Peer review history for:

Belelie MD, Ayob N, Burger RP, Venter AD, Piketh SJ. Atmospheric mercury dispersion over the South African Highveld. S Afr J Sci. 2025;121(3/4), Art. #17029. https://doi.org/10.17159/sajs.2025/17029

HOW TO CITE:
Atmospheric mercury dispersion over the South African Highveld [peer review history]. S Afr J Sci. 2025;121(3/4), Art. #17029. https://doi.org/10.17159/sajs.2025/17029/peerreview

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Reviewer 1: Round 1
Date completed: 29 November 2023
Recommendation: Accept / Revisions required / **Resubmit for review** / Resubmit elsewhere / Decline / See comments
Conflicts of interest: None

Does the manuscript fall within the scope of SAJS?

Yes/No

Is the manuscript written in a style suitable for a non-specialist and is it of wider interest than to specialists alone?

Yes/No

Does the manuscript contain sufficient novel and significant information to justify publication?

Yes/No

Do the Title and Abstract clearly and accurately reflect the content of the manuscript?

Yes/**No**

Is the research problem significant and concisely stated?

Yes/No

Are the methods described comprehensively?

Yes/**No**

Is the statistical treatment appropriate?

Yes/No/**Not applicable**/Not qualified to judge

Are the interpretations and conclusions justified by the research results?

Yes/**Partly**/No

Please rate the manuscript on overall contribution to the field

Excellent/**Good**/Average/Below average/Poor

Please rate the manuscript on language, grammar and tone

Excellent/Good/**Average**/Below average/Poor

Is the manuscript succinct and free of repetition and redundancies?

Yes/No

Are the results and discussion confined to relevance to the objective(s)?

Yes/No

The number of tables in the manuscript is

Too few/**Adequate**/Too many/Not applicable

The number of figures in the manuscript is

Too few/Adequate/Too many/Not applicable

Is the supplementary material relevant and separated appropriately from the main document?

Yes/No/**Not applicable**

Please rate the manuscript on overall quality

Excellent/Good/Average/**Below average**/Poor

Is appropriate and adequate reference made to other work in the field?

Yes/**No**

Is it stated that ethical approval was granted by an institutional ethics committee for studies involving human subjects and non-human vertebrates?

Yes/No/**Not applicable**

If accepted, would you recommend that the article receives priority publication?

Yes/**No**

Are you willing to review a revision of this manuscript?

Yes/No

With regard to our policy on ‘Publishing peer review reports’, do you give us permission to publish your anonymised peer review report alongside the authors’ response, as a supplementary file to the published article? Publication is voluntary and only with permission from both yourself and the author.

Yes/No

Comments to the Author:

Review of specific aspects:

Scope

The topic is appropriate for the scope and readership of the Journal.

Content

This is the first peer-reviewed study to model the dispersion of mercury emissions over the South African Highveld (i.e. at a local scale), and so I believe it is sufficiently novel to warrant publication.

The title is appropriate. I caution against the use of the rather alarmist statement in the abstract that ‘the population working and living near power plants may be at risk of acute adverse health impacts due to inhalation’ without explaining precisely how this was calculated, where it occurs and what the certainty is.

The literature review appears to be dated and there are several more recent (and not so recent) studies that need to be included e.g. Pacyna et al (2016) and perhaps some of the work of Brunke.

There are several issues with the methods that I feel need to be addressed before the study can be published. Please see my comments under Major Issues (and also some under Minor Issues).

The description and interpretation of the findings are somewhat vague and imprecise and need to be improved.

The formatting of references needs to be improved. Many references are incomplete.

Presentation

The clarity of the language needs to be improved. The manuscript is well structured and focused. The length of the paper is appropriate, although I have suggested in Minor Issues that a few more plots of the deposition results are needed.

Scientific conduct

There are no obvious conflicts of interest, and ethics approval is not required for this study.

Major Issues

There are several deficiencies in the dispersion modelling that need to be addressed and/or properly explained in the manuscript:

- The study period should be consistent for the meteorological data and the emissions data. It is currently not stated what year the emissions are for. Are they the average of emissions for the three-year study period?
- The mercury emissions information is not adequately justified, especially considering what an important input these are. How were the emissions derived? Why are emissions from an

unpublished source used, rather than those published by Garnham and Langerman (2016)? How do these emissions compare to those of Garnham and Langerman (2016)?

- Please explain how the CALPUFF model handled the conversion/transformation of mercury species in the atmosphere.
- It appears that the dry deposition parameters of Hg0 were assumed to be identical to those adopted for Hg2+. It is very difficult to justify this, considering that Hg0 is highly non-reactive and Hg2+ is highly reactive. The deposition values of Hg have been over-predicted and the Hg0 concentrations under-predicted. This needs to be corrected.
- The dispersion model output needs to be validated against measurements of mercury concentrations on the Highveld and mercury measured in rainwater (if available).

A secondary issue that needs to be addressed is that the literature review needs to be updated to include more recent studies.

Lastly, the interpretation of the results needs to be improved. I have highlighted several issues in the Minor Issues section of this review.

Minor Issues

Please address the following:

1. Line 7: The statement that the Highveld has the ‘poorest air quality in the country’ needs to be well referenced in the main text if this statement is made in the abstract.
2. Line 44: It is unclear what a ‘coal landfill’ is; please reword.
3. Line 44: ‘Metallurgy’ is not an emission source. Do you mean ‘metallurgical smelters’?
4. Line 51: The South African mercury emissions published in Pacyna et al (2006) have since been corrected because they were based on incorrect mercury content in coal values. Please update.
5. Lines 62-63: The form of mercury emissions from coal-fired power stations, which are stated to be the largest source of atmospheric mercury emissions, also depend largely on the PM abatement technology (fabric filter plant or electrostatic precipitator) installed at a power station, which removes some of the mercury from the flue gas stream. The form of global mercury emissions are not necessarily applicable to South African coal-fired power stations. Please address.
6. Line 80 and onwards: The choice of dispersion model should be discussed in the Methods section, and not in the Introduction.
7. Line 93: SAHA is not a recognized abbreviation. Rather don’t use it.
8. Line 116: The study period (2011-2013) is rather long ago. Please justify why this period was selected.
9. Line 133: Please justify why unpublished mercury emissions were used, rather than those published by Garnham and Langerman (2016).
10. For what year are the mercury emissions used in this study? What is the inter-annual variability in mercury emissions from Eskom’s power stations? Please clarify.
11. Lines 133-135: The Hg speciation depends on the PM removal technology installed at power stations, and so obviously varies per plant. A detailed discussion on this is needed, and justification for using the average values is required.
12. Table 3: The coordinates are shown in degrees S and E, not as x-y coordinates in metres. Also, the output capacities are incorrect. Please see Eskom’s Integrated Report for the power station capacities in 2011-2013.
13. Lines 142-144: If mercury is absorbed into the droplets (I assume this is the ‘aqueous phase of clouds’ although I don’t think clouds exist in other phases) then it will probably be removed from the atmosphere by wet deposition rather than by dry deposition.
14. Line 163: The units for 0.48 need to be included.
15. Section 2.3: Please explain how the CALPUFF model handled conversion/transformation of mercury species in the atmosphere.
16. Line 128: Reference 28 does not assess exposure to power plant emissions.

17. Section 2.3: It is not actually stated here what deposition parameters are used for Hg0 in this study. Please specify clearly.
18. Line 194: The statement that 'The primary exposure pathway is inhaling inorganic Hg0' is directly contradicted by the reference cited, which states that 'exposure of the general population is primarily to organic mercury from dietary exposure to methylmercury (e.g., fish, seafood, rice) and elemental mercury from dental amalgams. Relative to organic and elemental mercury, exposure of the general population to inorganic mercury compounds is minimal. Please correct.
19. Line 208: It is not clear why it is stated that 'However, this practice is not recommended in studies investigating inorganic compounds' since the focus in this study is on exposure to elemental mercury?
20. Table 5: The RELs need to be included in this table. Also, please clarify why an exposure continuity equivalent to the working week is suitable for evaluating the health risk of exposure to concentrations in the ambient air.
21. Line 224: OEHHA (2014) specifically states that the acute REL is based on maternal exposure. This needs to be included in the 'susceptible subgroups' mentioned.
22. Two methods of assessing risk are mentioned: the RFC and the REL. Please clarify which method is used for which purpose.
23. Line 253: What does it mean that Matla and Kriel (most readers won't know where these power stations are) have 'low emission profiles'? Both of these power stations have relatively high mercury emissions because they are fitted with ESPs.
24. Line 254: What are the 'measured concentrations in this study'? No measurements have been presented.
25. Lines 255-257: The meaning of the following is unclear: 'A comparison showed a significant difference in the number of sources modelled in the current study and those in international studies. One would subsequently expect the concentrations in the current study to be much higher'. What sources were included in this study that were not included in international studies? What are the international studies? Please cite them. Are the concentrations predicted here indeed higher than concentrations predicted in other studies?
26. Lines 261-262: The sentences 'the larger the domain, the more species may be removed by deposition processes. In this case, especially Hg0, given its solubility, reactivity and consequent atmospheric lifetime' do not follow. Hg0 is fairly unreactive and has a long atmospheric lifetime so why is it highlighted as being removed by deposition processes?
27. Line 271: The statement 'The results reveal that relatively low amounts of each species were removed from most modelled regions' needs to be improved. Only one region was modelled. By 'removal' do you mean deposition? Please refer to the figures and the amounts to substantiate your statement.
28. Line 273: The statement that removal occurs in the atmosphere above the power stations is odd; please reword. Perhaps you mean the atmosphere in he vicinity of the power stations?
29. Lines 283-285: References 37 and 62 pertain to Poland and China, not to the South African Highveld as implied here. Also, it appears you are comparing modelled mercury deposition values for South Africa to measured values for China. Is this a fair comparison? How do the mercury measurements from South Africa compare to those from China?
30. Line 287: The assumption that the dry deposition parameters of Hg0 were assumed to be identical to those adopted for Hg2+ cannot be justified. Hg0 is highly non-reactive; Hg2+ is highly reactive. The deposition values of Hg have been greatly over-predicted.
31. The mercury deposition results are not presented at all. It would be very helpful for the reader if at least the combined dry deposition and wet deposition plots could be included.
32. It needs to be stated in the heading of Table 6 that the Hazard Quotient is presented in the table.
33. The way in which the 'average predicted exposure' and the 'maximum predicted exposure' in Table 6 were calculated needs to be clearly explained. What is the time period for each measurement? What was averaged in each case?
34. Line 313: What is the 'worst-case scenario' mentioned here? It needs to be very clearly defined.

Earlier it is stated that ‘maximum annual values’ is the worst-case scenario. Is the worst-case scenario at the point of highest impact? But even adding the annual averages of all species of mercury at the point of maximum impact does not get close to 0.026 µg/m3

35. Line 328: The line ‘It could expose the population to depend on fishing to supplement their nutritional needs’ is odd. This is not a local fishing-dependent population. What is the basis for this statement? Bio-accumulation in fish in the ocean would be a much greater issue.
36. Line 331: The statement that ‘the population working and living near power plants may be at risk of acute adverse health impacts due to inhalation’ can only be made once it has convincingly been explained how the acute maximum concentrations were calculated and where they occur.
37. Measured mercury concentrations over this region are available (Belelie et al., 2019). Please used them to validate the CALPUFF modelling output.

Recommendation

I recommend that the authors of this manuscript be asked for major revisions. I am happy to review the revised manuscript.

Author response to Reviewer 1: Round 1

Reviewer comment	**Author response**
There are several deficiencies in the dispersion modelling that need to be addressed and/or properly explained in the manuscript: - The study period should be consistent for the meteorological data and the emissions data. It is currently not stated what year the emissions are for. Are they the average of emissions for the three-year study period?	It's now stated that the emission data was measured in 2014. As noted, we modelled per individual power 2011-2013 and combined the 12 outputs with the CALSUM tool. The CALSUM output shows the cumulative concentration and deposition, not the average, as previously stated – this has now been corrected in the paper.
The mercury emissions information is not adequately justified, especially considering what an important input these are. How were the emissions derived? Why are emissions from an unpublished source used, rather than those published by Garnham and Langerman (2016)? How do these emissions compare to those of Garnham and Langerman (2016)?	Power plant-specific Hg-coal content data was measured for each power plant in 2014 and obtained directly from ESKOM. In 2016, I presented a paper at the annual NACA conference, where I presented these estimates. The paper compared the assumed Hg coal contents from the literature with the actual Hg coal contents in 2014. Please see citation 7 in the reference list.
Please explain how the CALPUFF model handled the conversion/transformation of mercury species in the atmosphere.	Please advise whether I've acceptably addressed this comment. Since Hg's oxidation mechanisms in the atmosphere are not well understood yet, the model doesn't have a conversion scheme for the pollutant and its species. The model used the specified parameters (like diffusivity and reactivity, exit velocity) to determine dispersion/deposition. A 2019 study developed a CALPUFF-Hg version to model Hg specifically (please see citation 37). This scheme will be adopted for our prospective Hg modelling.
It appears that the dry deposition parameters of Hg0 were assumed to be identical to those adopted for Hg2+. It is very difficult to justify this, considering that Hg0 is highly non-reactive and Hg2+ is highly reactive. The deposition values of Hg have	The reviewer is correct, of course, and this was a slight oversight. The previous is why it is stated that the modelling is assumed to be conservative. We've added a discussion in the paper stating that the results are over/under-estimated. Unfortunately, this cannot be corrected given modelling constraints like time constraints. Nevertheless, we'd like to

been over-predicted and the Hg0 concentrations under-predicted. This needs to be corrected.	thank the reviewer for this comment, which can now be corrected in the subsequent modelling studies of Hg.
The dispersion model output needs to be validated against measurements of mercury concentrations on the Highveld and mercury measured in rainwater (if available).	I've compared the modelling concentrations to ambient in situ measurements from one of my past studies, as mentioned by the reviewer in a later comment (Belelie et al., 2019). We trust that the discussion is acceptable.
A secondary issue that needs to be addressed is that the literature review needs to be updated to include more recent studies.	We've updated some of the references but are unsure if the reviewer has deemed them to an adequate extent. Please advise.
Lastly, the interpretation of the results needs to be improved. I have highlighted several issues in the Minor Issues section of this review.	This was a major comment from both reviewers, so much of the text presented in the previously submitted manuscript has since been removed. On the other hand, much text has been added and/or improved upon based on the reviewer's comments. All changes are highlighted in yellow in the revised manuscript.
Minor Issues	All minor issues, as outlined by the reviewer, have been addressed. E.g. the deposition results are presented, the potentially alarming statements have been rewritten, and it's now stated that the sum was used. Not the average, and it's explained that the lowest and highest modelled exposures were used in the risk assessment, but at a specific location only and not generalised for the whole domain. Unclear statements have either been removed or rewritten for clarity. A discussion on emission control/abatement technologies was also added. Please advise whether the discussion requires more conversation. Also, I (the lead author) sensed that the reviewer was unhappy with the conclusion (alarming/confusing statements or otherwise). Please advise whether it's now acceptable.

