shots that correspond

to comparable periods of the day, but we must remember that with these transects the spatial patterns of dispersion of GEM are sought, and that the temporal pattern is studied through continuous measurements during a whole year with the Tekran device. Reviewer suggest the use of passive samplers as a good solution to solve this problem and this is a significative suggestion that we have not taken into account when drafting the manuscript. We have tried to solve this in the introduction section, adding the following paragraph: "These objectives can be accomplish sufficiently using passive samples (McLagan et al., 2018), with clear advantages in its low cost and the easier application, especially in areas with access difficulties. Some uncertainties remain in this approach, most important of them is the Hg compounds that these passive samplers' uptake. This uncertainty can be important in the vicinity of industrial sites (for instance, chloralkali plants), where RGM can be in higher proportions". And in the results and discussion section a new paragraph has been added: "All datasets measured for these three profiles correspond to a period (11:00–14:00) of stability in terms of micrometeorological parameters, i.e., in the middle of the day. This approach is essential to ensure the comparability of the different transects, but it is a limitation in the temporal evolution of GEM contents throughout the day. The present work complements these daytime measurements with night-time ones, based on the daily evolution described in the area (Esbrí et al., 2016, Tejero et al., 2015), but it should be mentioned that there is an alternative to carry out these monitoring tasks using passive samplers (McLagan et al., 2018), which offer a greater time range. Their use as a substitute for these direct measures or in combination with them will undoubtedly result in higher representativeness of the data obtained. These measures during summer nights reported higher GEM levels in the surroundings of mining-related GEM sources, with levels more than two times higher in Almadén, for instance." Another point in the review is the role of the mixing layer in the Hg distribution of the investigated area. May be it is not the creation of the mixing layer itself, but the consequence of this creation in terms of winds at the monitoring heights (not more than 3 meters). Other authors have described this process as a main process involved

in pollutants concentrations in the nearby town of Puertollano (Adame et al., 2012). We add a comment in this sense to clarify this point: “This phenomenon must be due to the confluence of three micrometeorological factors: high temperatures and solar radiation coincidental with low relative humidity values, which combine to increase the intensity of the formation of the mixing layer during the day, that has the consequence of an increment of wind speed in the investigated area.” Adame, J. A., Notario, A., Villanueva, F., & Albaladejo, J. (2012). Application of cluster analysis to surface ozone, NO 2 and SO 2 daily patterns in an industrial area in central-southern Spain measured with a DOAS system. Science of the Total Environment, 429, 281-291. In the point 4, the suggestion to give more details about what gaseous Hg specie has been measured with Tekran and Lumex was the most common discussion point in the previous reviews and short comments. We think that in the revised version has been solved satisfactorily with the aid of this suggestions. Specific comments: Abstract: Abstract is far too long. 680 words. It is heavy reading, where it should be a clear and concise summary. We have tried to summarize the abstract, we have this version in 562 words with all suggestion attended, not only of this reviewer, but also of the previous review and the short comments. “Mercury is a global pollutant that can be transported long distances after its emission by primary sources. The most common problem of gaseous Hg in the vicinity of anthropogenic sources is it presence in inorganic forms and in the gaseous state in the atmosphere. Risk assessments related to the presence of gaseous Hg in the atmosphere at these contaminated sites are often based on episodic and incomplete data, which do not properly characterize the Hg cycle in the area of interest or consider spatial or temporal terms. The aim of the work described was to identify criteria to obtain the minimum amount of data with the maximum meaning and representativeness in order to delimitate risk areas, both in a spatial and temporal respect. Data were acquired from May 2014 to August 2015 and included vertical and horizontal Hg measurements. A statistical analysis was carried out and this included the construction of a model of vertical Hg movements that could be used to predict the location and timing of Hg inhalation risk. A monitoring

strategy was designed in order to identify the relevant criteria and this involved the measurement of gaseous Hg in a vertical section at low altitude (i.e., where humans are present) and in horizontal transects to characterize appropriately the transport cycle of gaseous Hg in the lower layers of the atmosphere. The measurements were carried out over time in order to obtain information on daily and seasonal variability. The study site selected was Almadenejos (Ciudad Real, Spain), a village polluted with mercury related to decommissioned mining and metallurgical facilities belonging to the Almadén mercury mining district. The vertical profiles revealed that higher Total Gaseous Mercury concentrations are present at lower altitude during nocturnal hours and at higher altitude at dawn and dusk. On a daily basis the most important process involved in gaseous mercury movements is the mixing layer. Vertical transferences are predominant when this process is active, i.e., in all seasons except winter, while major sources act as constant suppliers of gaseous Hg to the mixing cell, thus producing Hg deposition at dusk. Conversely, horizontal transferences prevail during the hours of darkness and the main factors are major and minor sources, solar radiation, wind speed and topography. The study has shown that it is important: i) to identify the sources; ii) to get data about Hg movements in vertical and horizontal directions; iii) to extend the measurements over time in a sufficiently representative way, both daily and seasonally; iv) to determine the different populations of data to establish the background levels, this work proposes the use of Lepeltier graphs to do it. In terms of risk assessment, the nights carry greater risk than the days in all seasons except in autumn. The main factors involved in the creation of high-risk periods are those related to dilution (or its absence): namely wind speed and solar radiation at null levels. The results of this study highlight the possible importance of the relief in the distribution of gaseous mercury in the proximity of discrete sources. Furthermore, these systematic monitoring strategies can offer significant information in the Minamata Convention emission reduction scenario. Further studies, including a detailed topographic model of the area, are required in order to make precise estimations of the influence of this parameter, which appears in this study to be less important than the other factors but

