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 all 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 reviewers, which are also sincerely acknowledged by us; we particularly thanks their positive comments on the quality of our work, and we are sure that the proposal of one of the reviewers for 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.

#RC1 – Reviewer 1

General comments: The manuscript "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 Esbri et al. discusses criteria and a minimum amount of information needed to efficiently characterize Hg contaminated site as a result of past mining activities. The authors suggest a novel monitoring design and evaluate it based on results obtained during measurement campaigns in the Almaden mercury mining districts. Overall, the manuscript brings new insights into specific pathways of Hg at contaminated sites, as well as the methodology to determine risks associated

The paper is well written and structured, including visualizations, statistical treatment and the interpretation of the results. However, there are some parts of the manuscript that are a bit unclear in its present form and need to be revised and simplified, respectively. To this end, in the following they are some specific comments and suggestions to improve the quality of this work.

Specific comments:

- Abstract: In its present form the abstract contains too many details, the second and third paragraphs in particular. It is suggested to rewrite it, focusing on the main outcomes of this work, e.g. relevant criteria and data needs for characterization of contamination and associated risks in the spatio-temporal context.

Done. We have rewrite second and third paragraph to accomplish reviewer suggestion: 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. Horizontal profiles showed that the background values were close to 6 ng m–3 except in the spring months, when they rose to 13 ng m–3 and increased the area affected by mercury emissions to more than 4 km around the mining and metallurgical sites. On a daily basis the most important process involved in gaseous mercury movements is the mixing layer, which begins in the early morning and finishes at nightfall. 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, and based on the model constructed to infer atmospheric Hg concentrations based on micrometeorological parameters, the nights carry greater risk than the days in all seasons (54% in spring and winter, 72% in summer) except in autumn, when 99% of the hours of risk occurred during the day. 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 extent of the area affected by an emission source is independent of its importance in terms of absolute emissions. The affected zone did not extend beyond 100 metres from the location of the source during the daytime period and 200 metres in the night-time. Under the worst micrometeorological conditions, it was predicted that the affected area would cover almost the entire town of Almadenejos, although these risk conditions only represent 11.34% of the hours in an annual period.

- Line 46: Revise the definition of TGM

Done. Now the sentence is "GEM and RGM species constitute 'total gaseous mercury' (TGM)".

- Line 64: "altitudes in the range 500-11,000 metres from background and contaminated locations;. . ." . Not clear. Revise and support with some references.

Done. The sentence is now as follows: Most of the available information on this topic is on a kilometric scale, at high altitudes in the range 500–11,000 metres from background and contaminated locations (Slemr et al., 2018; Weigelt et al., 2016);

- Lines 73-75: It is not clear what is meant by "Risk assessment", ". . .worst theoretical conditions. . ." and ". . .the worst-case scenario. . .". Revise and provide relevant details.

Done. The sentence is now as follows: Risk assessments of areas with anthropic contamination of gaseous Hg are often carried out with scarce data, often corresponding to short periods of time, and these do not provide a representative view of the day-night contrast or the seasonality, not even at the level of hot and cold or dry and wet seasons (depending on the location of the case study). We have conducted studies based on sampling times selected in the worst theoretical conditions, with higher expected emission rates enhanced by temperature and solar radiation, with the aim of identifying the worst-case scenario in summer days without winds in a mining site in Almadén (Martinez-Coronado et al., 2011), in a mining complex in Mount Amiata-Italy (Vaselli et al., 2013) in a chloralkali plant in Tarragona (Esbrí et al., 2015), in a chloralkali plant in Romania (Esbri et al., ; 2018a) and in a period of time with higher Hg metallurgical works in Almadén (Tejero et al., 2015), the evaluation of background conditions (Higueras et al., 2014), and comparison of the worst and best scenarios (Higueras et al., 2013).

- Lines 80-88: Not clear how the mentioned reference (Deng et al., 2016) is linked with the rest of the paragraph. It is also suggested to shorten and simplify this whole paragraph.

Thanks for the suggestion, but we think it is important to put into perspective the argument that it is necessary to rethink the representativeness of the data when doing a mercury-related risk analysis. In many cases sampling (o monitoring?) is not performed (o carried out) in the worst conditions due to ignorance, since the variations in environmental concentrations of

mercury can be very large in space and time and may be due to local reasons, not predictable based on the scientist's previous experience. For these reasons, we think that cited a reference like Deng et al (among many others), is relevant to support the idea.

– Line 97: Provide more details on the “exhaustive identification” of sources in the study area. By what means these sources were identified?

Done. The sentence is now as follows: In this work we have tried to obtain the minimum information necessary about the emission, transport and deposition of atmospheric mercury to ensure the representativeness of such data with a minimum cost in terms of effort and money. Before designing the sampling locations, an exhaustive identification of the Almadenejos emission sources, represented in red in Fig. 1, was carried out with a Lumex RA-915M equipment in mobile monitoring mode using a car to cover the entire area.

- In Lines 100-103 emission sources in the study area are ranked according to their importance. Based on what criteria?

Done. A new sentence has been added: The importance of the sources has been stablished if the average concentrations are below 200 ng m-3 (low importance), in the range of 200-1000 ng m-3 (medium importance) or up to 1000 ng m-3 (high importance).

- Line 109: Check if coordinates of AWTP are written in a correct format

Checked.

- Line 115: I suggest leaving out the sentence starting with “This situation gives. . .”

Yes, we have deleted this sentence.

- Lines 242-243: How were the background locations defined and separated from the rest?

Background values were determined using Lepeltier graphs.

Technical corrections:

- Line 120: Check values indicated in brackets for Lower and Upper Gradient

Yes, we have checked and they are correct.

- Lines 174-177: In Figure 2 there are no A, B and C mentioned in the text

Yes, the reference to the figure were incorrect. We have deleted A, B and C in the text.

– Page 19: Location should be mentioned in Table 2 caption

Done. We have changed the sentence: Table 1. Statistical summary of TGM levels at different heights (3, 2 and 0.5 metres) and total gradient (3–0.5 m), upper gradient (3–2 m) and lower gradient (2–0.5 m) in Almadenejos WWTP. All TGM data are in ng m–3.

- Figure 5: units are not shown for scale bar in Profile 1 and Profile 3, respectively

Yes, the scale was missing. We have revised the figure, adding these scales.

- Figure 9: scale bar is missing

Done.

#SC1 – Short comment 1

The manuscript studies the alternatives that exist to make monitoring works in an area contaminated with anthropogenic gaseous mercury. It recommends measurements at different heights, over significant transects and the repetition of these measurements over time. Although the results seem to be appropriate for a complex area such as the one they have chosen as study area, the effort involved in obtaining this minimum number of data is great and perhaps could be simplified if a previous study were made of the most important factors involved in the local cycle of mercury, in a short period.

In any case, the manuscript presents a monitoring option that seems to offer very significant data and that could be applicable to any contaminated area.

Lines 44-47. Definition of TGM include wrongly particle-bound mercury fraction. Revise it.

Done. The new version explains this with the following sentence: GEM and RGM together these species constitute 'total gaseous mercury' (TGM).

Lines 51-52. If water is included in this transfer pathways, what about sediments?

Thanks for the comment. In principle, we did not consider it important to include sediments in this introduction, since we were going to study mercury emissions in an urban environment, but it is true that the results have shown that sediments are an important source of emission to consider in the area of study. For these reasons, we have included it in the following sentence: Numerous Hg transfer pathways are involved in this cycle, and these include soil-atmosphere, soil-plant, plant-atmosphere, and water-atmosphere, and sediments-water, amongst others.

Line 61. Again sediments are missing. . .

It is difficult to find references including data about gaseous mercury emissions from sediments, so we have included sediments with a reference to emissions from salt marshes, which are not a perfect analogue, but which well expresses the idea of the timing of mercury emissions in a river context. The new sentence is as follows: A maximum emission during diurnal hours was described for soils (Zhu et al., 2015), mine materials (Eckley et al., 2011), waters (O`Driscoll et al., 2003), sediments (Sizmur et al., 2017) and snow (Maxwell et al., 2013), while forb leaf (Stamenkovic et al., 2008) and growing broad leaf (Fu et al., 2016) reach their minimum emission rates during diurnal hours.

Line 100. Explain what are the sources of medium importance, polluted wastes? Ore outcrops?

Done. The new sentence is as follows: In the town centre of Almadenejos there are four emission sources of medium importance (cinnabar wastes), while in the vicinity there is one of very high importance (MMP), one of high importance (Nueva Concepción mine), and two of low importance (a contaminated road running North of the town and the course of the Valdeazogues river, since it passes through the El Entredicho mine).

Lines 128-131. Then there is no soil data, why?

The monitoring strategy was designed to study the vertical flows of mercury from dispersed emission sources in the urban area, not to study emissions from the soils of the Almadenejos treatment plant, which are not contaminated. For this reason, the possibility of monitoring the temperature and moisture of these soils was not considered necessary.

Line 147. Add a comma in 3,650 and unifies the way the figures are represented throughout the manuscript

Done.

Lines 181-183. Add a reference to support this sentence.

We have not fully understood this suggestion. The sentence has a first reference to the wastes that exist in the metallurgical complex, which could be referenced by the already mentioned Martinez-Coronado et al. (2011), and a second part that describes minor sources identified in this work, and that is why we do not refer to them. We have added the reference to the first part of the sentence.

Line 210. There is no reference in the methodology section to soil temperature measurements, explain this.

These soil temperature data are used as reference but do not belong to this work, but to a previous one in which a nearby soil was monitored to study its emissions. In the present work, these data are used as general trends that are expected to continue year after year without significant changes. Unfortunately, the work remains unpublished and we have not been able to reference it.

Line 250. Something is missed in the top of the figure, in the scale bars

Done. The figure has been edited to solve this problem.

Line 287. In Figure 7, is it possible to separate transitional populations in the spring charts of profiles 1 and 3?

Thanks for the suggestion. Although the trend seems to change, there is not a sufficient number of data to establish an anomaly threshold.