Reviewer 2: Round 1
Date completed: 16 February 2024
Recommendation: Accept / **Revisions required** / Resubmit for review / Resubmit elsewhere / Decline / See comments
Conflicts of interest: None

Does the manuscript fall within the scope of SAJS?

Yes/No

Is the manuscript written in a style suitable for a non-specialist and is it of wider interest than to specialists alone?

Yes/**No**

Does the manuscript contain sufficient novel and significant information to justify publication?

Yes/No

Do the Title and Abstract clearly and accurately reflect the content of the manuscript?

Yes/**No**

Is the research problem significant and concisely stated?

Yes/No

Are the methods described comprehensively?

Yes/**No**

Is the statistical treatment appropriate?

Yes/**No**/Not applicable/Not qualified to judge

Are the interpretations and conclusions justified by the research results?

Yes/**Partly**/No

Please rate the manuscript on overall contribution to the field

Excellent/Good/Average/**Below average**/Poor

Please rate the manuscript on language, grammar and tone

Excellent/Good/**Average**/Below average/Poor

Is the manuscript succinct and free of repetition and redundancies?

Yes/No

Are the results and discussion confined to relevance to the objective(s)?

Yes/No

The number of tables in the manuscript is

Too few/Adequate/Too many/Not applicable

The number of figures in the manuscript is

Too few/Adequate/Too many/Not applicable

Is the supplementary material relevant and separated appropriately from the main document?

Yes/No/**Not applicable**

Please rate the manuscript on overall quality

Excellent/Good/Average/**Below average**/Poor

Is appropriate and adequate reference made to other work in the field?

Yes/No

Is it stated that ethical approval was granted by an institutional ethics committee for studies involving human subjects and non-human vertebrates?

Yes/No/**Not applicable**

If accepted, would you recommend that the article receives priority publication?

Yes/**No**

Are you willing to review a revision of this manuscript?

Yes/No

With regard to our policy on 'Publishing peer review reports', do you give us permission to publish your anonymised peer review report alongside the authors' response, as a supplementary file to the published article? Publication is voluntary and only with permission from both yourself and the author.

Yes/No

Comments to the Author:

I have made detailed comments on the attached pdf.

The scope of the study and the overall findings would be of relevance to the SAJS community, and I do believe that this would be a good journal for such a study to be published in. However, I do not recommend that it is accepted in its current form. I recommend either resubmission after major revisions or rejection with a recommendation to resubmit later. I have made detailed comments in the attached pdf that outline my concerns. I will summarise them briefly here.

In many places there is just too little information to assess the work. I recommend more results are shown as well as information on previous studies. Many comments are highly generalized and the quantitative information isn't discussed often (much is more qualitative, e.g. the abstract that has no quantitative results). In addition, I have comments on the assumptions made to discuss firstly the average deposition over the domain and secondly the average HQ over the domain. I explain more in the attached on both of these, but the former is highly skewed by the size of the modelling domain, so I am not convinced it is the best metric to use to compare to other studies. Also, the average over some domain has less physical meaning as the plants, water and soils don't move across the domain. This last point is also valid for the HQ analysis that was not spatial in this study, but used average for this large domain. The HQ is estimating risk to people, and to average over the domain means a person would inhale the average of the domain. I think a spatial analysis would provide results that more accurately estimate health risk.

In addition, this modelling is similar to a thesis at NWU (M Belelie: https://repository.nwu.ac.za/handle/10394/30615). If this paper is based on this thesis, then that is fine. If it is not, then I would expect to see it referenced more and compared to in the manuscript.

[See Appendix 1 for Reviewer 2's comments made directly on the manuscript]

Author response to Reviewer 2: Round 1

All comments by the reviewer in the pdf document have been addressed. We want to thank the reviewer for a very detailed review.

As requested by both reviewers, we've shown the deposition results. The comparison table between this study and international modelling studies is not shown after thoroughly revising this reviewer's comments. The reviewer noted that the comparison was inappropriate and has since been removed.

More information, hopefully to the satisfaction of the reviewer, has been added throughout the manuscript – based on comments by both reviewers.

The abstract has been entirely changed.

Quantitative results are now also discussed based on comments from both reviewers.

The assumption was based on the sum, not the average – this is clearly stated now.

The risk assessment is now based on the sum of concentration in the vicinity of Kriel and Matla, and longer for the entire domain. The HQ discussion has also been entirely changed. The exposure values used for the chronic exposure were also in ng/m3 and not ug/m3, so this has also been corrected.

The modelling is based on the lead author's MSC dissertation.

Reviewer 2: Round 2
Date completed: 25 October 2024
Recommendation: Accept / **Revisions required** / Resubmit for review / Resubmit elsewhere / Decline / See comments
Conflicts of interest: None

Does the manuscript fall within the scope of SAJS?

Yes/No

Is the manuscript written in a style suitable for a non-specialist and is it of wider interest than to specialists alone?

Yes/No

Does the manuscript contain sufficient novel and significant information to justify publication?

Yes/No

Do the Title and Abstract clearly and accurately reflect the content of the manuscript?

Yes/No

Is the research problem significant and concisely stated?

Yes/No

Are the methods described comprehensively?

Yes/**No**

Is the statistical treatment appropriate?

Yes/No/**Not applicable**/Not qualified to judge

Are the interpretations and conclusions justified by the research results?

Yes/**Partly**/No

Please rate the manuscript on overall contribution to the field

Excellent/**Good**/Average/Below average/Poor

Please rate the manuscript on language, grammar and tone

Excellent/**Good**/Average/Below average/Poor

Is the manuscript succinct and free of repetition and redundancies?

Yes/No

Are the results and discussion confined to relevance to the objective(s)?

Yes/No

The number of tables in the manuscript is

Too few/**Adequate**/Too many/Not applicable

The number of figures in the manuscript is

Too few/**Adequate**/Too many/Not applicable

Is the supplementary material relevant and separated appropriately from the main document?

Yes/No/**Not applicable**

Please rate the manuscript on overall quality

Excellent/**Good**/Average/Below average/Poor

Is appropriate and adequate reference made to other work in the field?

Yes/No

Is it stated that ethical approval was granted by an institutional ethics committee for studies involving human subjects and non-human vertebrates?

Yes/No/**Not applicable**

If accepted, would you recommend that the article receives priority publication?

Yes/**No**

Are you willing to review a revision of this manuscript?

Yes/No

With regard to our policy on 'Publishing peer review reports', do you give us permission to publish your anonymised peer review report alongside the authors' response, as a supplementary file to the published article? Publication is voluntary and only with permission from both yourself and the author.

Yes/No

Comments to the Author:

The authors have done a lot of work on the manuscript and this version is a very strong manuscript. My recommendation that minor revisions are needed. I have noted some comments in the attached. I strongly recommend that they are all addressed before acceptance.

There is one method issue that I believe needs more clarity. It is that it is not clear to me why the human health risk assessment was based on only two stations, the exact definition of the two scenarios, where the receptors are for the analysed health impacts, and then also I have some questions on the RFC and REL (details in the attached).

The other comments are in the attached.

[See Appendix 2 for Reviewer 2's comments made directly on the manuscript]

Author response to Reviewer 2: Round 2

Reviewer comment	**Author response**
I recommend confirming here that the other sources are not modelled, and only Eskom emissions as in Table 2 are modelled.	The sentence has been rewritten to 'Other possible sources that were not modelled are combustion in gasification plants, ferrous and non-ferrous metal production, domestic burning, crude oil refining, cement production, waste deposition and incineration, and illegal artisanal gold mining.'
I would still recommend a little more explanation. To me "conservative"	As suggested by the reviewer, the following sentence was added: 'Here, conservative means that the selected

means that the values would err on the safe side - so in this case it would err on higher levels of deposition. However, the “conservative” part isn’t yet explained here, only that the authors knows there are uncertainties (i.e. it is not “correct”). Thus, I would recommend just one more sentence explaining how it is “conservative” (i.e. it errs on the safe side) to do it this way? I see that it is described more below. I will leave this comment to highlight that as a reader, I do not yet undersand what conservative means at this point as it does not mean “not correct”. Perhaps one sentence noting that it is conservative as the parameters selected, as detailed below, would lead to higher deposition and thus it is deemed “conservative”	parameters, as detailed below, lead to higher deposition.’
Generally these do have an associated time period (i.e. 24-hr average of xxx concentration). What acute and chronic exposure periods does IRIS give for its use?	The US EPA (https://www.epa.gov/mercury/health-effects-exposures-mercury) states that the value is a default value for long-term exposure.
Section 3.3 notes that only two power stations were modelled. The reasoning for that (why only two and not use the full domain? This is a really big assumption) and the definition of the two scenarios has to be detailed in the methods. I would recommend noting it here as it is the estimate of the exposure.	All the power stations were modelled. However, during the first round of reviews, a reviewer recommended that the full domain not be considered but rather a single location. I then thought of a location where the highest concentrations were modelled—near Kriel and Matla, which are very close together. All power stations were modelled, but only two were considered in the potential health risk assessment. A sentence defining the scenarios has been added: ‘Two scenarios were considered: a baseline scenario that evaluated the minimum concentrations, and a worst-case scenario that assessed the maximum concentrations for both acute and chronic exposure.
What is meant by cumulative? RFC is a concentration, which would normally be an average. Or is this referring to the mass inhaled? I am not certain. I recommend just a short explanation.	Here, cumulative refers to the modelled concentrations and not the RFC value. The sentence explains that it refers to the Hg^0 concentrations: ‘The simulation returned modelled hourly, 8-hourly, and periodic (cumulative annual) Hg0 concentrations’
Why were working hours selected? This is ap ublic health study and not an occupational health study. I don’t think this is a valid assumption.	The statement was meant to note that the exposure also aligns with working hours.
How was the REL used? The equation below only uses the RFC? It is not yet clear how the 0.3 reported above for the RFC and the REL discussed her and in the table are used together. I recommend more explanation of this. In addition, the	The following sentences were added to clarify: ‘In our analysis, we utilised the RfC value for assessing chronic exposure, while the US EPA-recommended REL values were employed for acute exposure scenarios. While RfC and REL serve distinct purposes, they were used interchangeably in the formula below for comparative purposes.’