is still appreciable." Lines 47-49: This sentence really sums up one of the problems with this article. The writing is at times very convoluted and could be improved by making sentences more concise. Here stating "PBM & RGM are deposited on local or regional scales" or "PBM & RGM are deposited nearer to source" is enough. We agree with the reviewer, we have tried to be concise and to include only relevant information in the manuscript, but we cannot always achieve this purpose because English is not our mother language, and we must to use a scientific reviewer (Dr. Neil Thompson, mentioned in the acknowledgements) to make our "spanglish" readable. We think that the revisor makes an excellent job with our way of writing, but perhaps along the writing process, the objective of being concise can be lost. We have tried to simplify sentences through the manuscript, following this suggestion. Lines 49-50: "Once Hg is being deposited" should be "Once Hg HAS BEEN deposited" Done. Line 54-58: long, convoluted and repetitive sentence. We agree with the reviewer, the sentence was hard to understand. Now it is as follow: "Results show that processes of Hg deposition and emission are included in a complex cycle with a large number of factors involved, mainly seasonality, vegetation coverage, temperature, solar radiation, relative humidity, diurnal atmospheric turbulence and the presence of Hg oxidants (Zhu et al., 2016)." Line 64: "Metric scale" metric is the system, using this word to describe metre scales is very confusing. State "on the scale of metres" Done. We have changed this and other previous of "kilometric scale" Lines 72-74: Break this into two sentences. Done. Lines 79-80: There have been more recent studies on this very topic using passive samplers see McLagan et al. (2018). This study is highly relevant to this manuscript. And here seasonal differences are compared and the longer-term nature of the sampling method is ideal for chronic exposure assessment. Although it cannot make any diurnal assessment. This study should be discussed in detail in this manuscript. We agree with the suggestion, but we think that this reference in the manuscript remains to be valid, because its meaning in the line of arguments about the importance of using representative data to make these statements. We think that the reference to the work of McLagan et al. (2018) can be added after this paragraph, to include another

valid approach to solve this, as an alternative of the proposed in the manuscript. We have included this text: “These objectives can be accomplish sufficiently using passive samples (McLagan et al., 2018), with clear advantages in its low cost and the easier application, especially in areas with access difficulties. Some uncertainties remain in this approach, most important of them is the Hg compounds that these passive samplers’ uptake. This uncertainty can be important in the vicinity of industrial sites (for instance, chloralkali plants), where RGM can be in higher proportions.” Line 92: “Secular” wrong use of this word. It describes not being associated with religion. i do not know of another definition such as that being the intention of the authors. We tried to solve this, but we see in Wikipedia that this term can be adequate if we read this definition of secular variation: “The secular variation of a time series is its long-term non-periodic variation (see Decomposition of time series).” Lines 93-95: This is not ok. This does not need a Wiki quote. People know what the four dimensions are. Just like them without the Wiki reference. We agree with this suggestion, but another previous reviewer suggests this. We have deleted this addition. Line 192: “. . .TGM concentrations close to zero. . .” Please change this to simply "lower". At no point do these concentrations get close to zero. especially considering typical background concentrations are less than 2ng/m3. Done. Lines 198-199: It seems difficult to state with much confidence that higher concentrations at ground level mean greater deposition. These are not flux measurements as there is a lot of influence of wind. It might be possible to also expect the higher elevation sample to be higher in mercury. Enrichment at the surface, especially in low wind conditions could suggests a source at the ground with decreasing concentration with elevation being caused by dilution with the less enriched air above. It makes sense there is little difference between the sampling heights in the day because the winds mix the system and little difference can be observed. This is not a study of vertical mercury fluxes from a contaminated surface (e.g., a polluted soil), but rather the vertical fluxes of Hg that came from nearby sources that were being monitored. In this sense, perhaps we should include these findings as suggestions since the vertical fluxes of Hg are not being quantified. We