Lines 307-312. The topographic profile is not enough to understand this, how are the river valleys? open or narrow? what is the difference in heights from the nearby mountains? and the slopes?

Done. A new sentence explaining this has been added: It is necessary to emphasize that the topography of the study area consists of mountainous alignments of smooth slopes, typical of the Appalachian relief, with maximum differences of heights of 220 meters.

Line 375. Indicate in the figure the inhabited area where risk from chronic exposure may occur

Done. The manuscript has a revised version of the figure highlighting the inhabited area

Line 515. Unify the decimals in the numbers

Done.

#SC2 – Short comment 2

The ACP-2019-1107 manuscript entitled “4D dispersion of total gaseous mercury derived from a mining source: identification of criteria to assess risks related with high concentrations of atmospheric mercury”, offers an alternative for the characterization of environments contaminated by anthropogenic mercury gas. The manuscript contains original work and will be a valuable addition to the literature since report data of mercury obtained in different spatial region and temporal time (daily and different seasonal period). The authors have studied the extent to which monitoring work must be extended to obtain sufficiently representative data. Ensuring the data representativeness in geochemical work has always been a major challenge. Working on soil geochemistry, this representativeness is highly dependent on heterogeneity for the elements studied, spatial distribution patterns, and aspects related to sample preparation and analysis. The gaseous character of mercury and atmospheric dynamics complicate the achievement of this purpose, and for this reason the manuscript proposes as necessary the extension in time and space of the monitoring works to ensure the representativeness of the data and thus be able to build a dispersion model of gaseous mercury in the study area. This approach of minimal monitoring work to do represents the main novelty of the manuscript and is adequately presented by the authors. Instead, there are limitations to this approach. The authors have selected a study area with passive mercury emission sources that are almost exclusively dependent on meteorology. It may be one of the simplest cases to monitor, but if the sources are active (for example, a chloralkali industry) or the emission sources are modified (for example, by remediation work on contaminated soils or mining environments), the constructed model shows weaknesses to offer useful data in a risk analysis context. The authors must explain these weaknesses of the model built in the discussion section or/and in the conclusions section. This explanation may be accompanied by a list of adaptation needs or its possible immediate application to different scenarios of interest: mercury contamination by artisanal gold mining, active industrial emissions (chlor-alkali industry, zinc ore smelters, etc) or including natural emissions of volcanism-related origin.

Thank you for the comments about our manuscript. As explained in the previous paragraph, the problem that this work set out to solve was ensuring the data representativeness in the monitoring of areas contaminated with gaseous mercury. As stated in the text, our research group has worked extensively on these characterization procedures, on many occasions detecting data gaps that left part of the local cycle of mercury unexplained or characterized. We often tried to perform the characterization in the worst possible theoretical conditions, but later we found that it is not possible to know the worst possible theoretical conditions in all scenarios. The manuscript proposes a method with minimum work to do to ensure this representativeness, but it is true that the constructed model is adapted to the case study, and in this area, meteorological data can be used to model gaseous mercury concentrations since in the area emissions are passive and dependent on variations in temperature, wind and solar radiation. A paragraph at the end of the discussion section has been added to explain this weakness: “This approach is applicable with little variation to any area affected by diffuse Hg emissions, but will require adaptations if Hg emissions are active, whether it is anthropogenic (mostly industrial) or natural (volcanic related). In these cases, the monitoring procedures must be extended to the emission processes, with the aim that these data will also be incorporated into the built model. In this way, the model will also serve to foresee changes in emission rates, either due to changes in technology in industrial activity, or due to changes in emission patterns in natural processes.”

Another important aspect to consider by the authors is the possibility of adapting this monitoring strategy to feed sufficiently representative data to models of dispersion of gaseous pollutants (Calpuff, ISC-Aermod, others).

This suggestion is very interesting for the future works. We believe that it goes beyond the main objective of the present work, the construction of a simple models based on correlations between parameters that allow the application of this methodology without much economic cost or learning time of the mentioned models. That is why we have not considered them in this work, although it could be an interesting future line of research.

The role of wet and dry deposition and particulate mercury in the local mercury cycle must also be better explained. There are some details in the introduction and a reference by the same authors studying the topic is cited, but there are no references in the text to this topic.

Dry deposition rates were published in a previous manuscript and seems not to be involved in the cycle of TGM in the area. Risk related with this solid material are more related with the incorporation to human trophic chain. We must take in consideration that a large proportion of Hg appears as bound to humic acids, a Hg compound more available for crops and vegetables. We have added some details about PBM in the methodology section: "Previous data of PBM of the area has shown that emissions are related with creation of diurnal mixing layer while dry deposition rates (317 $\mu g\ m^{-2}\ year^{-1}$) were in the order of other rural areas, and lower than urban areas (Esbri et al., 2018b)"

The manuscript deserves to be published after this minor revision based on its novelty, presentation and quality of the data provided.

#SC3 – Short comment 3.

This manuscript offers monitoring alternatives for contaminated areas that seem to offer very significant results in mining areas such as the chosen one. In the context of emission reductions required by the Minamata Convention, these procedures should offer valuable information about the evolution of the gaseous Hg concentration values in areas with real problems of risk for people.

Thanks for this suggestion. The new scenario generated after the approval of the Minamata Convention and its ratification by 120 countries will mean a major change in the levels of Hg available in the environmental compartments. This expected reduction should be monitored, to assess the evolution of the process and assess the adoption of more restrictions if the desired objectives are not achieved. In this sense, our systematic monitoring approach should offer comparable results over time and significant conclusions. Considering the importance of this suggestion, we have decided to include in the abstract a short sentence that indicates this aspect: " Furthermore, these systematic monitoring strategies can offer significant information in the Minamata Convention emission reduction scenario. " In addition, it is also commented in the last paragraph of the discussion section, which is now: " This approach is applicable with little variation to any area affected by diffuse Hg emissions, but will require adaptations if Hg emissions are active, whether it is anthropogenic (mostly industrial) or natural (volcanic related). In these cases, the monitoring procedures must be extended to the emission processes, with the aim of incorporating these data into the built model. In this way, the model will also serve to foresee changes in emission rates, either due to changes in technology in industrial activity, due to changes in emission patterns in natural processes or changes in emissions rates derived of restrictions of Minamata Convention (UN, 2019)."

And we have added a reference:

United Nation (2019). Minamata Convention on Mercury. Available at http://www.mercuryconvention.org/Convention/Text/tabid/3426/language/en-US/Default.aspx (Last access, 03/06/2020)

Among all the work presented in the manuscript, I am very interested in making transects that can be compared over time, both in daily cycles and at different seasons. The method seems to work well in the chosen mining environment, but I wonder if it would offer meaningful information in an environment with less spectacular emissions, for example, in a bay entering sediments contaminated with cinnabar and native mercury droplets. For the application of this transect monitoring method, is prior identification of the emission sources essential? What phenomena could I register in this case?

The better situation is to know the location of the most important emission sources prior to design the route of the transects, although locations of temporary sources (still unknown) can be incorporated into them, such as flood events that bring sediments rich in cinnabar and mercury droplets. The main advantage of this method of transects in different periods of time is the rapid and low-cost obtaining of comparable information that serves to establish background levels and anomalous levels and their evolution in the different meteorological seasons, in the day/night or in occasional events such as flood events, tides or that considered to have an influence on the activation of mercury gas emissions. As in other situations, prior knowledge improves the effectiveness of the approach.

Otherwise, the manuscript is very well written, and there are only a few minor errors that may have already spotted in the comments above. To name the ones that seemed most striking to me, the term TGM is not well defined on line 47

Done. Now the term is defined as: GEM and RGM Together these species constitute 'total gaseous mercury' (TGM).

on line 60 I don’t understand the term "forb"

It is not a common term, it does not correspond to a single plant, but to plants with herbaceous flowers.

, and the weather station is unclear where it is in Figure 1.

Done. We have added a detail in the sentence: “The location of this device (WGS84 30S 351714 E/4289255 N) is shown in Fig. 1, in the AWTP Almadenejos.”

#RC2 – Reviewer 2

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 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 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 km^2, 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.

4D dispersion of total gaseous mercury derived from a mining source: identification of criteria to assess risks related with high concentrations of atmospheric mercury.

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Abstract. Mercury is a global pollutant that can be transported long distances after its emission by primary sources. ~~Most of the problems associated with Hg as a toxic element dispersed worldwide arise due to its incorporation into the trophic chain and its conversion into organic forms. However, in the vicinity of anthropogenic sources, t~~The most common problem of gaseous Hg in the vicinity of anthropogenic sources is ~~the~~ it presence ~~of Hg~~ 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 ~~September~~ 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. ~~Horizontal profiles showed that the background values were close to 6 ng m^{-3} except in the spring months, when they rose to 13 ng m^{-3} and increased the area affected by mercury emissions to more than 4 km around the mining and metallurgical sites.~~ On a daily basis the most important process involved in gaseous mercury movements is the mixing layer~~, which begins in the early morning and finishes at nightfall~~. 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, ~~and based on the model constructed to infer atmospheric Hg concentrations based on micrometeorological parameters,~~ the nights carry greater risk than the days in all seasons ~~(54% in spring and winter, 72% in summer)~~ except in autumn, ~~when 99% of the hours of risk occurred during the day~~. 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 extent of the area affected by an emission source is independent of its importance in terms of absolute emissions. The affected zone did not extend beyond 100 metres from the location of the source during the daytime period and 200 metres in the night time. Under the worst~~

micrometeorological conditions, it was predicted that the affected area would cover almost the entire town of Almadenejos, although these risk conditions only represent 11.34% of the hours in an annual period.

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.

1 Introduction

Mercury (Hg) is considered to be a global pollutant due to its ability to be transferred between different environmental compartments and over long distances, which results in the contamination of pristine areas far from the sources. The Hg cycle in the environment begins with geogenic or anthropogenic emissions, which mainly consist of gaseous elemental mercury (GEM) along with minor proportions of particle-bound mercury (PBM) and reactive gaseous mercury (RGM). GEM and RGM Together these species constitute 'total gaseous mercury' (TGM). The residence time of each of these mercury species is different and is much longer for GEM, which means that this species can be deposited in remote areas such as the Arctic Sea, while PBM and RGM are often deposited on local or regional areas that are relatively close to thenearer to source (Radke et al., 2007, and references therein). Once Hg is has been being deposited, a cycle of re-emission/deposition, along with changes in Hg speciation, explains the flows of this element in the environment.