REL at 1-hour is higher than the RFC noted above, but how can that be as the REL is stated here as the level below which there are no health impacts. I recommend this is clarified.	The REL reflects a threshold below which no adverse health effects are expected during short-term exposure. Therefore, it may be higher than the chronic RfC, accounting for the cumulative risks associated with prolonged exposure.
I would recommend in 3.1 and 3.2 to bring in some literature to help the reader understand if these are large values or not. This region has a large amount of coal-fired power stations (really unique globally), so it would be interesting to know the general levels that other studies elsewhere that looked at Hg near coal fired power stations found. I think this is very important for a manuscript in SAJS as the readership is more broad and not just air quality people, and thus it would help readers to understand the scale of the problem.	More literature has been added to each section.
I recommend the significant figures of all of the maps are checked and updated to me more in-line with what is reported in the text. Having only one color in the map does make it hard to really understand the spatial distribution of the deposition. I assume this is because the high values close by the stations as noted below. But is there any way to show some more levels between 0.07 and 7 (in a) and similarly large in b. It may take some trial and error in th legend, but I think it would greatly improve this section.	Updated.
This is dry deposition, correct?	Correct, thank you! Corrected accordingly.
I noted in methods that this section is not yet clear to me as I can't follow why only two power stations were modelled. Why not do this analysis spatially? I would expect that to be described in the methods as well as the definition of the baseline and worst case. As it is written here, it is just not enough information for me to really understand. Also, where we the receptors placed/what distance was assessed to select the lower predicted exposure and the maximum predicted exposure? These are questions that I recommend are added into the methods, but I am noting them here as I read.	The receptors were the 12 power stations. The lower and upper exposures were selected from the full domain, initially. However, a reviewer from the first round of reviews suggested only considering the exposure at a single location (surrounding Kriel and Matla).
As shown in De Lange et al (2021) the simulated PBL also has a large impact on the dispersion - and as this region doesn't have information on the vertical structure of the atmosphere, which I	The information and citation were added to the discussion, as suggested by the reviewer.

would imagine makes it a similar uncertainty in many models.	
I think this is too strong of a word. The HHRA is of course an estimate and there are uncertainties, but “inaccurate” would make me as a reader think, well then why should I even read this? Rather, it is uncertain and it seems the authors believe the HQ could be higher than what it really is. However, in health research there is the precautionary principle that does support using more conservative (i.e.t o err on the safe side, so here to use a higher HQ) results to protect health. I recommend this is rewritten.	The word has been changed to ‘uncertain’ as suggested by the reviewer.
Do these exist?	Unfortunately not yet, no.
If compared to ambient, then all sources should be included.	The sentence has been changed to state that all sources should be included.
Are there many or do we need more? It would seem this study suggests we do need more around Eskom stations (this study could help to place some I would think). I would note that here as it is a key finding from this.	There aren’t many for the interior, no. To date, the only publication on Hg over the interior is the lead author’s publication in 2019. Two other unpublished sources are theses by Meyer (2019) (Highveld) and Bredenkamp (2019) (Welgegund background site) from the NWU. The latter is currently writing a manuscript for Welgegund for her PhD. A paper by the lead author for the Highveld region is also currently pending a second round of reviews at the Science of The Total Environment journal.

Reviewer 3: Round 2

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Appendix 1: Reviewer 2's comments on manuscript (round 1)

Atmospheric Mercury Dispersion over the South African Highveld

Abstract

Coal combustion in coal-fired power plants has been identified as the dominant source of mercury (Hg) emissions in South Africa. Most South African coal-fired power plants are located in a region afflicted by the poorest air quality in the country - the South African Highveld area. However, the state of Hg emitted by the power sector on the South African Highveld is unclear. It is thus essential to generate knowledge on Hg emissions in this region as it represents one of the world's most concentrated source regions of Hg. This study presents the results of the first-ever dispersion modelling study regarding Hg concentrations and wet and dry deposition over this region using CALPUFF. The atmospherically significant forms of Hg (Hg^0, Hg^{2+}, and HgP) were modelled from 12 coal-fired power plants during 2011-2014. As Hg^0 has been identified as the only Hg species to pose a threat via the inhalation pathway, a ~~brief~~ health risk assessment was conducted to put the modelling results into perspective. The concentrations of the Hg species are highest over the cluster of power plants situated in the centre of the domain. The results convey that concentrations of the species are accumulating in an area of already high concentrations over two of the plants. This part of the domain also yielded maximum wet and dry deposition - which makes it clear that the proximity of the power plants leads to higher deposition. The health risk assessment suggests that the population working and living near power plants may be at risk of acute adverse health impacts due to inhalation. The findings also indicate that studies characterizing and quantifying methylmercury concentrations are needed, as this is Hg's most toxic environmental form.

Keywords: coal-fired power plants, mercury, South African Highveld, CALPUFF, deposition.

Significance

The research presents the results of the first-ever dispersion modelling study regarding mercury concentrations and wet and dry deposition over this region using CALPUFF. This is a significant contribution to scientific knowledge on mercury emissions in this region. The study conducts a brief health risk assessment, suggesting that the population working and living near power plants may be at risk of acute adverse health impacts due to inhalation of Hg^0. The findings indicate that further studies are needed to characterize and quantify methylmercury concentrations, as this is mercury's most toxic environmental form. This points to important future research directions.

1. Introduction

The South African Highveld area has been identified as an area associated with poor air quality due to high emissions of criteria pollutants such as particulate matter (PM), SO_2 and NO_x, and a potential area of high concentration of atmospheric mercury (Hg) species [1]. This region is well-known for its various anthropogenic emission sources: coal-fired power plants, coal landfills, metallurgy and mines, agriculture, and transportation [2,3].

Globally and annually, combustion in coal-fired power plants is the dominant anthropogenic source of environmental Hg [4], contributing approximately 56% [5]. Coal-fired power plants were estimated as the leading possible anthropogenic source of ambient Hg emissions in South Africa (72-78 %) [1]. Moreover, a past study listed South Africa as the second-highest global atmospheric Hg emissions source. It contributed to about 16% of global Hg emissions [5].

Mercury is a highly toxic and ubiquitous volatile metal, which is environmentally persistent and prone to long-range atmospheric transport [6]. It subsequently leads to adverse health effects in distant regions where it is emitted [7]. Mercury is, therefore, regarded as a global pollutant threatening both the health of humans and ecosystems [8,9,7,6]. It can be assumed that the ecological behaviour of the Hg emitted depends on the different environmental forms, as these chemical forms have other chemical properties [8, 9].

Unlike other heavy metals in the environment, atmospheric Hg generally occurs in its gaseous phase [10]. It may be emitted into the atmosphere as inorganic gaseous elemental (Hg^0), inorganic reactive gaseous (Hg^{2+}), and inorganic particle-bound Hg (HgP) [11,12]. Atmospheric emissions of Hg are dominated by Hg^0 (53%), followed by Hg^{2+} (37%) and HgP (10%) [13]. Although Hg^0 is the predominant form in the gaseous phase [13, 14], Hg^{2+} significantly influences the total deposition of atmospheric Hg [15]. Under certain conditions, Hg^0 may be removed by dry deposition processes [16]. Mercury is transported over long distances in the atmosphere, even reaching the poles [7]. Due to the concentration of significant sources over the Highveld, it is expected that Hg is transported and deposited over large portions of South Africa [2].

To investigate and better understand the environmental fate and behaviour of Hg, and given the complex nature of air quality evaluation, air quality models have been developed and established. Understanding the difficulties related to source-specific air pollution control and air quality management can be quite challenging because a wide range of contaminants is emitted from various sources over different spatial and temporal scales. Therefore, specialists in controlling and managing air pollution rely on these models to aid them in decision-making processes for different pollution control settings. Rather than comparing an air pollution source's compliance to results obtained from air pollution sampling, they are based on emission estimates from atmospheric dispersion models [17].

These models use different tools and strategies, such as Lagrangian, Eulerian, Computational Fluid Dynamics, and Gaussian models [18]. It was decided that the Lagrangian California Puff (CALPUFF) modelling system is the most suitable for this study as it can handle complex three-dimensional wind fields on large domains between 50 km–and 300 km [19]. The US EPA also endorses the model for complex topographies and for modelling the atmospheric dispersion of pollutants prone to long-range transport [20]. The model has been used to approximate population exposure from power-generating plant emissions to $PM_{2.5}$, SO_2, SO_4, NOx, NO_3, and HNO_3 in Beijing, China [21]; an exposure assessment to Zn, Pb, and Cd from a Zinc smelter in Spelter, West Virginia [22]; and for a health risk assessment to Hg emissions from a solid waste gasification plant located southeast of Milan, Italy [23].

In South Africa, the atmospheric dispersion of Hg has been simulated at Cape Point using GEOS-Chem [24, 25], GLEMOS, and ECHMERIT [25] and the CAM-Chem [26] models. No literature has been found to describe air pollution dispersion modelling of Hg on the SAHA or with CALPUFF for South Africa. This research aims to fill this knowledge gap and build upon the region's recent and first-ever Hg concentration characterization study [27]. Additionally, a health risk assessment is conducted based on the results obtained from the model for Hg species concentrations and its simulated wet and dry deposition.

2. Material and Methods

2.1 Modelling Structure and Domain

A 250 km by 250 km modelling domain was selected for this study, spanning the South African Highveld Area (Figure 1). The modelling domain hosts various anthropogenic sources of Hg, including the 12 power plants illustrated in Figure 1. Other possible sources are combustion in gasification plants, ferrous and non-ferrous metal production, domestic burning, crude oil refining, cement production, waste deposition and incineration, and illegal artisanal gold mining. The Lambert Conic Conformal projection minimizes map distortion over this domain size. The components of the CALPUFF modelling system sequentially consist of CALMET, CALPUFF, and CALPOST. In the most recent version of the model, a new feature known as CALSUM was introduced, which allows the user to combine multiple outputs from CALPUFF into a single file to lessen the runtime considerably.

2.2 CALMET

CALMET meteorological model generates hourly temperature and wind files for the selected domain on a three-dimensional grid [21]. In addition, two-dimensional surface and dispersion characteristics, properties, and atmospheric mixing height files are created [28]. For this study, CALMET was run in a hybrid mode from January 2011 to December 2013 at a resolution of 1 km by 1 km on a 12 km by 12 km grid—Mesoscale Model (MM5) prognostic meteorological data obtained from the input data fields. The MM5 dataset comprises precipitation, wind speeds and vectors, boundary layer heights, and temperatures. A recent study by Pretorius et al. [29] used the same domain and meteorological fields from CALMET to evaluate health risk exposure to PM, SO_4, and NO_3. This study assessed the performance of CALMET for the Highveld region and found the created fields to adequately simulate the actual fields [29]. The default CALMET options were mainly used, but some were altered to suit the needs of this study. These alterations and their motivations are summarised in Table 1 and were based on a peer-reviewed report [30]. South Africa does not have the MM5 dataset commercially available yet, and it was bought from Lakes Environmental Software, Canada. At a resolution of 12 km along with 18 vertical heights, it was the best accessible dataset, with its centre at 26.47 S 29.03 E.

2.3 *CALPUFF*

The model was used to simulate the hourly dispersion concentrations of the three critical atmospheric species of Hg (Hg^0, Hg^{2+}, and HgP) and concurrent wet and dry deposition at selected receptor locations [28]. The emission rates of Hg utilized in this study were calculated using estimated emission rates for each power-generating plant [31] (Table 2). The Hg speciation was assumed to be consistent with values reported by Carpi [13], namely, Hg^0 (53%), Hg^{2+} (37%), and HgP (10%). Source-specific characteristics of the 12 power-generating plants are summarised in Table 3. Chemical and deposition parameters required for the wet and dry deposition simulation during the period were obtained from a past study [32] and summarised in Table 4.

The atmospheric lifetime of Hg^0 is approximately one year [33-35) due to its stability and low solubility and reactivity in the atmosphere [11, 36). The wet scavenging of Hg^0 has been described as trivial [37]. It is thought to be primarily removed after oxidizing to Hg^{2+} and consequent deposition. It may, however, occasionally be adsorbed by soot and PM in gas and aqueous phases of clouds [38]. When this occurs, dry deposition may remove it from the atmosphere, provided that the surface air Hg^0 concentration is high enough [16, 39]. A recent study adopted dry deposition parameters for Hg^0 [40]. The study specifies that the values were used as the CALPUFF model indicates them. Presumably, the study used a newer version of the model, as these values are unavailable in the version utilized in this study.

The Hg^{2+} and HgP species are believed to be dispersed locally, and their deposition patterns depend on local sources [37]. The deposition parameters for Hg^{2+} are assumed to be like those of nitric acid (HNO_3) provided in the model [28]. These parameters were also adopted by McGuire et al. [32] as they provide a conservative basis of deposition for this species. The previous is usually assumed in many settings [41], as both these species are highly soluble and reactive [42, 41]. From the limited measurements made regarding the deposition of Hg^{2+}, it may be derived that its deposition velocity magnitude is analogous to HNO_3 [41]. The parameters for HgP were adopted from those given for NO_3 in the model [28]. McGuire et al. [40] made this assumption to provide a conservative basis for the deposition of this species, and it was decided to make this same assumption. Theoretically, this assumption seems plausible because HgP mainly consists of particles smaller than 2.5 µg/m^3 [42,43].

According to Aneja et al. [44] and Tsai et al. [45], to further justify this assumption, NO_3 is one of the dominant constituents of the fine PM fraction. Deposition velocities of particulate species mainly depend on their size distribution [41]. Therefore, a mass mean diameter of 0.48 was selected as particulates resulting from combustion sources are generally less than one micron [40], providing an additional conservative basis for this study. An earlier study used similar deposition parameters for this species, assuming the same geometric mass mean diameter [46]. To make deposition modelling of HgP more reliable, Zhang et al. [41] suggest that prospective studies regarding the size of these particles should be improved. The deposition parameters for Hg^{2+} and HgP were selected because it implies that the highest possible amount of these deposition-prone species can be removed from the atmosphere, which will have a subsequent and indefinite impact on the modelled Hg concentration. This supposition is not made for Hg^0 as [8] describe both deposition processes to be inefficient in the removal thereof.

After completing each individual run, the 36 output files (12(concentration + wet deposition + dry deposition) were combined using CALSUM. The previous was possible because the modelling period during each run was alike, and the species were identical and in the same order for each run. In order to calculate the accumulative concentration and wet and dry deposition averages during the period, use was made of CALPOST.