have made changes in this regard to the text: “These positive differences between heights in terms of TGM suggest that mercury can remain accumulated at lower heights during the night, rising while the mixing layer is being created, and falling when this mixing layer disappears. These data could indicate that a diurnal cycle of emission and deposition is active in the studied area, and that deposition could be intense – especially at dusk – in the transitional hours between higher and lower winds.” Figure 3: This is a poor figure. Simply categorizing the data as high medium or low removes any quantitative assessment of the data. This could be vastly improved by taking the mean of the three height measurements for teach hourly time period and then plotting the residuals of each sampling height against time. Thus describing the magnitude of differences. Yes, the original design of the figure was as the reviewer suggest, but we think that the meaning of the data provided was hard to understand, and we tried to simplify the figure in the same spirit as heat maps, commonly used nowadays. Some meaning has been lost with this simplification, but we think that the essential meaning of data to be discuss in the text is in the figure. Figure 4: Instead of presenting typical days with these weather patterns, why not present the mean data (and the number of days described by this weather) for each meteorological condition. The goes to the very heart of the purpose of the manuscript – to eliminate “snap-shots-in-time” and give better time integrated data. We have assumed that there were exceptional micrometeorological conditions that must be explained and that they are not sufficiently represented in the general data since their influence is diluted in the prevailing conditions. This is the sense of this figure. Figure 5: why is the data so much more noisy in spring and autime than winter and summer in profile 3? This could be an analytical issue. We think that the noise that the reviewer has seen is related with the changes in micrometeorological conditions in these transitional seasons. We have explained this effect in previous works, such as Esbri et al. (2016). Esbrí, J. M., Martínez-Coronado, A., & Higueras, P. L. (2016). Temporal variations in gaseous elemental mercury concentrations at a contaminated site: Main factors affecting nocturnal maxima in daily cycles. Atmospheric Environment, 125, 8-14. Lines

265-268: Couldn't this easily be confirmed with river water and sediment samples at each river crossing site? Yes, we have added a new reference of García-Ordiales et al. (2018) in this sense. Garcia-Ordiales, E., Higueras, P., Esbrí, J. M., Roqueñí, N., & Loredo, J. (2018). Seasonal and spatial distribution of mercury in stream sediments from Almadén mining district. Geochemistry: Exploration, Environment, Analysis, 19(2), 121-128. Lines 279-281: Are they though? there looks to be little if any differences in overall concentrations of these profiles particularly for background concentrations based on Figure 5. Yes, we propose Lepeltier approach to avoid personal interpretation based on box and whistler graphs. In soil geochemistry, this approach provides more precise information about background values and anomalous populations. Also, differences between them appears as more significative. We have worked with this approach in Higueras et al. (2003) Higueras, P.; Oyarzun, R.; Biester, H.; Lillo, J.; Lorenzo, S. (2003) A first insight into mercury distribution and speciation in the Almadén mining district, Spain. Journal of Geochemical Exploration, 80: 95-104. Lines 290-292: This may well be the case, but the sampling methods chosen do not relay any information as to whether this is a random and very short term spike in concentration or a longer-term trend. The measurement is merely a "snap-shot-intime", making it exceedingly difficult to produce any assessment of chronic exposures. We think that we have answered this misunderstood previously, but we insist that these profiles are not merely snap-shot, we have made these monitoring in the middle of the day, with a more stable wind condition, because is the unique way to have comparable data for all points considered. And is important to remember that the objective was to search spatial variations, not temporal variations, and a try to identify patterns of Hg distribution and factors. Chronic exposure must be assessed with secular data of a whole year, as it has been our research plan. Lines 298-299: again this is a short-coming of the method and an example of a timerelated change in concentration rather than simply a spatial related change. Sorry, we do not understand this comment. Does the review consider this as reiterative? Or invalid? Lines 299-301: of course it is because wind increases dilution - it blows concentrations

away and the mix with surrounding air depleted in TGM more rapidly. We agree. Line 301: Why are we now talking about GEM and not TGM? This simply switched. Consistency of terminology please. Yes, we have solved this problem with the previous suggestions of other reviewers. Line 307: But Profile 3 certainly does have emissions sources. You only have to look at the large spikes in TGM concentrations. The authors really needed to have a control profile, without any sources (rivers or mines) to make such a statement. We added "significant" sources to indicate that in this profile the source has very low capacity to emit Hg. It will be preferably to have a blank profile in the area, but in the Almadén mining district is impossible to find a profile like this. Centuries of mining exploitation and the dissemination of artisanal furnace to recover Hg from cinnabar make impossible the search of such blank profile. Conclusions: This point form conclusions is a little strange. REFERENCES: McLagan, D. S., Monaci, F., Huang, H., Lei, Y. D., Mitchell, C. P., & Wania, F. (2019). Characterization and quantification of atmospheric mercury sources using passive air samplers. Journal of Geophysical Research: Atmospheres, 124(4), 2351-2362.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2019-1107/acp-2019-1107-AC5-supplement.pdf

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