Numerous Hg transfer pathways are involved in this cycle, and these include soil-atmosphere, soil-plant, plant-atmosphere, and water-atmosphere, and sediments-water, amongst others. These fluxes have been quantified by different approaches, most of which employ dynamic flow chambers, micrometeorological methods and bulk methods (Carpi and Lindberg, 1997; O'Driscoll et al., 2003; Stamenkovic et al., 2008; Eckley et al., 2011; Zhu et al., 2015; Fu et al., 2016; Zhu et al., 2016, amongst others). Some doubts remain concerning the comparison of these methods, but the rResults show that processes of Hg deposition and emission are included in a complex cycle in which verywith different factors influence the flows from one environmental compartment to another and a large number of factors are involved between these, mainly seasonality, vegetation coverage, temperature, solar radiation, relative humidity, diurnal atmospheric turbulence and the presence of Hg oxidants (Zhu et al., 2016). A maximum emission during diurnal hours was described for soils (Zhu et al., 2015), mine materials (Eckley et al., 2011), waters (O`Driscoll et al., 2003), sediments (Sizmur et al., 2017) and snow (Maxwell et al., 2013), while forb leaf (Stamenkovic et al., 2008) and growing broad leaf (Fu et al., 2016) reach their minimum emission rates during diurnal hours. These daily cycles of Hg emissions from soils, waters or plants contribute to the increase of the atmospheric mercury pool, especially in the lower layers of the troposphere. Most of the available information on this topic is on a kilometric scalescale of kilometres, at high altitudes in the range 500–11,000 metres from background and contaminated locations (Slemr et al., 2018; Weigelt et al., 2016); however, information about TGM dispersion on a metric scalescale of meters is scarce. Some information about these distances comes from episodic monitoring by means of LIDAR techniques, such as those measured in China, where maximum levels at lower altitudes were detected during night-time hours (Guan et al., 2010). Saiz-Lopez et al. (2008) modeled the vertical profile of GEM over Antarctica and found that maximum levels were located at lower altitudes during daytime hours. Tackett et al. (2007) described a vertical GEM profile in the Arctic troposphere and found maximum levels of GEM at heights of 20–80 metres above ground under different conditions. Steffen et al. (2002) studied vertical profiles on snowpack before and during depletion events and found that GEM levels increased sharply at the surface during the depletion event on a two-metre profile. Ferrara et al. (1998) identified higher TGM concentrations a few centimetres above the ground and background values at heights 10–20 metres above ground at the Eastern border of Almadén village.

Risk assessments of areas with anthropic contamination of gaseous Hg are often carried out with scarce data, often corresponding to short periods of time, , and tThese do not provide a representative view of the day-night contrast or the seasonality, not even at

the level of hot and cold or dry and wet seasons (depending on the location of the case study). We have conducted studies based on sampling times selected in the worst theoretical conditions, with higher expected emission rates enhanced by temperature and solar radiation, with the aim of identifying the worst-case scenario in summer days without winds in a mining site in Almadén (Martinez-Coronado et al., 2011), in a mining complex in Mount Amiata-Italy (; Vaselli et al., 2013) in a chloralkali plant in Tarragona (; Esbrí et al., 2015), in a chloralkali plant in Romania (Esbri et al., ; 2018a) and in a period of time with higher Hg metallurgical works in Almadén (; Tejero et al., 2015), the evaluation of background conditions (Higueras et al., 2014), and comparison of the worst and best scenarios (Higueras et al., 2013). However, we realized that the mercury cycles in all of the studied sites were not exactly the same, and that the most important factors that control the emission, transport and deposition processes also differed from one area to another. This idea can be exemplified by the most recent reference found for risk assessment related to gaseous mercury (Deng et al., 2016). The authors found correlations between methylmercury (MeHg) in blood and TGM in the air after only seven gaseous Hg measurements without covering a full annual period. There are many confounding variables that may produce this correlation due to the low representativeness of the gaseous Hg sampling. It therefore seems necessary to carry out a sufficiently representative sampling effort in order to understand the peculiarities of the Hg cycle in the study area to achieve a realistic risk assessment. In this sense, it is necessary to gain a knowledge of the Hg flows from the moment that it is emitted and to understand the main mechanisms of dilution and/or concentration. It is also necessary to obtain information on the evolution in the vertical direction with respect to the source and also horizontally, as this information that will provide the dispersion of the contaminant in the area. It is also highly recommended to obtain information on the temporal evolution of these vertical and horizontal processes, both daily and seasonally. 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.

The main objective of the work described here was to obtain information on vertical and horizontal profiles of TGM in an environment contaminated by decommissioned mercury mining facilities, with the ultimate objective of locating the risk areas around the main sources of emission and the moment at which the risk in these areas was significant. Data acquisition was carried out over a whole year in order to identify relationships between TGM data and secular variations in local micrometeorological and topographical data. ~~In this way, the title of the manuscript refers to a new type of 4d monitoring, in the sense that Wikipedia defines the term: "meaning the 4 common dimensions, is an important idea in physics referring to three-dimensional space (3D), which adds the dimension of time to the other three dimensions of length, width, and depth".~~

2 Methodology

In this work we have tried to obtain the minimum information necessary about the emission, transport and deposition of atmospheric mercury to ensure the representativeness of such data with a minimum cost in terms of effort and money. Before designing the sampling locations, an exhaustive identification of the Almadenejos emission sources, represented in red in Fig. 1, was carried out with a Lumex RA-915M equipment in mobile monitoring mode using a car to cover the entire area. In the town centre of Almadenejos there are four emission sources of medium importance (cinnabar wastes), while in the vicinity there is one of very high importance (MMP), one of high importance (Nueva Concepción mine), and two of low importance (a contaminated road running North of the town and the course of the Valdeazogues river, since it passes through the El Entredicho mine). The importance of the sources has been stablished if the average concentrations are below 200 ng m^{-3} (low importance), in the range of 200-1000 ng m^{-3} (medium importance) or up to 1000 ng m^{-3} (high importance).

In an effort to achieve the main objective of this work, it was decided to obtain data in the three directions of space, including a short vertical transect and long horizontal transects that include emission sources of high, medium and low importance. These data

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were also obtained serially over time to cover both the daytime cycles of light and darkness, as well as the seasonal cycles of hot and cold periods.

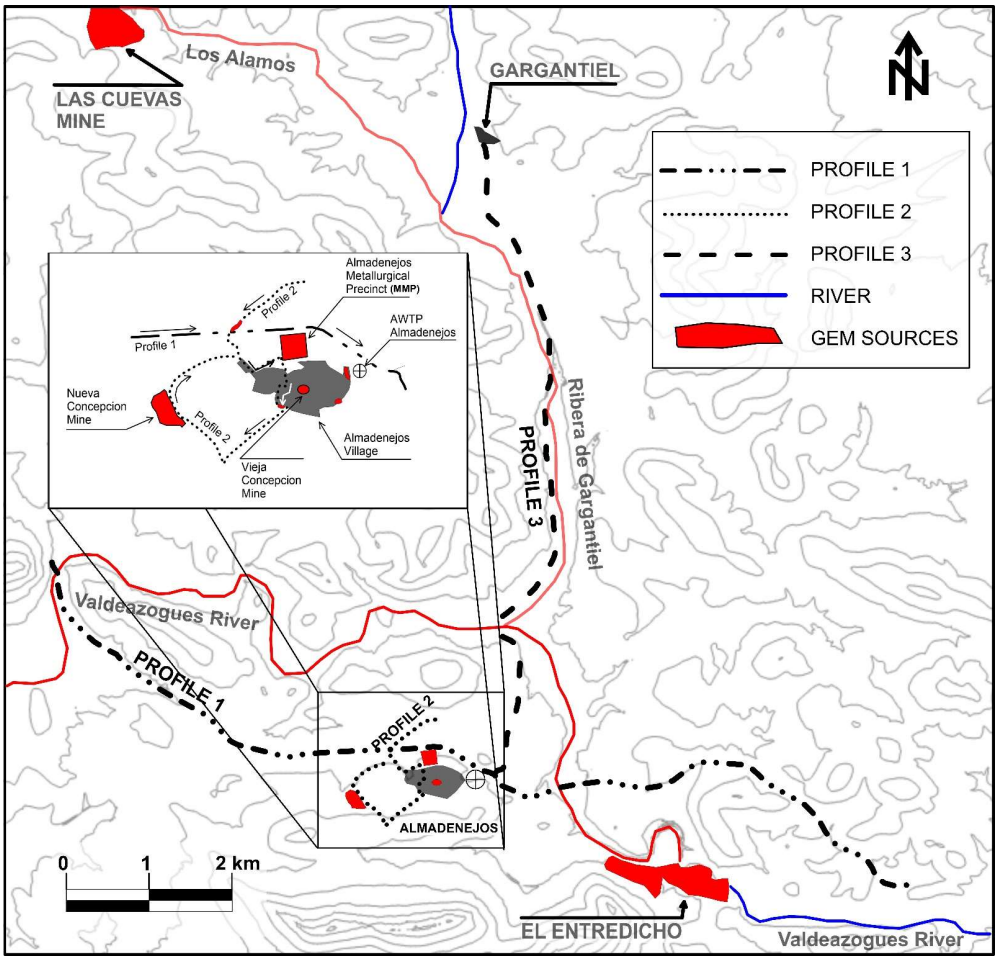
2.1 Vertical profile measurements

Total Gaseous Mercury (TGM) was measured at a site located in the proximity of Almadenejos village (Fig. 1) and corresponding to a closed precinct that encompasses the Almadenejos wastewater treatment plant (AWTP) (WGS84 30S 351707 E/4289235 N). Almadenejos was a secondary mining and metallurgical centre in the so-called Almadén mercury-mining district (Higueras et al., 2006). This area includes three large mines, which are now closed, and a metallurgical precinct located immediately to the North of the urban area and representing the only significant active local source of gaseous mercury (Martínez-Coronado et al., 2011). This is an excellent area for the study of Hg transference between environmental compartments (Naharro et al., 2018; Campos et al., 2018; ~~Esbrí et al., 2018b~~) due to the scarce remediation works that have been carried out in recent centuries, which has left a legacy of anomalous Hg presence in the soils, roads and rivers. ~~This situation gives rise to a very interesting mercury cycle to carry out environmental studies.~~ Previous data of PBM of the area has shown that emissions are related with creation of diurnal mixing layer while dry deposition rates (317 µg m^{-2} $year^{-1}$) were in the order of other rural areas, and lower than urban areas (Esbri et al., 2018b)