2.4 Assessment of Potential Health Risk

As described previously, exposure to Hg could cause adverse human impacts on human health. To put the model results into perspective, the potential impact of the simulated emissions from the power plants on health is assessed. A previous study in this region assessed human health exposure to PM, SO_2, and NO_x emissions from power plants based on intake and intake fraction [28]. The methodology used in this assessment is discussed in detail in previous publications [47- 49]. It was recently utilized in a health risk study [50], where Hg was one of the pollutants under investigation. It essentially entails the execution of four steps, which are discussed in the following sections.

2.4.1 Hazard Identification

Hazard identification is an exercise to determine whether the exposure to the pollutant under investigation can cause an intensification in the occurrence of a specific severe health effect in humans. Mercury, a non-carcinogenic pollutant [51], may cause neurological and behavioural conditions in humans [52]. These conditions can be acute, chronic, and even fatal [53], and their severity depends on the level of exposure [52]. The primary exposure pathway is inhaling inorganic Hg^0 [53]. Reactive and particulate Hg are commonly removed near their sources due to their high atmospheric solubility and reactivity [54,55]. They pose a risk to human health after deposition, when methylmercury, the most toxic form of Hg, may be formed [56,57]. This study, however, only considers the inhalation exposure pathway to Hg^0.

2.4.2 Dose-response

Fundamentally, this step of the risk assessment process establishes an exposure-response relationship. The toxicological factors that establish this relationship are Reference Concentration (RFC) and Reference Dose (RFD). The RFC evaluates inhalation risks, while the RFD assesses the risks associated with oral exposure. Both reference doses are benchmarks of daily human exposure. Barnes and Dourson et al. [47] and IRIS [51] define them as average daily exposure levels that are not likely to threaten human health throughout a lifetime. Typically, this step requires the implementation of an equation to calculate an RFD value, which can be adjusted to calculate RFC. However, this practice is not recommended in studies investigating inorganic compounds [49]. Since an RFC value was readily available, this study deviates from the standard procedure. The RFC value used in this risk assessment, associated with Hg^0 inhalation, is adopted from IRIS [51] (0.3 µg/m^3). This value is used to characterize the risk exposure to Hg^0 in the fourth step of this process. It is also assumed to be identical for acute and chronic exposure periods.

2.4.3 Assessment of Exposure

The exposure of the human population to Hg^0 was predicted using CALPUFF as described in the CALPUFF section previously. The simulation returned average modelled hourly, 8-hourly, and periodic (annual average) Hg^0 concentrations. These values assessed potential acute and chronic impacts on human health.

2.4.4 Characterization of Risk

The US EPA [49] recommends Risk Exposure Levels (REL) [58] as the preferred choice to assess acute inhalation values. Like an RCF, a REL is the air concentration at or beneath which no severe health impacts are expected in the population over a given exposure period. The population includes susceptible subgroups such as children and senior citizens [49]. The average hourly, 8-hourly, and annual Hg^0 concentrations are compared to acute (1 hourly and 8-hourly) and chronic REL values to assess potential health impact. Additional information, including associated uncertainty factors, is provided in Table 5 below.

For the characterization of a health risk for a non-carcinogenic pollutant by way of inhalation, the hazard must be quantified through the use of the Hazard Quotient (HQ) [49] given by:

$$HQ = EC/RFC \qquad (1)$$

, where EC represents the exposure concentration in the air (µg/m^3), and RFC is the reference concentration (µg/m^3). If HQ is smaller than 1, it indicates that the pollutant concentration is less than the RFC benchmark value. If this is the case, no subsequent action is necessary because the likely risk is within the admissible threshold. In other words, it means that HQ<1 is considered safe. It does not mean that HQ>1 should be construed as causing potential severe health impacts. It should instead be deduced as an indication of potential severe health impacts [59].

3. Results and Discussion

3.1 Atmospheric Dispersion of Hg Species

The modelled spatial distribution of Hg^0, Hg^{2+}, and HgP concentrations are illustrated in Figures 2, 3, and 4, respectively. The highest ambient concentrations of all three Hg species were calculated over the central parts of the modelled domain. As expected, this is the same spatial distribution as the other significant pollutants from power plants modelled for the Highveld region [29]. Moreover, as expected, the highest modelled concentrations were observed for Hg^0 and the lowest for HgP, given the conservative basis of this study. The modelled Hg^0, Hg^{2+}, and HgP concentrations ranged from 0.0028–0.0631, 0.0028–0.0497, and 0.0008–0.0137 ng/m^3, respectively.

Kriel and Matla may collectively act as one stack in the centre of the domain, as they are very close to each other. Polluted air from the other power plants is thus accumulating in an already polluted area of high concentrations. These two plants have relatively low emission profiles and shorter stacks, leading to lower emission heights and dispersion potential. The measured concentrations in this study are compared to those obtained by other selected studies. A comparison showed a significant difference in the number of sources modelled in the current study and those in international studies. One would subsequently expect the concentrations in the current study to be much higher. In addition, because we modelled the atmospheric dispersion of Hg over a larger domain, one expects higher modelled concentrations.

Theoretically, the larger the domain, the more species may be removed by deposition processes. In this case, especially Hg^0, given its solubility, reactivity and consequent atmospheric lifetime. In addition, the different considered emission rates coupled with meteorology and the difference in deposition parameters should provide for different modelled concentrations. Furthermore, this does not entail modelling Hg species using an identical model. The previous is vital because atmospheric dispersion models use different schemes and strategies in their respective computations. Modelled Hg^0 concentrations are somewhat lower than the results of [40,60]. However, the modelled concentrations are moderately higher than those by [23].

3.2 *Wet and Dry Deposition*

The results reveal that relatively low amounts of each species were removed from most modelled regions. However, over four locations on the domain, higher amounts were removed in the locations' immediate vicinity (<1km). The previous was simulated in the atmosphere above Kriel and Matla, Lethabo, Kendal, and Tutuka. This observation may be explained by the fact that species of Hg tend to be deposited near their emission source [13,61]. The simulated wet deposition of Hg^{2+} and HgP at the specified receptors during the modelling period ranged from 0.07–7.46 and 0.03–3.33 (g/ha)/yr, respectively. Critical for wet deposition to occur, of course, is precipitation. The average deposition rate during the modelling period over the domain was 1.0125 x 10^{-2} mm/hr. The average wet deposition over Kriel and Matla was simulated at 5.18091 x 10^{-1} mm/hr. Compared to the amount of wet deposition measured for total Hg at rural and urban sites in China (0.02–0.07 and 0.12 (g/ha)/yr, respectively) [62], the values in the current study are somewhat higher. Given the conservative basis of the current study, the modelled deposition of HgP is much higher than Hg^{2+}. Fu et al. (2016) utilized direct precipitation measurements, which should provide for more refined deposition estimates. Zysk et al. [37] modelled very similar total wet deposition values (0.08–0.8 kg/ha/annum) to those measured by Fu et al. [62] for Hg.

Notably, the dry deposition of Hg^0 was interpreted cautiously, as its dry deposition parameters were assumed to be identical to those adopted for $Hg^{2+,}$ which provides conservative estimates of this species' highest potential dry deposition. Dry deposition is another mechanism by which species of Hg may be transferred from the atmosphere to aquatic and terrestrial surfaces.

This mechanism, of course, occurs in the absence of precipitation. The modelled dry deposition of the species closely resembles one another, with the central parts of the domain being the region most affected, followed by the southwestern part. Dry deposition rates decrease from the centre of the domain to the outskirts. The results reveal that deficient species were removed from most modelled regions. The dry deposition of Hg^0, Hg^{2+}, and HgP ranged from 0.003–0.104, 0.002–0.081, and 0.00002–0.00052 (g/ha)/yr, respectively. The average modelled deposition of Hg^0 (1.4 (g/ha)/yr) is smaller than what was observed by [40] (4.4 (g/ha)/yr) (for a coal-fired power plant in Mexico) and more prominent compared to the average reported by [37] (0.25 (g/ha)/yr) (modelled for the Polish power sector). Their study accounted for natural emissions and chemical transformation, which indicates that the dry deposition of Hg^0 in this study is considerably overestimated. The previous may subsequently be derived for Hg^{2+} and HgP as well.

3.3 Assessment of Potential Health Risk

The Hazard Quotient (HQ) has been calculated for the Highveld as an annual spatial average (baseline scenario) as well as maximum annual values (worst-case scenario) within the study area (Table 6). These values represent an HQ range which, at its highest level, gives a conservative estimate of the health risk to the population on the Highveld. The quantified acute and chronic HQ values for the baseline scenario show a tolerable exposure level to concentrations of Hg^0 (HQ <1 in all cases). The average exposure concentrations for this scenario are also lower than the recommended REL values.

In terms of the worst-case scenario, however, acute (1 hour and 8 hours) quotients exceed one (HQ>1). This result suggests a potentially severe health effect. The maximum predicted exposure levels are also above the REL values for the corresponding exposure periods. The HQ value for the chronic exposure period is below one (HQ <1), suggesting the likely risk is negligible. Considering the uncertainty in the modelled concentrations of Hg^0, these values may either be higher or lower. There is currently no South African national ambient standard for comparison.

4. Conclusions

As expected, the concentrations of the Hg species are highest over the cluster of power plants situated in the centre of the domain. Moreover, the results convey that concentrations of the species are accumulating in an area of already high concentrations over Kriel and Matla. This part of the domain also yielded maximum wet and dry deposition. It is thus clear that the proximity of the power plants leads to higher deposition. The formation of methylmercury is, therefore, likely to occur due to the possibility of these high-modelled concentrations being removed by deposition. The high wet deposition results for Hg^{2+} cover the same spatial area as the modelled concentration, corroborating the above statement. It could expose the population to depend on fishing to supplement their nutritional needs. Although conservative estimates, the results identify a potential need to assess the possible impact of toxic methylmercury on the South African Highveld. The health risk assessment suggests that the population working and living near power plants may be at risk of acute adverse health impacts due to inhalation. The prospective modelling of Hg over this region should be evaluated against ambient monitored concentrations to account for uncertainty and fractional bias. Concurrent direct precipitation measurements may enhance this to provide more refined deposition modelling.

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Figures and Tables

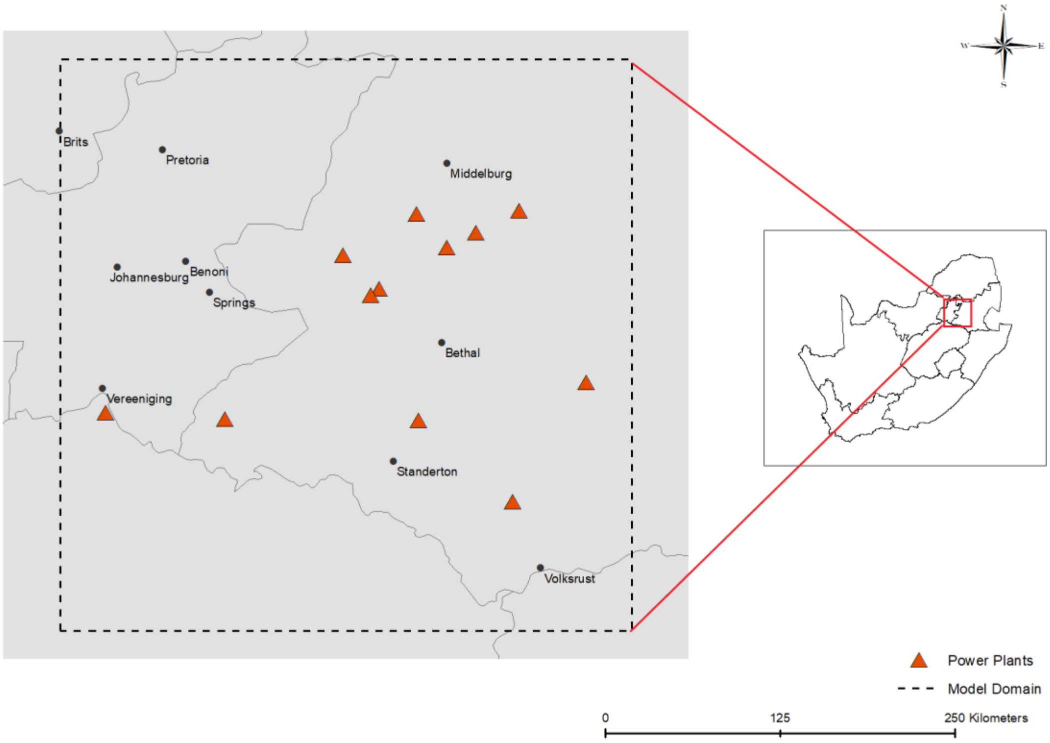

Figure 1: Locations of the 12 coal-fired power plants used to model the atmospheric dispersion of Hg^0, Hg^{2+}, and HgP in this study. The black box represents the modelling domain.

Table 1: CALMET options were altered from the default settings (Exponent Inc., 2014).

Description	**Default setting**	**Used setting**	**Motivation**
Map projection	UTM	LCC	To keep map distortion to a minimum
No observation mode	Observations only	No surface, overwater, or upper air observation. Use of MM5 data for these observations	Limited observational data
Extrapolation of surface wind	Ignore upper air station data	No extrapolation	Exclusion of observations
Gridded prognostic wind field	No	Yes	Exclusion of observations
3D Relative humidity	Use observations	Use prognostic data	Exclusion of observations
3D temperature	Use observations	Use prognostic data	Exclusion of observations

Table 2: Per annum emission rate of Hg^0, Hg^{2+}, and HgP, in grams per second (g/s) investigated in this study, and the emission control device/s installed at each power-generating plant.

Power Plant	**Emission Control Device**	**Emission rate per annum (g/s)**		
		Hg^0	**Hg^{2+}**	**HgP**
ARNOT	FF	0.00212	0.00148	0.0004
CAMDEN	FF	0.00318	0.00222	0.0006
DUVHA	ESP+FF	0.01431	0.00999	0.0027
GROOTVLEI	ESP+FF	0.00848	0.00592	0.0016
HENDRINA	FF	0.00212	0.00148	0.0004
KENDAL	ESP	0.05406	0.03774	0.0102
KOMATI	ESP	0.00954	0.00666	0.0018
KRIEL	ESP	0.02915	0.02035	0.0055
LETHABO	ESP	0.0636	0.0444	0.0102
MAJUBA	FF	0.00689	0.00481	0.0013
MATLA	ESP	0.03233	0.02257	0.0061
TUTUKA	ESP	0.03339	0.02331	0.0063

Table 3: Source-specific parameters of each power-generating plant investigated in this study.

Power Plant	Coordinates		Output Capacity (MW.)	Stack Height (m)	Effective Stack Diameter (m)	Exit Velocity (m/s)	Exit Temperature (K)
	x (m)	y (m)					
ARNOT	-25.944	29.792	1680	195	16	25	418
CAMDEN	-26.62	30.091	1650	155	17	14	423
DUVHA	-25.961	29.339	1590	300	18	27	413
GROOTVLEI	-26.77	28.5	1600	152	13	22	418
HENDRINA	-26.031	29.601	1610	155	16	22	418
KENDAL	-26.088	28.969	1550	275	19	24	413
KOMATI	-26.091	29.422	1650	220	17	10	418
KRIEL	-26.254	29.18	1550	213	20	19	413
LETHABO	-26.740	27.975	1440	275	17	28	433
MAJUBA	-27.28	29.771	1700	250	17	35	398
MATLA	-26.28	29.142	1610	275	19	26	408
TUTUKA	-26.776	29.352	1600	275	17	19	413

Table 4: Deposition and Chemical Parameters of the three species modelled in this study

Dry Deposition (Gases)

Species	Diffusivity (cm^{-2} s^{-1})	Alpha Star	Reactivity	Meso. Resistance	Henry's Law Coefficient.
Hg^{0}	0.1628	1	18	0	1.00E-07
Hg^{2+}	0.1628	1	18	0	1.00E-07

Dry Deposition (Particles)

Species	Geometric Mass mean diameter (microns)	Geometric Standard Deviation (microns)
HgP	0.48	2

Wet Deposition

Species	Scavenging Coefficient (liquid) s^{-1}	Scavenging Coefficient (Frozen) s^{-1}
Hg^{2+}	6.00E-05	0
HgP	0.0001	3.00E-05

Table 5: Uncertainty associated with REL values (OEHHA, 2014) used for comparison.

RFC comparison	Species	Study population	Exposure continuity	Exposure duration	Composite uncertainty factor
Acute (1 hour)	Rats	12	-	1 hour per day	3000
Acute (8 hours)	Humans	236	8 hours per day, five days a week	13.7–15.6 years	3000
Chronic	Humans	236	8 hours per day, five days a week	13.7–15.6 years	300

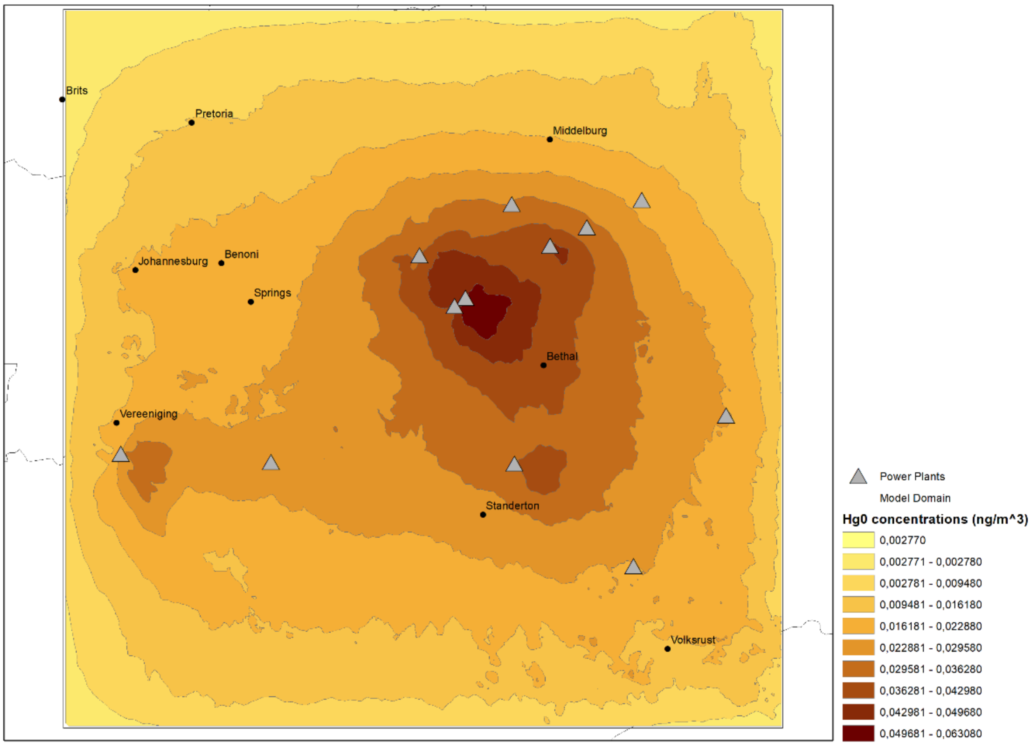

Figure 2: The spatial distribution of three-year (2011-2013) modelled average Hg^0 concentrations (ng/m^3) originating from power-generating plants on the South African Highveld.

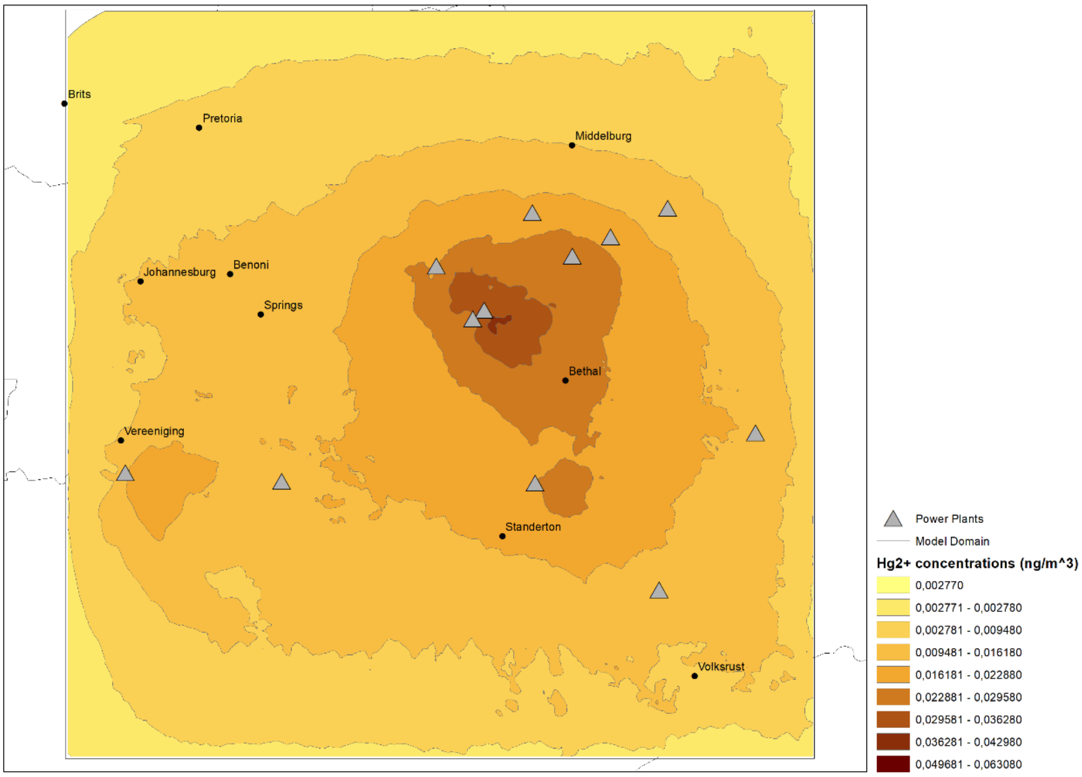

Figure 3. The spatial distribution of three-year modelled average Hg2+ concentrations (ng/m^3) originating from power-generating plants on the South African Highveld.

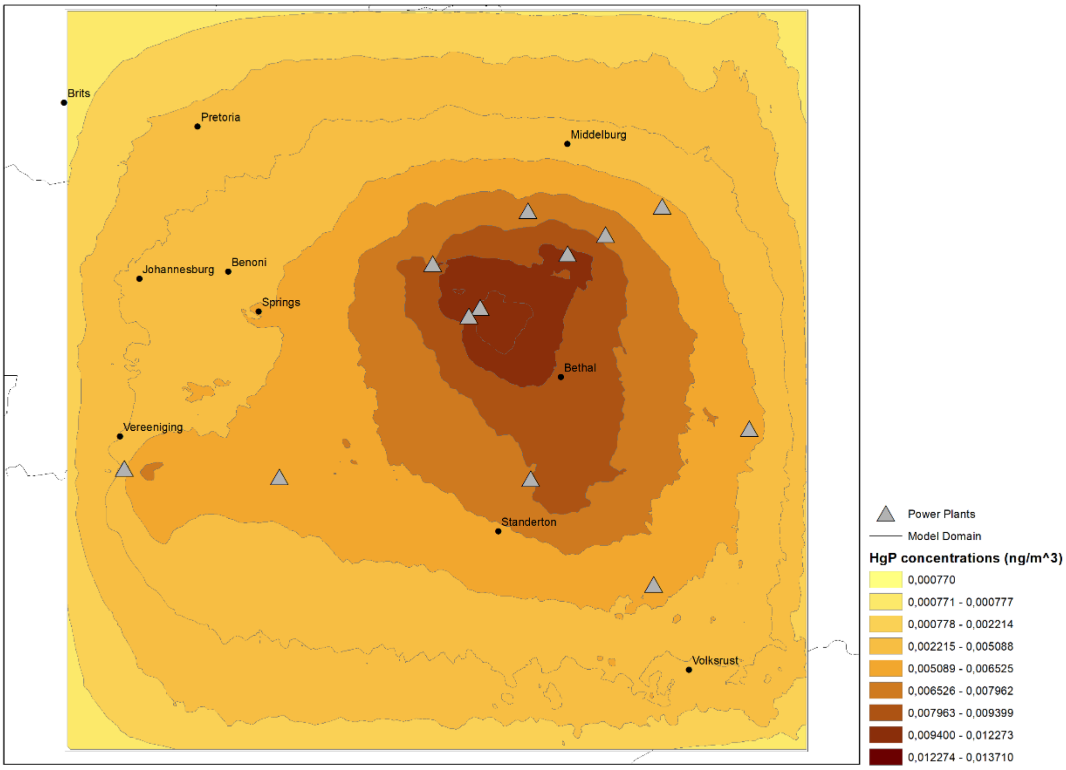

Figure 4. The spatial distribution of three-year modelled average HgP concentrations (ng/m^3) originating from power-generating plants on the South African Highveld.

Table 6: Assessment of potential health risk to emissions of Hg^0 from modelled power plants.

Exposure period	**Average predicted exposure ($\mu g/m^3$)**	**Maximum predicted exposure (ug/m^3)**	**REL ($\mu g/m^3$)**	**RFC ($\mu g/m^3$) used for HQ quantification**	**Baseline HQ.**	**Worst case HQ.**
Acute (1 hour)	0.002	2.001	0.6	0.3	0.007	6.67
Acute (8 hours)	0.001	0.791	0.06	0.3	0.003	2.637
Chronic	0.00003	0.02625	0.03	0.3	0.0001	0.0875

Appendix 2: Reviewer 2's comments on manuscript (round 2)

Atmospheric Mercury Dispersion over the South African Highveld

Coal combustion in coal-fired power plants is the dominant source of mercury (Hg) emissions in South Africa, with most plants located in the South African Highveld, an area suffering from poor air quality. Despite this, the specifics of Hg emissions from these plants remain unclear. This study presents the first dispersion modelling of Hg concentrations and wet and dry deposition in the Highveld using CALPUFF. It focuses on inorganic gaseous elemental (Hg^0), inorganic reactive gaseous (Hg^{2+}), and inorganic particle-bound Hg (HgP) emissions from 12 coal-fired power plants from 2011-2014. Results show that Hg concentrations are highest near the central cluster of power plants, with levels ranging from 0.0028–0.0631 ng/m^3 for Hg^0, 0.0028–0.0497 ng/m^3 for Hg^{2+}, and 0.0008–0.0137 ng/m^3 for HgP. Significant wet and dry deposition, measured at 0.07–7.46 and 0.03–3.33 (g/ha)/yr, respectively, also occurs in these areas, indicating that proximity to power plants leads to higher deposition. A health risk assessment suggests that nearby populations may be at risk of acute health impacts from Hg^0 inhalation. However, the accuracy of this assessment is limited by the overestimation of Hg^0 concentrations in dry deposition modelling. The findings highlight the need for further studies to characterise and quantify methylmercury, the most toxic form of Hg, in the environment.