The equipment used to make the measurements was a Tekran 2537B with a synchronized multi-port sampler (model 1115) that allowed alternate measurement of up to six separate input streams. In this work only three of these six sampling possibilities were used, and these corresponded to sampling points located at 0.5, 2 and 3 metres above ground, with measurements made from September 2014 to August 2015. An external pump working at 15 m^3 h^{-1} was employed, with the sampling lines purged with Hg-free air (GEM < 2 ng m^{-3}) when not in use. Various gradients were used in order to study differences in TGM contents at different altitudes: Total Gradient (TGM_{3metre}–$TGM_{0.5metre}$), Lower Gradient (TGM_{3metre}–TGM_{2metre}) and Upper Gradient (TGM_{2metre}–$TGM_{0.5metre}$).

The device was calibrated every seven days by means of an internal permeation source. An intercomparison exercise between Lumex RA-915M and Tekran 2537B systems was carried out in 2011 in conjunction with the Spanish *Instituto de Salud Carlos III*, and a compatibility index (see ref. ISO/IEC, 1997) of less than 1 was found during all experiments (Fernández-Patier and Ramos-Diaz, 2011).

Micrometeorological data were acquired using a Davis Vantage Pro meteorological station, which is a fully automated device that allows data to be collected every 15 minutes, including temperature, relative humidity, wind speed and direction, atmospheric pressure, rain, solar radiation and ultraviolet radiation. The location of this device (WGS84 30S 351714 E/4289255 N) is shown in Fig. 1, in the AWTP Almadenejos.



150 **Figure 1: Location of the three horizontal profiles in the study area and main mercury mining sites. AWTP: Almadenejos Wastewater Treatment Plant. Main known gaseous mercury sources are shown in red (including rivers with Hg-contaminated sediments); uncontaminated streams are shown in blue.**

2.2 Horizontal profile measurements

155 The sampling strategy was designed to cover not only anomalous GEM data from local emission sources, but also background GEM data around major and minor sources at locations far from Almadenejos. As shown in Fig. 1, three transects were chosen to achieve these objectives:

- Profile 1 has a length of 12,350 metres, including two crosscuts with the Valdeazogues River, which transports sediments moderately contaminated with Hg (García-Ordiales et al., 2016), especially in the vicinity of El Entredicho open pit mine
160 (Fig. 1). This profile passes close to Almadenejos village, 40 metres from the main GEM source in the studied area, which is a decommissioned mining and metallurgical plant (MMP) (Martínez-Coronado et al., 2011). This profile was selected

with the aim of identifying relationships between background GEM data, at large distances from Almadenejos, and local anomalous GEM data from the main source area.

- Profile 2 has a length of 3,650 metres and it crosscuts the main GEM sources of the village: La Nueva Concepción mine, MMP and two minor GEM sources in tracks paved with contaminated materials from the MMP. This profile was selected with the aim of identifying possible relationships between anomalous GEM data from local sources and background data from the hills located to the South and North of Almadenejos.
- Profile 3 covers 8,450 metres from Almadenejos village limits to the village of Gargantiel. This profile mainly represents the background values, including a crosscut over two minor GEM sources of polluted sediments: the Valdeazogues River and its tributary, the Gargantiel River.

Data acquisition of GEM was performed using a Lumex RA-915M device, which is a portable Atomic Absorption Spectrometer that is able to collect one GEM data point every second (Higueras et al., 2014). The device was installed on an automobile, with the sampling line located on the front side of the vehicle. The speed was kept constant during the sampling time, i.e., in the range 40–50 km h^{-1}. Baseline checks were carried out at the beginning and the end of each profile, and a baseline correction was performed when differences were up to 1 ng m^{-3}, assuming that the lamp derive was linear during measurements. 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. The profiles had differences in the number of data points and precise locations along the profile. In order to enable direct comparison of the collected data and to minimize erraticism, an average for each 100 metres was calculated and each average was assigned to the centre of the corresponding distance range.

2.3 Statistical treatment

Data analysis was carried out with different software packages: Microsoft Excel, Minitab 15 and Golden Surfer 9. A multiple linear regression analysis (MLRA) on the normalized dataset of vertical profiles was performed using Minitab 15. A best subset regression analysis was performed using Mallows' CP to identify the best predictors prior to performing a multiple linear regression analysis on each dataset. A fitted line graph was constructed using the equation obtained in the MLRA to obtain an R^2 value based on a new equation between measured gradient (or TGM) and predicted gradient. Lepeltier graphs were used to find the distribution pattern that best fitted the various sets of GEM data in horizontal profiles. A lognormal distribution curve (Lepeltier, 1969) is defined by two parameters: one is dependent on the mean value and the other is dependent on the character of the distribution of values. These parameters were determined graphically by means of cumulative frequency curves in log-probability plots using Minitab 15. Finally, the delimitation maps of risk areas due to the presence of gaseous Hg were produced using Surfer 9.

3 Results and discussion

3.1 Vertical profiles

The daily evolution pattern of TGM (Fig. 2~~A~~) is similar to that described by Esbrí et al. (2016) for Almadén town, which is located 11 km to the west of Almadenejos: the pattern shows low TGM levels during diurnal hours and higher levels during the rest of the day, a finding that has been interpreted as being due to a decrease in the wind speed during the night (Fig. 2~~B~~). In terms of TGM levels (see Table 1 and Fig. 2~~C~~ for more details), the site studied in Almadenejos has TGM concentrations that are at least three times higher than those measured in the Almadén site described by Esbrí et al. (2016) and a more marked difference between maximum and minimum daily TGM concentrations was observed. This behaviour is probably due to the fact that in Almadén the main dump was reclaimed during the years 2008–2010, which led to a very significant decrease in local TGM (Higueras et al., 2013), whereas reclamation of the metallurgical precinct has never been performed in Almadenejos. As a result, a huge amount of metallurgical waste remains in the MMP (Martinez-Coronado et al., 2011), in addition to the presence of some minor sources

produced by the network of roads and tracks or uncontrolled accumulation of contaminated waste (Fig. 1). Seasonally, the main pattern is similar to that described by Esbrí et al. (2016) in the nearby population of Almadén, with lower TGM levels in winter and higher levels in summer. However, transitional seasons show a different trend, especially in springtime, when TGM levels are at an intermediate level between winter and autumn.

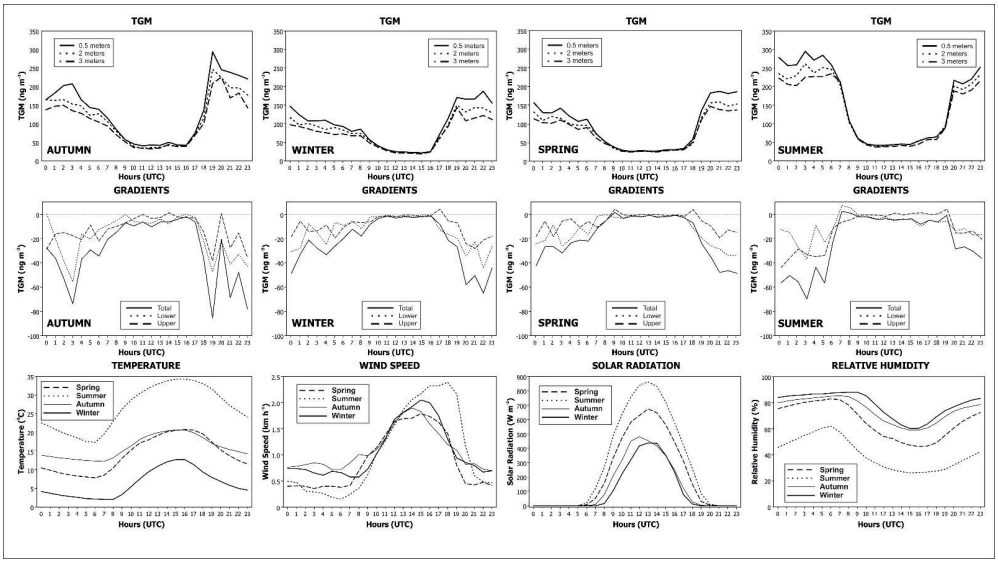


Figure 2: Daily and seasonal evolution of TGM contents at 3, 2 and 0.5 metres above ground in the AWTP site (Upper row); daily and seasonal evolution of gradients at between 3–0.5 metres, 3–2 metres and 2–0.5 metres above ground in the AWTP site (Middle row); and daily and seasonal evolution of micrometeorological parameters (temperature, solar radiation, relative humidity and wind speed) in the AWTP site (Lower row).

Vertical gradients in the AWTP (Table 2 and Fig. 2) show TGM concentrations ~~close to zero~~lower during diurnal and windy hours, with higher concentrations at lower heights above ground in all three sections considered (3–0.5; 3–2; 2–0.5). Variability according to season does not appear to have any evident pattern, except for summer versus autumn/winter/spring: Summer data reached positive levels only in the first few hours before and after the atmospheric mixing process was active, i.e., at dawn and dusk, especially for gradients 3–0.5 and 2–0.5. These positive differences between heights in terms of TGM suggest~~indicate~~ that mercury can remain~~s~~ accumulated at lower heights during the night, ~~it rises~~ rising while the mixing layer is being created, and ~~it falls~~ falling when this mixing layer disappears. These data could indicate that a diurnal cycle of emission and deposition ~~is~~ could be active in the studied area, and that deposition is intense – especially at dusk – in the transitional hours between higher and lower winds. Llanos et al. (2011) estimated the annual emissions of the MMP to be 16.4 kg y^{-1}, but the dispersion/dilution process of these emissions in the surrounding environment was unknown and it was impossible to perform a similar measurement with a crane over this MMP facility.