Keywords: coal-fired power plants, mercury, South African Highveld, CALPUFF, deposition.

Significance

The research presents the results of the first-ever dispersion modelling study regarding mercury concentrations and wet and dry deposition over this region using CALPUFF. This finding significantly contributes to scientific knowledge on mercury emissions in this region. The study conducts a brief health risk assessment, suggesting that the population working and living near power plants may be at risk of acute adverse health impacts due to inhalation of Hg^0. The findings indicate that further studies are needed to characterise and quantify methylmercury concentrations, as this is mercury's most toxic environmental form—the previous points to important future research directions.

Data Availability

On request of authors.

1. Introduction

The industrialised South African Highveld Area has been identified as an area associated with poor air quality due to high emissions of criteria pollutants such as particulate matter (PM), SO_2 and NO_x, and a potential area of high concentration of atmospheric mercury (Hg) species [1]. This region is well-known for its various anthropogenic emission sources: coal-fired power plants, coal ash disposal sites, metallurgical smelters and mines, agriculture, and transportation [2,3].

Commented [A1]: Neither of these references are primary literature that identified the emissions in the region. 3 is but only for Hg emissions, but I believe this statement is more general. If it is, then I recommend a reference that studied the sources is included. If it is just about Hg, then I recommend the sentence and references are updated to reflect that.

Globally and annually, combustion in coal-fired power plants is the dominant anthropogenic source of environmental Hg [4], contributing approximately 56% [5]. Coal-fired power plants were estimated as the leading possible anthropogenic source of ambient Hg emissions in South Africa (72-78%) [1]. The concentration of Hg emitted by the power plants is mainly dependent on the type of emission control device installed. The emission control devices South African power plants use are electrostatic precipitators, fabric filters, desulphurisation/flue-gas conditioning, or a combination thereof [6]. These devices reduce the amounts of particulate matter and sulphur, as well as Hg, with the power plants fitted with fabric filters reducing the highest Hg per GWh (7, 8).

Moreover, a past study listed South Africa as the second-highest global atmospheric Hg emissions source. According to their study, the country contributed to about 16% of global Hg emissions [5]. However, these estimates were based on incorrect Hg-content coal values and triggered subsequent Hg studies. Using correct values, the Hg inventory was updated, and South Africa was listed as the 6th leading emitter of the pollutant [3].

Mercury is a highly toxic and ubiquitous volatile metal, which is environmentally persistent and prone to long-range atmospheric transport [9]. It subsequently leads to adverse health effects in distant regions far from where it was emitted [10]. Mercury is, therefore, regarded as a global pollutant threatening both the health of humans and ecosystems [11,12,10,9]. It is known that the ecological behaviour of the Hg emitted depends on the different environmental forms, as these chemical forms have other chemical properties [11, 12].

Unlike other heavy metals in the environment, atmospheric Hg generally occurs in its gaseous phase [13]. It may be emitted into the atmosphere as inorganic gaseous elemental (Hg^0), inorganic reactive gaseous (Hg^{2+}), and inorganic particle-bound Hg (HgP) [14,15]. Atmospheric emissions of Hg are dominated by Hg^0 (53%), followed by Hg^{2+} (37%) and HgP (10%) [16]. Although Hg^0 is the predominant form in the gaseous phase [16, 17], Hg^{2+} significantly influences the total deposition of atmospheric Hg as it's more reactive and soluble [18]. Under certain conditions, Hg^0 may be removed by dry deposition processes [19]. Mercury is transported over long distances in the atmosphere, even reaching the poles [20]. Due to the concentration of significant sources over the Highveld, it is expected that Hg is transported and deposited over large portions of South Africa [2]. However, there aren't many measurements to support this, except for some over the Highveld [21,22] and at background sites (e.g. [23]).

To investigate and better understand the environmental fate and behaviour of Hg, and given the complex nature of air quality evaluation, air quality models have been developed and established. In South Africa, the atmospheric dispersion of Hg has been simulated at Cape Point using GEOS-Chem [24, 25], GLEMOS, ECHMERIT [25] and the CAM-Chem [26] models. No literature has been found to describe air pollution dispersion modelling of Hg on the industrialised Highveld or with CALPUFF for South Africa. This research aims to fill this knowledge gap and build upon the region's recent and first-ever Hg concentration characterisation study [21]. A health risk assessment is also conducted based on the results obtained from the model for Hg species concentrations.

2. Material and Methods

Understanding the difficulties related to source-specific air pollution control and air quality management can be quite challenging because a wide range of contaminants is emitted from various sources over different spatial and temporal scales. Therefore, specialists in controlling and managing air pollution rely on these models to aid them in decision-making processes for different pollution control settings. Rather than comparing an air pollution source's compliance to results obtained from air pollution sampling, they are based on emission estimates from atmospheric dispersion models [27].

These models use different tools and strategies, such as Lagrangian, Eulerian, Computational Fluid Dynamics, and Gaussian models [28]. It was decided that the Lagrangian California Puff (CALPUFF) modelling system is the best for this study based on its pros and cons and regulatory approval by the South African government [29]. The US EPA also endorses the model for complex topographies and for modelling the atmospheric dispersion of pollutants prone to long-range transport [30]. The model has been used to approximate population exposure from power-generating plant emissions to $PM_{2.5}$, SO_2, SO_4, NOx, NO_3, and HNO_3 in Beijing, China [31]; an exposure assessment to Zn, Pb, and Cd from a Zinc smelter in Spelter, West Virginia [32]; and for a health risk assessment to Hg emissions from a solid waste gasification plant located southeast of Milan, Italy [33].

2.1 Modelling Structure and Domain

A 250 km by 250 km modelling domain spanning the South African Highveld Area was selected for this study (Figure 1). The modelling domain hosts various anthropogenic sources of Hg, including the 12 power plants illustrated in Figure 1. The power plants, arranged alphabetically, are labelled from 'a to l'. Other possible sources are combustion in gasification plants, ferrous and non-ferrous metal production, domestic burning, crude oil refining, cement production, waste deposition and incineration, and illegal artisanal gold mining. The Lambert Conic Conformal projection minimises map distortion over this domain size. The components of the CALPUFF modelling system (version 6.42) sequentially consist of CALMET, CALPUFF, and CALPOST. In addition, CALSUM was used, which allows the user to combine multiple outputs from CALPUFF into a single file to lessen the runtime considerably.

Commented [A2]: I recommend confirming here that the other sources are not modelled, and only Eskom emissions as in Table 2 are modelled.

2.2 CALMET

CALMET meteorological model generates hourly temperature and wind files for the selected domain on a three-dimensional grid [31]. In addition, two-dimensional surface and dispersion characteristics, properties, and atmospheric mixing height files are created [34]. For this study, CALMET was run in a hybrid mode from January 2011 to December 2013 at a resolution of 1 km by 1 km using 5th-generation prognostic Mesoscale Model (MM5) data. The MM5 model had a grid resolution of 12 km by 12 km resolution, incorporating Dudhia's simple-ice microphysics, the medium-range forecast Planetary Boundary Layer scheme, and a multilayer soil model. The MM5 model was set up using the NCEP Global Reanalysis data, featuring a global grid resolution of 2.5 by 2.5 degrees. The MM5 dataset comprises precipitation, wind speeds and vectors, boundary layer heights, and temperatures. A study by [35] used the same domain and meteorological fields from CALMET to evaluate health risk exposure to PM, SO_4, and NO_3. The study by [35] assessed the performance of CALMET for the Highveld region and found the created fields to adequately simulate the actual fields. The default CALMET options were mainly used, but some were altered to suit the needs of this study. These alterations and their motivations are summarised in Table 1 and were based on a peer-reviewed report [36]. South Africa does not have the MM5 dataset commercially available yet, and it was bought from Lakes Environmental Software, Canada. At a resolution of 12 km along with 18 vertical heights, it was the best accessible dataset, with its centre at 26.47 S 29.03 E.

2.3 CALPUFF

CALPUFF does not have a dedicated chemical scheme to handle the conversion and transformation of Hg in the atmosphere. A recent study addressed this absence by modifying version 7 of the software to simulate Hg in flue gases and airsheds [37]. However, the present study used the default HNO_3 scheme of the model for reasons discussed hereafter.

The model was used to simulate the hourly concentrations of the three critical atmospheric species of Hg (Hg^0, Hg^{2+}, and HgP) and concurrent wet and dry deposition over the domain. The emission rates of Hg utilised in this study were calculated using emission rates for each power-generating plant, obtained directly from ESKOM based on their 2014 Hg emission calculations from each power plant stack (Table 2). The Hg speciation was assumed to be consistent with values reported by [16], namely, Hg^0 (53%), Hg^{2+} (37%), and HgP (10%). Source-specific characteristics of the 12 power-generating plants are summarised in Table 3. The chemical and deposition parameters required for the wet and dry deposition simulation were obtained from [37,38] and are summarised in Table 4.

Generally, the Hg^{2+} and HgP species are dispersed locally, and their deposition patterns depend on local sources [39]. In this study, similar to a previous one, the deposition parameters for Hg^{2+} are assumed to be like those of nitric acid (HNO_3) provided in the model [34], as they provide a conservative basis of deposition for this species [38]. This assumption is conservative as one cannot be sure that the deposition prediction is 'correct'. Hg^{2+} and HNO_3 have similar [37] but not precisely the same aqueous solubility. The modelling parameters for Hg^{2+} are usually assumed to be similar to those of HNO_3 in many settings [40], as both these species are highly soluble and reactive [40, 41]. From the limited measurements made regarding the deposition of Hg^{2+}, it may be derived that its deposition velocity magnitude is analogous to HNO_3 [40]. The parameters for HgP were adopted from those given for NO_3 in the model [34]. [40] made this assumption to provide a conservative basis

Commented [A3]: I would still recommend a little more explanation. To me “conservative” means that the values would err on the safe side - so in this case it would err on higher levels of deposition. However, the “conservative” part isn’t yet explained here, only that the authors knows there are uncertainties (i.e. it is not “correct”). Thus, I would recommend just one more sentence explaining how it is “conservative” (i.e. it errs on the safe side) to do it this way?

Commented [A4R3]: I see that it is described more below. I will leave this comment to highlight that as a reader, I do not yet undersand what conservative means at this point as it does not mean “not correct”. Perhaps one sentence noting that it is conservative as the parameters selected, as detailed below, would lead to higher deposition and thus it is deemed “conservative” for the deposition of this species, and it was decided to make the same assumption. Theoretically, this assumption seems plausible because HgP mainly consists of particles smaller than 2.5 µg/m^3 [41,42].

According to [43] and [44], to further justify this assumption, NO_3 is one of the dominant constituents of the fine PM fraction. Deposition velocities of particulate species mainly depend on their size distribution [40]. Therefore, a mass mean diameter of 0.48 µm was selected as particulates resulting from combustion sources are generally less than one micron [38], providing an additional conservative basis for this study. An earlier study used similar deposition parameters for this species, assuming the same geometric mass mean diameter [45]. To make deposition modelling of HgP more reliable, [40] suggests that prospective studies regarding the size of these particles should be improved. The deposition parameters for Hg^{2+} and HgP were selected because they imply that the highest possible amount of these deposition-prone species can be removed from the atmosphere, which will have a subsequent and indefinite impact on the modelled Hg concentration. This supposition is not made for Hg^0 as [11] describes wet deposition processes as being inefficient in the removal thereof. For its dry deposition, however, it was modelled to have dry deposition parameters identical to those of Hg^{2+}. A subsequent study by [37] indicated that the dry deposition of Hg^0 should be modelled using a diffusivity value of 0.1194 cm²/s—lower than the 0.1628 cm²/s applied in this study. The reactivity value was also supposed to be 8 and not 18. Additionally, the study suggested that the diffusivity for Hg^{2+} should be aligned with that of mercury chloride ($HgCl_2$), which is 0.086 cm²/s, rather than the 0.1628 cm²/s previously used. In other words, the dry deposition values reported here are conservative in that the assumed parameters will greatly overestimate the dry deposition of Hg^0 and maybe underestimate the ambient concentrations underpredicted.

After each run, the 36 output files (12 each for concentration, wet deposition, and dry deposition) were merged using CALSUM. This merging was feasible because the modelling periods were consistent, and the species were identical and in the same sequence across runs. Subsequently, CALPOST processed these files to determine the combined concentrations and total wet and dry deposition.

2.4 Assessment of Potential Health Risk

As described previously, exposure to Hg could cause adverse human impacts on human health. To put the model results into perspective, the potential impact of the simulated emissions from the power plants on health is assessed. A previous study in this region assessed human health exposure to PM, SO_2, and NO_x emissions from power plants based on intake and intake fraction [35]. The methodology used in this assessment is discussed in detail in previous publications [46,47,48]. Examples of the method application include evaluating the health risk to Hg from a Malaysian coal-fired power plant [49] and, more recently, exposure to total gaseous mercury from industrially influenced Polish sites [50]. It essentially entails executing four steps, which are discussed in the following sections.

2.4.1 Hazard Identification

Hazard identification is an exercise to determine whether the exposure to the pollutant under investigation can cause an intensification in the occurrence of a specific severe health effect in humans. Mercury, a non-carcinogenic pollutant [51], may cause neurological and behavioural conditions in humans [52]. These conditions can be acute, chronic, and even fatal [53], and their severity depends on the level of exposure [52]. The primary exposure pathway for Hg^0 is inhalation, particularly in occupational settings where Hg-vapour is present. However, exposure to Hg^0 compounds through ambient air is minimal for the general population.

In contrast, exposure to organic methylmercury primarily occurs via ingestion from dietary sources such as seafood, fish, and sea mammals [53]. Reactive and particulate Hg are commonly removed near their sources due to their high atmospheric solubility and reactivity [54,55]. They risk human health after deposition, when methylmercury, the most toxic form of Hg, may be formed [56,57]. This study, however, only considers the inhalation exposure pathway to Hg^0.

2.4.2 Dose-response

Fundamentally, this step of the risk assessment process establishes an exposure-response relationship. The toxicological factors demonstrating this relationship are Reference Concentration (RFC) and Reference Dose (RFD). The RFC evaluates inhalation risks, while the RFD assesses the risks associated with oral exposure. Both reference doses are benchmarks of daily human exposure. [46] and [51] define them as average daily exposure levels that are not likely to threaten human health throughout a lifetime. Typically, this step requires the implementation of an equation to calculate an RFD value, which can be adjusted to calculate RFC. However, this practice is not recommended in studies investigating inorganic compounds [58] because they differ fundamentally from organic compounds containing carbon-hydrogen bonds. Since an RFC value was readily available, this study deviates from the standard procedure. The RFC value used in this risk assessment, associated with Hg^0 inhalation, is adopted from IRIS [51] (0.3 $\mu g/m^3$). This value is used to characterise the risk exposure to Hg^0 in the fourth step of this process. It is also assumed to be identical for acute and chronic exposure periods [51].

2.4.3 Assessment of Exposure

The exposure of the human population to Hg^0 was predicted, where the highest cumulative concentration of Hg^0 was simulated during the three years using CALPUFF as described in the CALPUFF section previously. The simulation returned modelled hourly, 8-hourly, and periodic (cumulative annual) Hg^0 concentrations. These values assessed potential acute and chronic impacts

Commented [A5]: Generally these do have an associated time period (i.e. 24-hr average of xxx concentration). What acute and chronic exposure periods does IRIS give for its use?

Commented [A6]: Section 3.3 notes that only two power stations were modelled. The reasoning for that (why only two and not use the full domain? This is a really big assumption) and the definition of the two scenarios has to be detailed in the methods. I would recommend noting it here as it is the estimate of the exposure.

Commented [A7]: What is meant by cumulative? RFC is a concentration, which would normally be an average. Or is this referring to the mass inhaled? I am not certain. I recommend just a short explanation.

on human health. Notably, the chosen exposure continuity—reflecting typical working hours—allows for a comprehensive evaluation of health risks associated with ambient air concentrations [59].

Commented [A8]: Why were working hours selected? This is ap ublic health study and not an occupational health study. I don't think this is a valid assumption.

2.4.4 Characterisation of Risk

The US EPA [58] recommends Risk Exposure Levels (REL) [60] as the preferred choice to assess acute inhalation values. Like an RCF, a REL is the air concentration at or beneath which no severe health impacts are expected in the population over a given exposure period. The population includes susceptible subgroups such as children, senior citizens, and maternal exposure [58]. The cumulative hourly, 8-hourly, and annual Hg^0 concentrations are compared to acute (1 hourly and 8-hourly) and chronic REL values to assess potential health impact. Additional information, including associated uncertainty factors, is provided in Table 5 below.

Commented [A9]: How was the REL used? The equation below only uses the RFC? It is not yet clear how the 0.3 reported above for the RFC and the REL discussed her and in the table are used together. I recommend more explanation of this. In addition, the REL at 1-hour is higher than the RFC noted above, but how can that be as the REL is stated here as the level below which there are no health impacts. I recommend this is clarified.

For the characterisation of a health risk for a non-carcinogenic pollutant by way of inhalation, the hazard must be quantified through the use of the Hazard Quotient (HQ) [58] given by:

$$HQ = EC/RFC \tag{1}$$

, where EC represents the exposure concentration in the air (µg/m^3), and RFC is the reference concentration (µg/m^3). If HQ is smaller than 1, it indicates that the pollutant concentration is less than the RFC benchmark value. If this is the case, no subsequent action is necessary because the likely risk is within the permissible threshold. In other words, it means that HQ<1 is considered safe. It does not mean that HQ>1 should be construed as causing potential severe health impacts. It should instead be deduced as an indication of potential severe health impacts [61].

3. Results and Discussion

3.1 Atmospheric Dispersion of Hg Species

The modelled spatial distribution of Hg^0, Hg^{2+}, and HgP concentrations are illustrated in Figure 2. The highest cumulative ambient concentrations of all three Hg species were calculated over the central parts of the modelled domain (0.0497–0.0631 ng/m^3 for Hg^0 and Hg^{2+} and 0.0123–0.0137 ng/m^3). As expected, this is the same spatial distribution as the other primary pollutants from power plants modelled for the Highveld region [35]. Moreover, as expected, the highest modelled concentrations were observed for Hg^0 and the lowest for HgP. The modelled concentrations for Hg^0, Hg^{2+}, and HgP ranged from 0.0028 to 0.0631 ng/m^3, 0.0028 to 0.0497 ng/m^3, and 0.0008 to 0.0137 ng/m^3, respectively. These results are comparatively lower than the ambient monitored total gaseous mercury concentrations (comprising Hg^0 and Hg^{2+}) at three study domain sites (Balfour, Middelburg, and Standerton) (Belelie et al., 2019). During a one-year monitoring period in 2009, average concentrations at the sites were measured at 1.99±0.94 ng/m^3, 1.04±0.62 ng/m^3, and 1.25±1.38 ng/m^3, respectively. The monitoring sites, depicted in Figure 1, were influenced by different Hg

Commented [A10]: I would recommend in 3.1 and 3.2 to bring in some literature to help the reader understand if these are large values or not. This region has a large amount of coal-fired power stations (really unique globally), so it would be interesting to know the general levels that other studies elsewhere that looked at Hg near coal fired power stations found. I think this is very important for a manuscript in SAJS as the readership is more broad and not just air quality people, and thus it would help readers to understand the scale of the problem.

emission sources, from local fossil fuel combustion to sparse regional contributions. A notable finding from the study was that domestic burning constituted the most significant source of emissions throughout the monitoring period. Domestic burning is a low-level source with emissions likely to be confined beneath the boundary layer, so this source should be factored into future Hg modelling efforts. The proximity of Kriel and Matla power plants, which may act as a single emission source due to their closeness, contributes to an accumulation of polluted air in an area already burdened with high Hg concentrations. Their proximity and lower emission heights and dispersion potential could lead to localised increases in Hg levels. Nevertheless, it is crucial to acknowledge that the peak concentrations are influenced by specific source characteristics and local atmospheric conditions rather than the mere expansion of the modelling domain.

The size of the modelling domain can influence the extent to which deposition processes remove Hg species. This influence on removal potential is particularly true for Hg^0, which, due to its solubility and reactivity, has a longer atmospheric lifetime and, thus, a greater potential for deposition over a larger area. However, it is essential to recognise that the concentration gradients of Hg species, including Hg^0, are primarily governed by their emission rates, atmospheric chemistry, and local meteorological conditions. These factors collectively determine the dispersion and deposition patterns observed in our model.

3.2 Wet and Dry Deposition

The modelled spatial wet distribution of Hg^{2+} and HgP concentrations is illustrated in Figure 3. The wet deposition of Hg^0, due to reasons discussed previously, is ignored. The results reveal that relatively low amounts of each species were removed from most of the modelled region. However, over four locations on the domain, higher amounts were removed in the locations' immediate vicinity (<1km) – not visible on the maps unless zoomed in to a power plant. The previous was simulated in the atmosphere surrounding Kriel, Matla, Lethabo, Kendal, and Tutuka. This observation may be explained by the fact that species of Hg tend to be deposited near their emission source [16,62]. The simulated wet deposition of Hg^{2+} and HgP during the modelling period ranged from 0.07–7.46 and 0.03–3.33 (g/ha)/yr, respectively.

Commented [A11]: I recommend the significant figures of all of the maps are checked and updated to me more in-line with what is reported in the text. Having only one color in the map does make it hard to really understand the spatial distribution of the deposition. I assume this is because the high values close by the stations as noted below. But is there any way to show some more levels between 0.07 and 7 (in a) and similarly large in b. It may take some trial and error in th legend, but I think it would greatly improve this section.

The modelled spatial wet distribution of Hg^{2+} and HgP concentrations is illustrated in Figure 4. Notably, the dry deposition of Hg^0 was interpreted cautiously, as its dry deposition parameters were assumed to be identical to those adopted for $Hg^{2+,}$ which provides conservative estimates of this species' highest potential dry deposition. Dry deposition is another mechanism by which species of Hg may be transferred from the atmosphere to aquatic and terrestrial surfaces. This mechanism, of course, occurs in the absence of precipitation. The modelled dry deposition of Hg^0 and Hg^{2+} closely resembles one another, with the central parts of the domain being the region most affected, followed by the southwestern part. Dry deposition rates decrease from the centre of the domain to the

Commented [A12]: This is dry deposition, correct?

outskirts. The dry deposition of Hg^0, Hg^{2+}, and HgP ranged from 0.003–0.104, 0.002–0.081, and 0.00002–0.00052 (g/ha)/yr, respectively. The maximum modelled deposition of Hg^0 (1.4 (g/ha)/yr) was simulated to occur mainly over Kriel town (also known as Ga-Nala) and its immediate vicinity (including Thubelihle settlement). The dry deposition of Hg^{2+} was somewhat different, occurring predominantly near Kriel and Matla power plants. On the other hand, the highest dry deposition of HgP was simulated on the outskirts of the domain, increasing from the centre of the domain. While Hg^0 and Hg^{2+} share similar diffusivity and reactivity (due to the similarity assumption made in the present study), leading to comparable dry deposition rates, HgP's distinct physical properties, such as its geometric mean diameter and standard deviation, result in different deposition behaviour. This variance in physical characteristics may contribute to the observed disparity in dry deposition rates across the domain.

3.3 Assessment of Potential Health Risk

The Hazard Quotient (HQ) has been calculated for emissions of Hg^0 from surrounding Kriel and Matla as a spatial minimum (baseline scenario) and maximum (worst-case scenario) within the study area (Table 6). These values provide a range of HQ that, at its highest, offers an estimate of health risk to the population within 20-40km from the two power plants. The calculated acute (1 hour and 8 hours) and chronic HQ values for the baseline scenario indicate a tolerable exposure level to concentrations of Hg^0, with all HQ values being less than one (HQ<1). This scenario's minimum predicted exposure concentrations are below the recommended REL values.

Commented [A13]: I noted in methods that this section is not yet clear to me as I can't follow why only two power stations were modelled. Why not do this analysis spatially? I would expect that to be described in the methods as well as the definition of the baseline and worst case. As it is written here, it is just not enough information for me to really understand. Also, where we the receptors placed/what distance was assessed to select the lower predicted exposure and the maximum predicted exposure? These are questions that I recommend are added into the methods, but I am noting them here as I read.

In contrast, for the worst-case scenario, the acute (1 hour and 8 hours) HQ values exceed one (HQ>1), indicating a potential for severe health effects due to peak emission events. The maximum predicted exposure levels are also above the REL values for these acute exposure periods. However, the HQ value for chronic exposure remains below one (HQ<1), suggesting that while short-term risks may be significant, long-term risks are within acceptable limits.

In atmospheric dispersion modelling, particularly for hazardous air pollutants Hg^0, several known uncertainties can influence the accuracy of predicted concentrations. Variability in emission factors is a primary source of uncertainty, as actual emissions can fluctuate due to changes in power plant operations, fuel composition, and the effectiveness of emission control technologies. Meteorological data like those from MM5 drive the dispersion patterns in models like CALPUFF and may introduce another layer of uncertainty. Examples include inaccuracies in wind speed, direction, atmospheric stability, and other weather-related variables that can significantly alter the model outputs. The specified deposition rates, chemical transformation rates, and mixing heights are often based on assumptions or limited data, which can lead to either overestimation or underestimation of concentrations. Despite these uncertainties, modelling remains vital for assessing potential health

Commented [A14]: As shown in De Lange et al (2021) the simulated PBL also has a large impact on the dispersion - and as this region doesn't have information on the vertical structure of the atmosphere, which I would imagine makes it a similar uncertainty in many models.
De Lange et al. 2021, The sensitivity of simulated surface-level pollution concentrations to WRF-ARW-model PBL parameterisation schemes over the Highveld of South Africa
https://www-sciencedirect-com.uplib.idm.oclc.org/science/article/pii/S0169809521000697

risks from air pollution. However, it is essential to interpret the results within the context of these limitations and the lack of a South African national ambient standard for mercury.