The daily evolution of the maximum, medium and minimum values for each of the three heights monitored is represented in Fig. 3, with the aim of visualizing the vertical movements of Hg and the heights at which they occur, both ascending and descending. It can be observed that in the summer the flows in the highest monitored sector occur only in the early hours of the morning, thus precluding the movement of Hg from the lowest to the highest monitored height. Instead, the exchange in the lower part is continuous throughout the day, i.e., from dawn to dusk. 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. In spring a similar exchange of maximum and minimum values also occurs early in the day, but in this case the exchange is maintained

throughout the day only in the highest monitored sector. The main difference between these two seasons is the soil temperature, which is much lower in spring (16 ºC) than in summer (27 ºC). In the spring, the lower soil temperature would promote a thinner mixing layer, which would be unable to promote Hg transfers in the region close to the ground, while in summer the high ambient and soil temperatures would increase the thickness of the mixing layer, thus producing Hg transfers in lower areas. Autumn, the other transition season, shows flows in the upper sector during the day and in the lower part only at dawn, when wind had ceased. Finally, in winter, when micrometeorological factors attenuate the creation of the mixing layer, flows were not detected during the day and only at dusk was a single exchange in the upper part of the monitored sectors measurable.

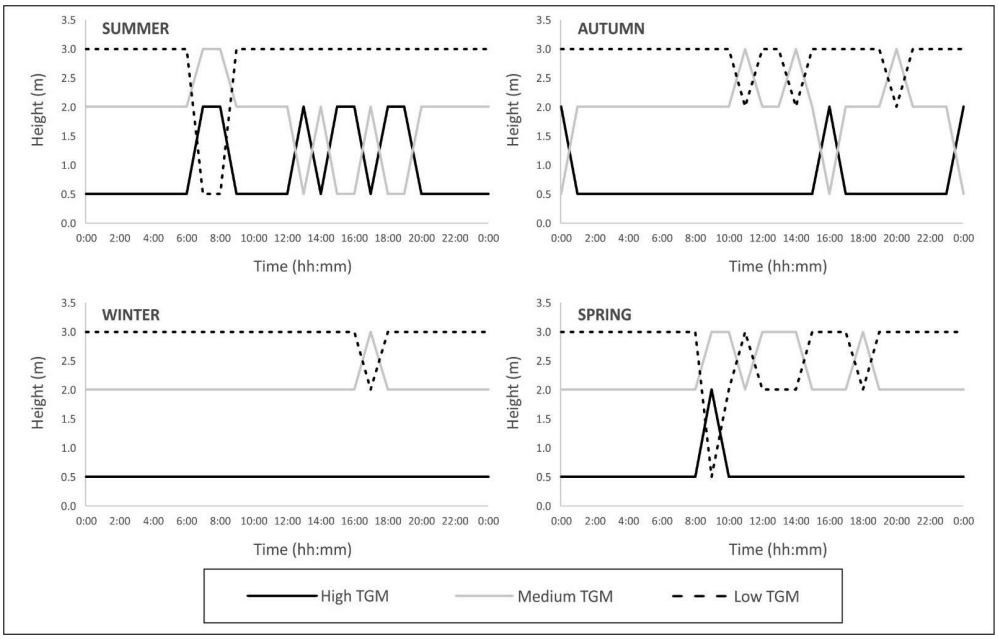


Figure 3: Schematic representation of the daily evolution of the maximum, medium and minimum levels of gaseous Hg at the three measuring points in the vertical profile.

The evolution of the TGM gradient during a typical summer day (with symmetrical temperature and solar radiation profiles during daytime hours) exemplifies this process perfectly (Fig. 4a), with positive gradients observed as solar radiation declined and an increase in the early morning. Negative gradients were observed during night-time hours, probably as a consequence of the stratification of lower atmospheric layers when the wind speed was zero or close to zero. A similar trend was observed on a winter day (Fig. 4b) or on a day with thermal inversion in the morning (Fig. 4c), but this tendency was not observed during rainy periods, such as a rainy day in November (Fig. 4d), on windy days (Fig. 4e) or on misty days (Fig. 4f).

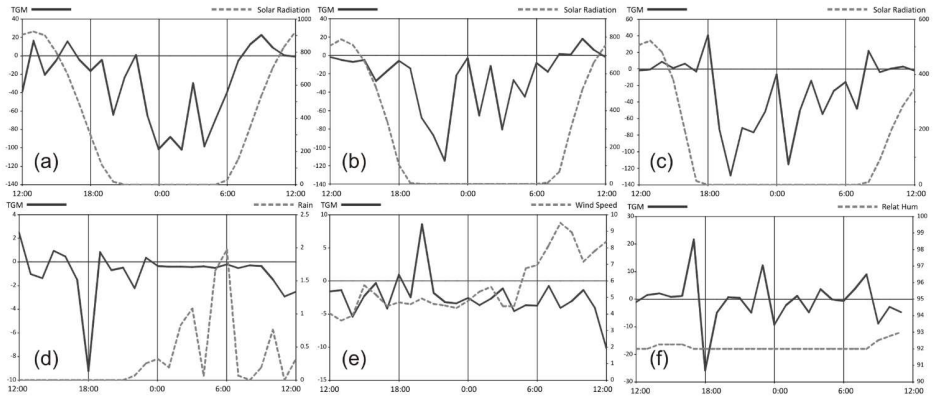


Figure 4: Evolution of TGM total gradients during typical contrasting meteorological conditions: (a) typical summer day; (b) typical winter day; (c) thermal inversion day; (d) rainy day; (e) windy day; and (f) foggy day.

On considering the weight of each factor by applying a multiple linear regression analysis (Table 3), it was observed that solar radiation is the key factor in spring, autumn and winter, but that wind speed can better explain gradient data in summer. Surprisingly, temperature appears to be a secondary factor in all seasons, and only in the summer period and in the lower gradient does this appear to be an important factor. The identification of wind speed as a primary factor in the lower gradient in autumn is consistent with the Hg exchange found at dusk in this period (Fig. 3). Wind speed is also important in the upper gradient in winter, i.e., the sector where the exchange of Hg is appreciable in Fig. 3.

3.2 Horizontal profiles

Profile 1 (Fig. 5a) represents the longest transect (12,350 m) and it includes two Valdeazogues river crosscuts: one near the El Entredicho open pit mine (located 2,500 metres upstream) and the other at the beginning of the transect (10,800 metres downstream from El Entredicho). Higher GEM contents were found in summer and spring, especially in the Valdeazogues river crosscut closest to El Entredicho. In terms of data variability, transition seasons (spring and autumn) show the highest differences between maximum and minimum GEM concentrations, while winter presents the lowest term. This data variability reaches its maximum amplitude in anomalous values (up to 60 ng m^{-3} during summer and spring near the MMP). Furthermore, data variability shows clear differences in background values between seasons, i.e., highest for transition seasons and lowest for summer and winter. Background levels are close to 6 ng m^{-3} during all seasons except for spring, which gave a value of 13 ng m^{-3}. Springtime is characterized in Almadenejos by a marked increase in temperature and solar radiation (Fig. 2), as compared with previous winter months, and an intense soil moisture release occurs that could enhance soil mercury emissions through the volatilization of more labile soil mercury species (Llanos et al., 2011). This process significantly increases the extent of higher background GEM levels, thus increasing the area affected directly by mercury emissions to more than 4 km taking into consideration the distance in profile 1 (Fig. 5a) from the Valdeazogues River to the MMP.