4. Conclusions

As expected, the concentrations of the Hg species are highest over the cluster of power plants situated in the centre of the domain. Moreover, the results convey that concentrations of the species are accumulating in an area of already high concentrations over Kriel and Matla. The concentrations are already high given the proximity of the power plants and other Hg sources to one another and because power plants are the predominant source of Hg in South Africa. This part of the domain also yielded maximum wet and dry deposition. It is thus clear that the proximity of the power plants leads to higher deposition. Wet deposition refers to Hg removed from the atmosphere by rain or snow and deposited onto land or water surfaces. Once deposited, inorganic mercury can be converted into methylmercury, a highly toxic form that bioaccumulates in aquatic food chains, by certain microbial processes in water systems. The formation of methylmercury is, therefore, likely to occur due to the possibility of these high-modelled concentrations being removed by deposition. The high wet deposition results for Hg^{2+} cover the same spatial area as the modelled concentration, corroborating the above statement. It could expose the population that depends on fishing to supplement their nutritional needs, such as the Rietspruitdam and Steenkoolspruit rivers near Kriel town. Although conservative estimates, the results identify a potential need to assess the possible impact of toxic methylmercury on the South African Highveld. While acute exposure to peak emissions of Hg^0 from the power plants in the study area may pose severe health risks, chronic exposure remains within acceptable limits. The conservative assumptions used in dry deposition modelling overestimated the expected concentrations of Hg^0 in the ambient air. This discrepancy underscores that this study's health risk assessment is inaccurate. Prospective Hg modelling studies and related health risk assessments should improve on this study using the appropriate dry deposition values of Hg^0. The prospective modelling of Hg over this region should include domestic burning as a source and be evaluated against ambient monitored concentrations during the modelling period to account for uncertainty and fractional bias. The concurrent use of reanalysis datasets of precipitation may enhance this to provide more refined deposition modelling.

Commented [A15]: I think this is too strong of a word. The HHRA is of course an estimate and there are uncertainties, but "inaccurate" would make me as a reader think, well then why should I even read this? Rather, it is uncertain and it seems the authors believe the HQ could be higher than what it really is. However, in health research there is the precautionary principle that does support using more conservative (i.e.t o err on the safe side, so here to use a higher HQ) results to protect health. I recommend this is rewritten.

Commented [A16]: Do these exist?

Commented [A17]: If compared to ambient, then all sources should be included.

Commented [A18]: Are there many or do we need more? It would seem this study suggests we do need more around Eskom stations (this study could help to place some I would think). I would note that here as it is a key finding from this.

Author Contributions
Anonymised

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Figures and Table

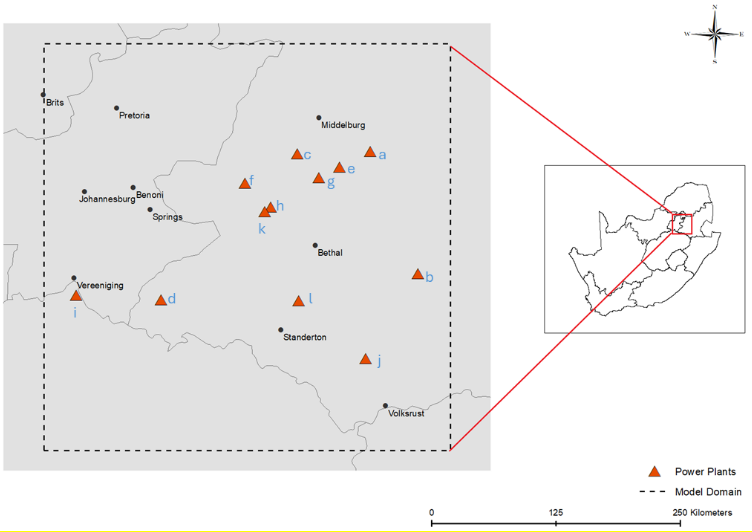

Figure 1: Locations of the 12 coal-fired power plants used to model the atmospheric dispersion of Hg^0, Hg^{2+}, and HgP in this study. The black box represents the modelling domain.

Table 1: CALMET options were altered from the default settings (Exponent Inc., 2014).

Description	**Default setting**	**Used setting**	**Motivation**
Map projection	UTM	LCC	To keep map distortion to a minimum
No observation mode	Observations only	No surface, overwater, or upper air observation. Use of MM5 data for these observations	Limited observational data
Extrapolation of surface wind	Ignore upper air station data	No extrapolation	Exclusion of observations
Gridded prognostic wind field	No	Yes	Exclusion of observations
3D Relative humidity	Use observations	Use prognostic data	Exclusion of observations

3D temperature	Use observations	Use prognostic data	Exclusion of observations

Table 2: Per annum emission rate of Hg^0, Hg^{2+}, and HgP, in grams per second (g/s) investigated in this study, and the emission control device/s installed at each power-generating plant.

Power Plant	**Emission Control Device**	**Emission rate per annum (g/s)**			**Power Plant Figure Label**
		Hg^0	**Hg^{2+}**	**HgP**	
ARNOT	FF	0.00212	0.00148	0.0004	a
CAMDEN	FF	0.00318	0.00222	0.0006	b
DUVHA	ESP+FF	0.01431	0.00999	0.0027	c
GROOTVLEI	ESP+FF	0.00848	0.00592	0.0016	d
HENDRINA	FF	0.00212	0.00148	0.0004	e
KENDAL	ESP	0.05406	0.03774	0.0102	f
KOMATI	ESP	0.00954	0.00666	0.0018	g
KRIEL	ESP	0.02915	0.02035	0.0055	h
LETHABO	ESP	0.0636	0.0444	0.0102	i
MAJUBA	FF	0.00689	0.00481	0.0013	j
MATLA	ESP	0.03233	0.02257	0.0061	k
TUTUKA	ESP	0.03339	0.02331	0.0063	l

Table 3: Source-specific parameters of each power-generating plant investigated in this study.

Power Plant	**Coordinates**		**Output Capacity (MW.)**	**Stack Height (m)**	**Effective Stack Diameter (m)**	**Exit Velocity (m/s)**	**Exit Temperature (K)**
	x (Easting)	**y (Northing)**					
ARNOT	-25.944	29.792	2100	195	16	25	418
CAMDEN	-26.62	30.091	1600	155	17	14	423
DUVHA	-25.961	29.339	3600	300	18	27	413
GROOTVLEI	-26.77	28.5	1200	152	13	22	418
HENDRINA	-26.031	29.601	2000	155	16	22	418
KENDAL	-26.088	28.969	4100	275	19	24	413
KOMATI	-26.091	29.422	1000	220	17	10	418
KRIEL	-26.254	29.18	3000	213	20	19	413
LETHABO	-26.740	27.975	3700	275	17	28	433
MAJUBA	-27.28	29.771	4100	250	17	35	398
MATLA	-26.28	29.142	3500	275	19	26	408
TUTUKA	-26.776	29.352	3600	275	17	19	413

Table 4: Deposition and Chemical Parameters of the three species modelled in this study (Scire et al., 2005; Mcguire et al., 2009; Xu et al., 2019).

Dry Deposition (Gases)

Species	Diffusivity (cm^2/s)	Alpha Star	Reactivity	Meso. Resistance	Henry's Law Coefficient.
Hg^0	0.1628	1	18	0	1.00E-07
Hg^{2+}	0.1628	1	18	0	1.00E-07

Dry Deposition (Particles)

Species	Geometric Mass mean diameter (microns)	Geometric Standard Deviation (microns)
HgP	0.48	2

Wet Deposition

Species	Scavenging Coefficient (liquid) s^{-1}	Scavenging Coefficient (Frozen) s^{-1}
Hg^{2+}	6.00E-05	0
HgP	0.0001	3.00E-05

Table 5: Uncertainty associated with REL values (OEHHA, 2014**)** used for comparison.

RFC comparison	REL (µg/m^3)	Species	Study population	Exposure continuity	Exposure duration	Composite uncertainty factor
Acute (1 hour)	0.6	Rats	12	-	1 hour per day	3000
Acute (8 hours)	0.06	Humans	236	8 hours per day, five days a week	13.7–15.6 years	3000
Chronic	0.03	Humans	236	8 hours per day, five days a week	13.7–15.6 years	300

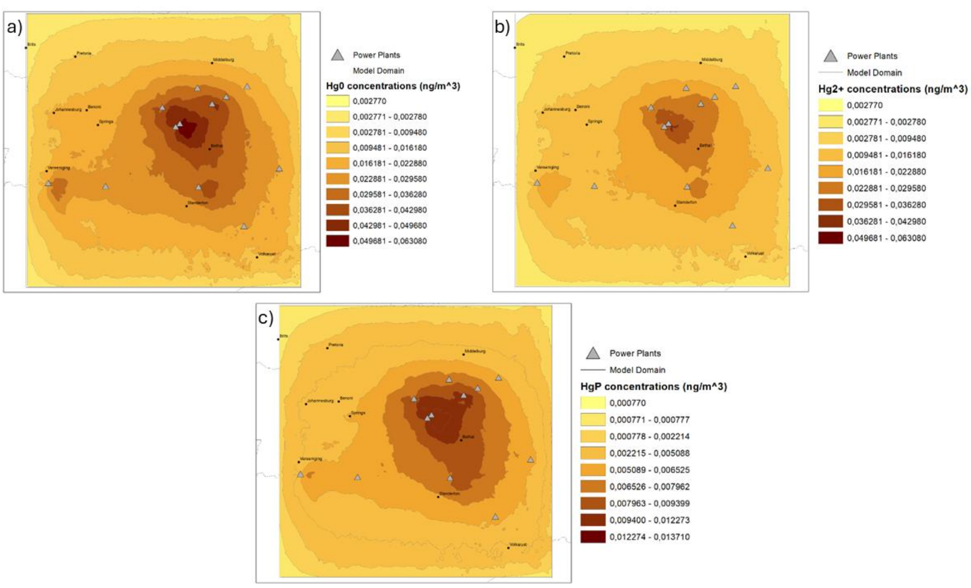

Figure 2: The spatial distribution of three-year (2011-2013) modelled average a) Hg^0, b) Hg^{2+}, and c) HgP concentrations (ng/m^3) originating from power plants on the South African Highveld.

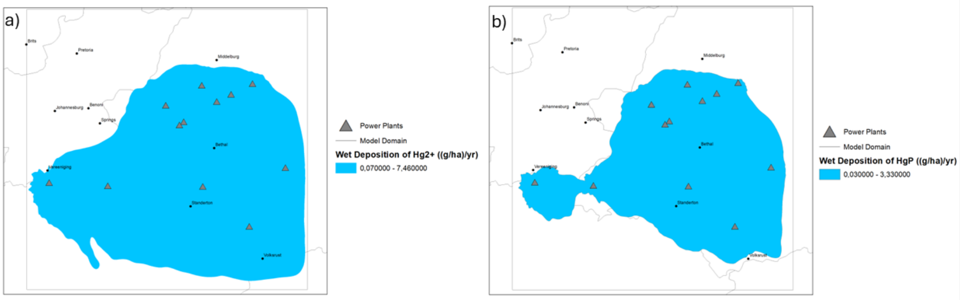

Figure 3: The spatial distribution of averaged three-year modelled wet deposition ((g/ha)/yr) of a) Hg^{2+} and b) HgP on the South African Highveld.

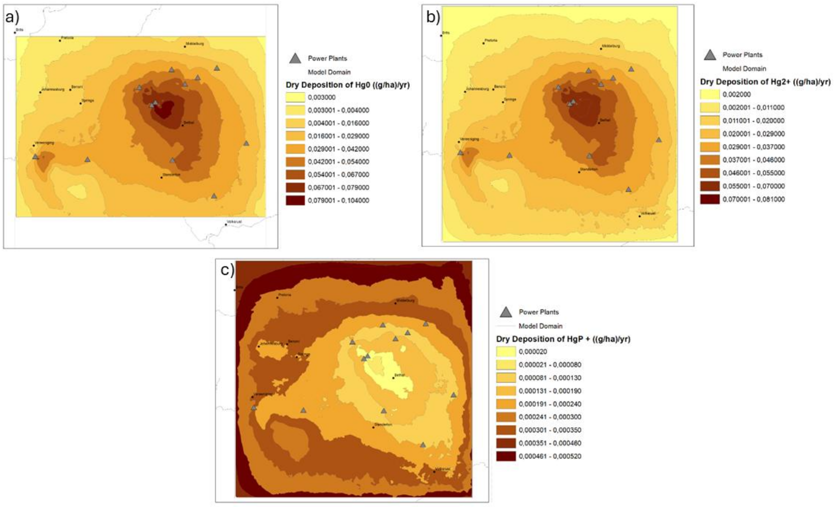

Figure 4: The spatial distribution of averaged three-year modelled dry deposition ((g/ha)/yr) of a) Hg^0, b) Hg^{2+} and c) HgP on the South African Highveld.

Table 6: Hazard Quotient (HQ) Assessment of potential health risk to emissions of Hg^0 from modelled power plants.

Exposure period	**Lowest predicted exposure (µg/m³)**	**Maximum predicted exposure (ug/m³)**	**REL (µg/m³)**	**RFC (µg/m³) used for HQ quantification**	**Baseline HQ.**	**Worst case HQ.**
Acute (1 hour)	0.002	2.001	0.6	0.3	0.007	6.67
Acute (8 hours)	0.001	0.791	0.06	0.3	0.003	2.637
Chronic	0.0000497	0.0000631	0.03	0.3	0.0001657	0.0875