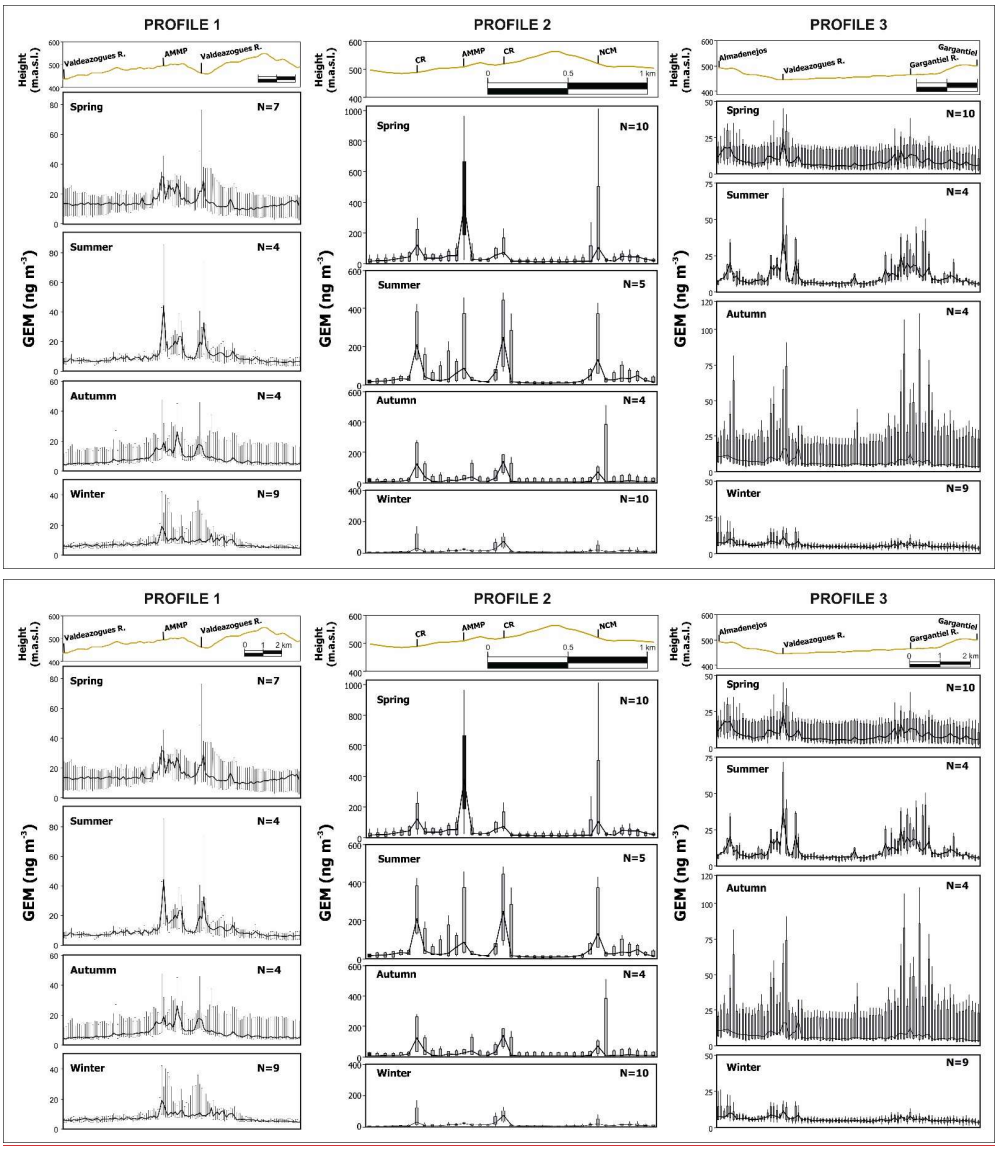


Figure 5: Boxplot of GEM in the horizontal profiles along the Almadenejos area. Each box represents the average of 100 metres. The location of these profiles is shown in detail in Fig. 1.

Profile 2 passes through minor and major mercury sources in the studied area, namely an abandoned metallurgical precinct (MMP), a closed underground mine (NCM) and two points with contaminated roads (CR in Fig. 5b). The maximum GEM concentrations were found during spring months, especially in the proximity of the MMP and NCM, and the lowest concentrations were measured during winter months (Fig. 5b). The extent of the anomalous high values reaches maximum distances in summer, with higher data variability along the transect, and minimum distances in winter, when anomalous values appear within the background values.

Profile 3 represents the local background profile and it crosses only one minor GEM source, the Valdeazogues River, 5,000 metres downstream from the El Entredicho mine (Fig. 5c). Maximum levels and variability in this transect were observed during autumn months, while winter represents the minimum for these two aspects. Background values were slightly lower (4–5 ng m^{-3}) for each season considered when compared to those for profile 1, although this profile represents a low-grade contaminated area in the mining district, with mercury present in sediments of the Valdeazogues and Rivera de Gargantiel Rivers (García-Ordiales et al., 2016), in soils (Rodríguez et al., 2003) and incorporated into the road as polluted waste from the El Entredicho closure works.

The Valdeazogues River represents a strip of contaminated materials (Garcia-Ordiales et al., 2018) that comprises the alluvial plain, and it is probably the most important minor source of GEM in the region. This river crosses the district for 30 km from the easternmost Hg mine (El Entredicho) to the confluence with the Guadalmez River outside the mining district. The GEM levels for all seasons in a section of the Valdeazogues River affected mainly by El Entredicho wastes are represented in Fig. 6 and it can be seen that the GEM average and range decrease with increasing distance from the mine.

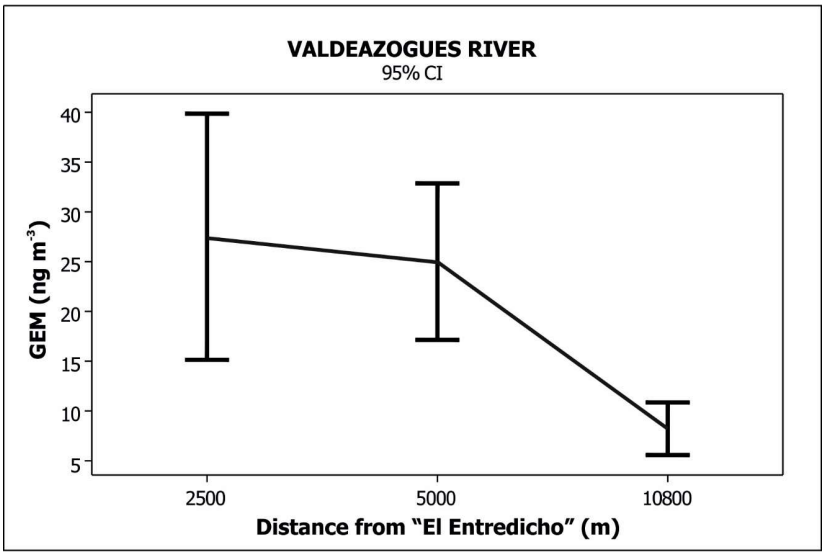


Figure 6: Variability in GEM levels on crosscuts of the Valdeazogues River according to distance from El Entredicho mine.

The profiles dataset was represented as lognormal distribution curves (Fig. 7) in an effort to determine the evolution of the main GEM sources in the studied area. The idea behind these graphs was to separate dataset populations, with the Y axis representing cumulative Gaussian distributions. The changes in the slope of each probabilistic curve (breaks) mark the boundaries between subpopulations. Profile 1 shows clear differences between 'classic' seasons and 'transition' seasons in terms of limits between normal and anomalous populations. In this sense, in summer and winter there is a break between normal and transitional populations at similar levels (6.76 ng m^{-3} in winter and 7.73 ng m^{-3} in summer), while in spring this break occurs at higher levels (14.81 ng m^{-3}) and autumn it occurs at 10.36 ng m^{-3}. In profile 1 the anomalous population corresponds to the emissions of Valdeazogues riverbank sediments and these are detectable at Hg levels of 10 ng m^{-3} in drier seasons (autumn and summer) and up to 30.14 ng m^{-3} in wet seasons (winter and spring); it should be remembered that this profile does not have any significant emission sources, except for polluted sediments, and the background values are below 10–14 ng m^{-3} in all seasons. A scenario in which emission sources are absent is best represented by profile 3, since it only has two points of contact with contaminated sediments (3.5 kilometres away from the nearby El Entredicho mine) and therefore its total Hg contents are much lower than in profile 1. Normal values appear in profile 3 at around 5 ng m^{-3} in summer and winter, and at around 10 ng m^{-3} in spring and autumn. These values can be considered as the local geochemical background values for the study area. It should be noted that a second transition population appears in

autumn and winter and this does not have an obvious explanation based on the appearance of a second source of emission in this background value profile.

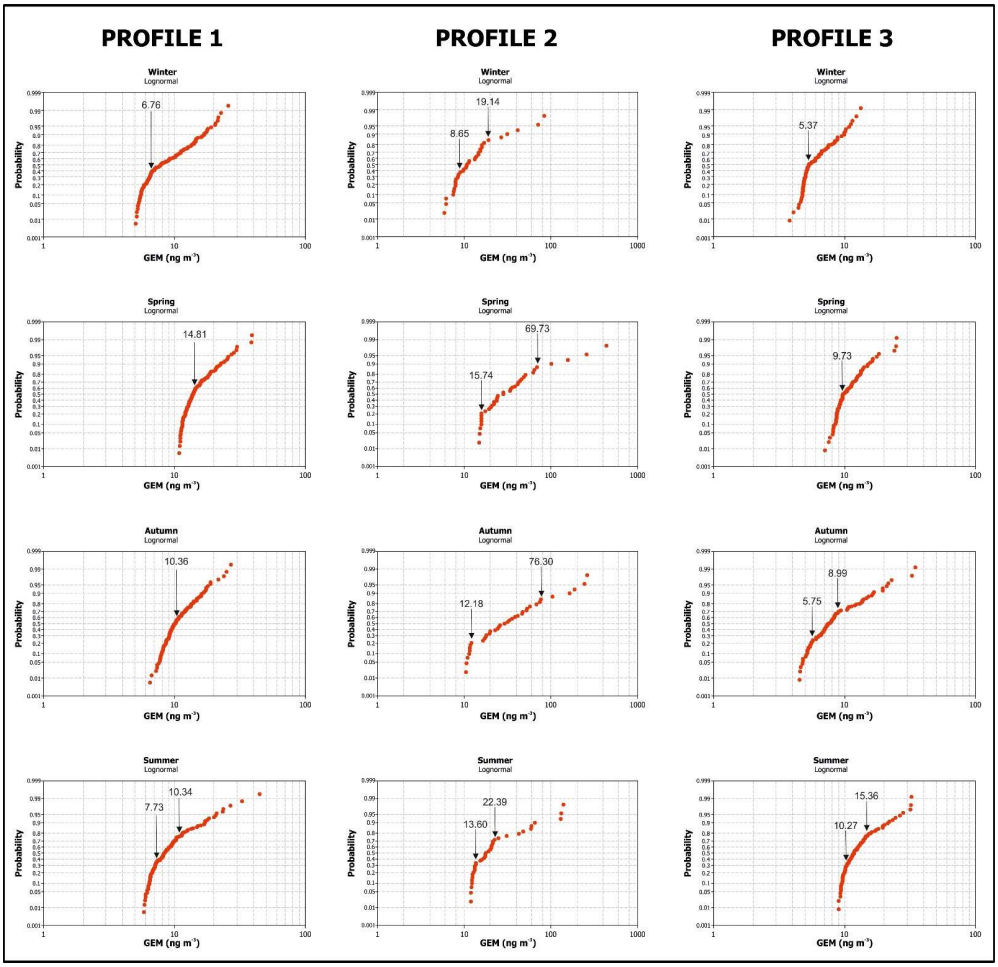


Figure 7: Lepeltier graphs for each profile according to the season.

Profile 2 has two emission sources of medium importance and one of high importance that produces an increase in the limit values of the normal population (around 15 ng m^{-3} in all seasons except winter, which has a value of 8.6 ng m^{-3}). This scenario with multiple emission sources leads to the appearance of a second transition population in winter, autumn and summer. The existence of an emission source as important as the MMP produces an increase in the limit of anomalous values from around 70 ng m^{-3} in winter and spring to 243 ng m^{-3} in summer, i.e., well above the WHO (2000) limit for chronic exposure of 200 ng m^{-3}.

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. ~~but we also offer data~~Night-time ~~measured~~ measures ~~during the night in summer because Esbrí et al. (2016) and Tejero et al. (2015)~~during summer nights reported higher GEM levels ~~during nocturnal hours~~ in the surroundings of mining-related GEM sources, with levels more than two times higher in Almadén, for instance. The present study provides information about the extent of this increase in nocturnal GEM levels. The evolution of Hg contents at three different time points, during the day when the wind ceases, and the probabilistic graph for each dataset are presented in Fig. 8. In profile 2 the maximum values are observed at the end of the monitoring, after the cessation of the wind, in all of the sources considered except for a contaminated road. This finding indicates that the wind is a determining factor for the increase in the environmental concentrations of Hg despite the fact that the emissions are probably lower. The evolution of the increase in the GEM values from the beginning to the end is difficult to observe in the distance vs GEM graph, but the Lepeltier graph (Fig. 8B) offers a better view of the situation for all of the data populations. In profile 2 the shift towards higher GEM values occurs only in the transition population and not in normal or anomalous values. The reason for this increase in the medium values (transition population) but not in normal or anomalous populations could be explained by the absence of dispersion processes, with background values and anomalous values remaining at similar levels because they are more dependent on emission factors (essentially temperature). So, what happens in profiles that do not have important emission sources? In profile 3 there are clearer increases towards the end of the monitoring without exception, and the increases in GEM contents affect all populations, i.e., normal, transitional and anomalous data. This trend provides evidence that the nocturnal increase in GEM values is homogeneous in the absence of significant sources of high emission and only the topography seems to be an important factor that drives this process, as can be seen in Fig. 8C: gaseous mercury emitted by minor sources tends to move downslope and becomes more dilute during this dispersion process. It is necessary to emphasize that the topography of the study area consists of mountainous alignments of smooth slopes, typical of the Appalachian relief, with maximum differences of heights of 220 meters. In the case of profile 3, this accumulation process happens in the bottom of the valleys. The Valdeazogues River and its sediments are a minor Hg source and the extent of higher nocturnal GEM levels reaches more than 1000 metres around the riverbed through a combination of both accumulation process, i.e., local emissions from sediments and topography.

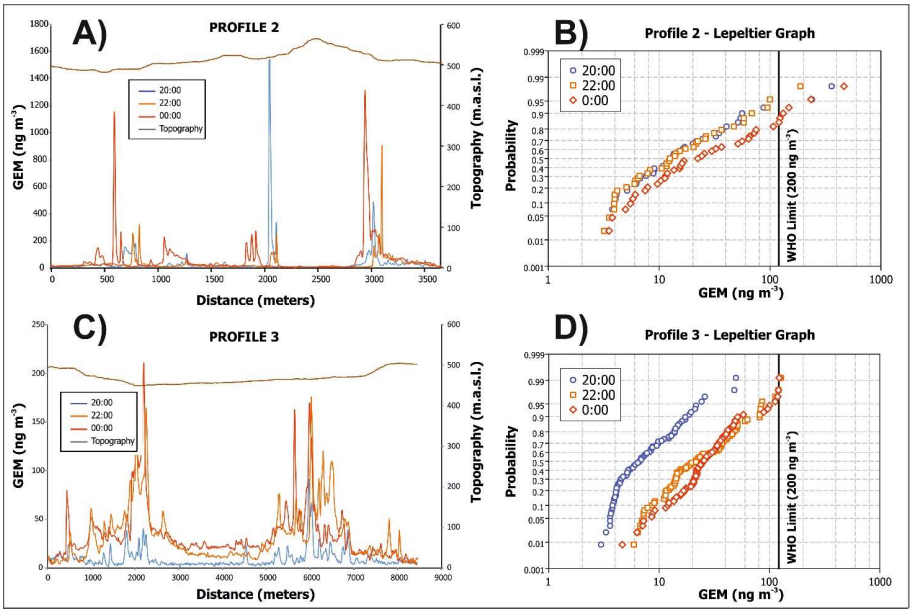


Figure 8: Nocturnal GEM levels in Almadenejos and surroundings. Summer average represents the average of diurnal GEM measurements in summer surveys. Graphs B and D are the Lepeltier curves of datasets A and C, respectively.

3.3 4D dispersion of TGM in the Almadenejos area

The preliminary conclusions from the monitoring work on the vertical and horizontal gradients suggest that dilution processes are the key for explaining the movements of Hg in a mining-metallurgical environment with multiple emission sources scattered throughout the study area. The creation of the mixing layer in the early morning hours represents an increment in Hg dilution and this is driven by increases in solar radiation, temperature and winds, which simultaneously lead to enhanced mercury emissions due to the same factors (Carpi and Lindberg, 1997; Gustin et al., 2002; Lindberg et al., 1999). Major gaseous Hg sources act as a constant supplier to the mixing layer, thus promoting movements to the closest areas and the deposition of this mercury when the convective forces cease and the mixing layer disappears. In terms of risk assessment, the existence of the mixing layer dilutes gaseous mercury and prevents the appearance of TGM levels up to 200 ng m^{-3} in populated areas, thus restricting the zone affected to some tens of metres, even with a huge gaseous mercury source (MMP) very close to the houses in Almadenejos. Conversely, this process causes the dispersion of a large amount of mercury to the surroundings and this increases the risk of air-plant transfer, even to edible vegetables grown in local orchards. The most favourable seasons to activate this process are the driest and warmest (i.e., spring and summer), while the micrometeorological conditions that can inhibit this process are rain, regional winds or persistent fog on winter days.

An opposite scenario occurs when local winds cease in twilight hours: emission rates decline with the absence of solar radiation and the decrease in temperature, while a wind speed close to zero produces an increase of TGM concentrations and strong negative gradients (Fig. 2) at human heights (from 0 to 3 metres above ground). Once again, summer is the season that has the most negative gradients and this is due to the contrasting differences in micrometeorological parameters (Fig. 2). During these nocturnal hours, horizontal movements play the most important role in the transference of gaseous mercury in the area. Clear differences in processes between diurnal and nocturnal hours can be highlighted: dispersion/diffusion, dilution/concentration and the predominance of vertical/horizontal transferences. As a consequence, the extent of the areas affected by higher TGM levels increases, and it is not only the well-known major sources that play an important role, but also minor sources, which produce extended areas with more than 200 ng m^{-3} during summer nights without winds. Contaminated sediments of the Valdeazogues River act as the main secondary source in the Almadenejos area. This river receives polluted fine-grained mine materials, particularly from the El Entredicho mine (Fig. 1) but also from other nearby old mines such as Las Cuevas, Vieja Concepción and Nueva Concepción.

In terms of risk assessment, the monitoring strategy presented in this work was able to identify the main zones of the urban area that can reach TGM concentrations above the WHO limit for chronic exposure (200 ng m^{-3}) and also the period of time during the day or throughout the year in which this limit is exceeded. The vertical gradients dataset obtained in the immediate vicinity of a medium emission source (AWTP) seems to indicate that, in terms of average values, only the night-time periods in summer and autumn produce concentrations above the WHO limit. To identify the hours during which inhalation of gaseous Hg may occur, one must take into account the whole dataset and not only these average values. Likewise, we identified the most favourable conditions for the WHO limit for chronic exposure to be exceeded (Table 4). This was achieved using the MLRA equations for the dataset at 2 metres (Table 3), i.e., the approximate height of a human being. It can be seen from the results in Table 4 that the nights are riskier than the days in all seasons (54% in spring and winter, 72% in summer) but in autumn this trend is reversed, with 99% of the hours of risk occurring during the day. The main factors are those related to dilution (or its absence): wind speed and solar radiation at null levels. It should be noted that the temperature in the hours at risk of inhalation of gaseous Hg can be as low as –4 °C in winter, which is consistent with the idea expressed above that it is the dilution processes (or their absence) that most decisively influence in the creation of periods of risk for the inhalation of gaseous Hg.

Once we had identified the micrometeorological conditions in which there was a risk, we proceeded to identify the extent of this risk in space. Profile 2 shows that the extent of the area affected by an emission source is independent of its importance in terms of absolute emissions, with the area not extending during the daytime period beyond 100 metres from the location of the source (Fig.

5). In the night, however, the extent of the affected area can reach more than 200 metres around the emission source (Fig. 8). Likewise, it can be seen from profile 3 (Fig. 8) that the risk associated with the increase of TGM values as a result of the emissions of contaminated sediments from the Valdeazogues River is null, with values of 100 ng m^{-3} not exceeded even under the worst micrometeorological conditions: i.e., summer nights without wind. The displacement of the Lepeltier curves in Fig. 8 shows that the cessation of wind during the night produces an increase of up to 33 ng m^{-3} in the population of anomalous values, with only three values exceeding the WHO limit of 200 ng m^{-2}, while in profile 2 this increase reaches 178 ng m^{-3} and, in this case, the micrometeorological conditions prevalent at night mean that almost all of the anomalous population exceeds the WHO limit of 200 ng m^{-3}.

From the data discussed above one can estimate the extent of the risk areas in a basic way from the micrometeorological conditions. Two extreme cases for day and night, in summer and in the absence of wind, are represented in Fig. 9. It can be observed that during the night the affected area can reach almost 100% of the homes in Almadenejos, although it is necessary to remember that the results of the MLRA indicated that only 11.34% of the hours of the studied year presented a risk of exceeding the WHO limit for chronic exposure (200 ng m^{-3}).

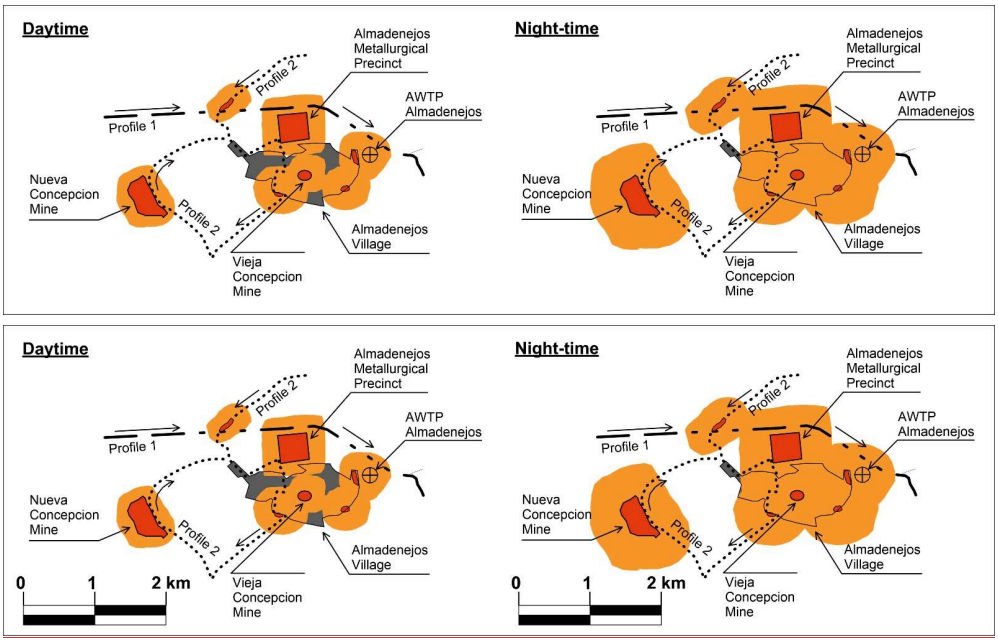


Figure 9: Extent of areas with Hg inhalation risk in the worst scenarios (orange) in relation to the different source areas (red), during daytime (left) and night-time (right).

This approach is applicable with little variation to any area affected by diffuse Hg emissions, but will require adaptations if Hg emissions are active, whether it is anthropogenic (mostly industrial) or natural (volcanic related). In these cases, the monitoring procedures must be extended to the emission processes, with the aim of incorporating these data into the built model. In this way, the model will also serve to foresee changes in emission rates, either due to changes in technology in industrial activity, due to changes in emission patterns in natural processes or changes in emissions rates derived of restrictions of Minamata Convention.

4 Conclusions

The study of transfer pathways of gaseous mercury in a mining-related environment has shown higher TGM levels at lower heights during nocturnal hours, relatively homogeneous and low levels during diurnal hours, and brief inversion periods during dawn and dusk.

Major sources act as constant suppliers of gaseous mercury to the diurnal mixing cell, while minor sources play an important role in mercury dispersion during nocturnal hours.

Vertical transferences occur preferentially during diurnal hours, while horizontal transferences predominate during nocturnal hours.

The monitoring strategy provided sufficient data to delineate spatial and temporal risk areas. This monitoring work established the following as minimum data to be obtained in any given area affected by gaseous Hg emissions:

- identification of emission sources, with special emphasis on location and importance
- collection of data in a vertical transect at a fixed point during all seasons of the year
- collection of GEM data in horizontal transects that may include a combination of background and anomalous GEM values in its path, as well as day and night values.

A significant statistical treatment must be added to this TGM data acquisition strategy. It is proposed here that models should be established using MLRA in order to allow the estimation of the times of risk based on past or expected micrometeorological data, without the need to re-measure after performing the risk assessment.

The results of this risk assessment show that nights are riskier than days in all seasons (54–72% in winter, spring and summer) but in autumn 99% of the higher-risk hours are diurnal. The main factors involved in the creation of periods of risk are those related to dilution (or its absence), e.g., wind speed and solar radiation at null levels. The extent of the affected area is independent of the importance of the source in terms of absolute emissions, with the affected area not extending more than 100 metres from the location of the source during the daytime period and 200 metres in the night-time. The worst scenario produced an affected area that covered almost the entire town of Almadenejos, although these risk conditions only represent 11.34% of the hours in an annual period.

Authors contribution

The manuscript was written through contributions of all authors. JME and RN acquired all experimental data. JME and AMC applied MLRA analysis to the dataset. JME, PHH and AMC produced the probabilistic Lepeltier graphs. All co-authors contributed to the writing of the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Authors contribution

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Con formato: Español (España)

Tables.

Table 1. Statistical summary of TGM levels at different heights (3, 2 and 0.5 metres) and total gradient (3–0.5 m), upper gradient (3–2 m) and lower gradient (2–0.5 m) in Almadenejos WWTP. All TGM data are in ng m^{-3}.

	N	Maximum	Minimum	Average
All data				
TGM (3 m)	6518	3012	2	125
TGM (2 m)	6518	2807	1	111
TGM (0.5 m)	6510	1971	1	102
Autumn				
TGM (3 m)	1570	2378	2	134
TGM (2 m)	1570	1544	1	116
TGM (0.5 m)	1570	1360	1	104
Winter				
TGM (3 m)	1222	1056	5	93
TGM (2 m)	1222	813	5	79
TGM (0.5 m)	1221	525	4	70
Spring				
TGM (3 m)	1589	1506	7	93
TGM (2 m)	1589	837	5	80
TGM (0.5 m)	1582	819	4	75
Summer				
TGM (3 m)	2137	3012	7	160
TGM (2 m)	2137	2807	7	147
TGM (0.5 m)	2137	1971	7	137
	Almadén *(Esbrí* et al.*, 2016)*			
TGM Autumn	*2025*	*281*	*0.8*	*23*
TGM Winter	*1159*	*122*	*0.8*	*13*
TGM Spring	*1067*	*280*	*3.1*	*23*
TGM Summer	*2019*	*687*	*2.5*	*52*

Tabla con formato

Table 2. Statistical summary of gradients: total gradient (3–0.5 m), upper gradient (3–2 m) and lower gradient (2–0.5 m). All TGM data are in ng m^{-3}.

	N	Maximum	Minimum	Average
All data				
Gradient (3–0.5 m)	6510	398	–1270	–23
Gradient (3–2 m)	6510	578	–1066	–9
Gradient (2–0.5 m)	6518	566	–1280	–14
Autumn				
Gradient (3–0.5 m)	1570	398	–1166	–30
Gradient (3–2 m)	1570	578	–756	–12
Gradient (2–0.5m)	1570	566	–1280	–18
Winter				
Gradient (3–0.5 m)	1221	164	–531	–23
Gradient (3–2 m)	1221	160	–484	–9
Gradient (2–0.5 m)	1222	468	–400	–14
Spring				
Gradient (3–0.5 m)	1582	171	–691	–18
Gradient (3–2 m)	1582	263	–559	–6
Gradient (2–0.5 m)	1589	149	–789	–12
Summer				
Gradient (3–0.5 m)	2137	371	–1270	–22
Gradient (3–2 m)	2137	433	–1066	–10
Gradient (2–0.5 m)	2137	318	–801	–13

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Table 3. Predictor coefficients resulting from a multiple linear regression analysis (MLRA). The main predictors by season are shown in bold type. Abbreviations: Temp: outside temperature; Hum: outside humidity; WindSp.: Wind speed; Bar.Pres.: Barometric pressure; SolarRad.: Solar radiation; n.c.: not considered in the MLRA.

	Constant	Temp	Hum	WindSp	Bar.Pres	Rain	SolarRad	r^2
Grad tot								
SUMMER	0.010	0.112	n.c.	**0.143**	0.034	-0.022	0.079	57.4
SPRING	0.001	n.c.	0.087	0.161	–0.047	0.015	**0.215**	77.6
AUTUMN	0.000	–0.068	0.043	0.164	–0.101	n.c.	**0.175**	83.9
WINTER	0.001	0.127	0.092	0.165	n.c.	0.036	**0.172**	74.8
Grad inf								
SUMMER	0.008	**0.101**	–0.021	**0.1**	–0.001	n.c.	0.056	85.8
SPRING	0.002	n.c.	0.063	0.133	–0.037	0.013	**0.156**	85.0
AUTUMN	0.000	–0.072	n.c.	**0.114**	–0.054	n.c.	0.112	91.5
WINTER	0.000	0.083	0.091	0.117	–0.045	n.c.	**0.144**	84.3
Grad sup								
SUMMER	0.014	0.001	n.c.	**0.07**	0.015	0.002	0.052	84.1
SPRING	0.000	n.c.	0.044	0.067	–0.025	0.032	**0.121**	78.6
AUTUMN	0.000	n.c.	0.059	0.094	–0.084	0.038	**0.117**	82.9
WINTER	0.000	0.068	n.c.	**0.097**	0.034	0.030	0.073	78.3
TGM at 2 m. height								
SUMMER	–0.035	–0.101	0.144	**–0.236**	–0.139	–0.052	–0.197	82.4
SPRING	–0.002	–0.114	–0.108	**–0.345**	–0.065	–0.085	–0.282	81.6
AUTUMN	–0.008	0.242	0.038	–0.269	–0.079	–0.125	**–0.390**	84.5
WINTER	0.000	–0.120	–0.088	–0.287	0.158	–0.027	**0.307**	79.3

560 Table 4. Micrometeorological conditions for TGM outdoor values to exceed the WHO limit for chronic exposure of 200 ng m^{-3}. Abbreviations: T: temperature; RH: relative humidity; WindSp: wind speed; and SR: solar radiation.

		T (ºC) *min*	RH (%) *min*	Windsp (m s^{-2}) *max*	SR (W m^{-2}) *max*	Time (h) *N*
Summer	Night	11.5	29.2	1.9	0	204
	Day	10.5	33.5	1.7	0.2	93
Autumn	Night	22.8		0	0	3
	Day	7.8		3.4	0.5	280
Winter	Night	–4.1		0.3	0	155
	Day	–4.2		0.1	0.2	19
Spring	Night	7.7		1.3	0	155
	Day	9.5		2.3	0.2	85