

## ***Interactive comment on “HR3DHG version 1: modelling the spatio-temporal dynamics of mercury in the Augusta Bay (southern Italy)” by Giovanni Denaro et al.***

**Ginevra Rosati (Referee)**

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Received and published: 23 December 2019

Dear Editor, Dear Authors,

please find my comments on the manuscript “HR3DHG version 1: modelling the spatio-temporal dynamics of mercury in the Augusta Bay (southern Italy)”.

Kind regards,

Ginevra Rosati (Referee)

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## General comments

I appreciated the multidisciplinary effort, but the work is flawed by the lack of a thorough revision of the biogeochemical processes of mercury in the marine environment and of the existing scientific background for mercury modeling. References are indeed not exhaustive and often misused, and the parameterizations chosen appear to be questionable in some cases. There are repeated attempts in the Introduction and Discussion to convince the reader that the model has new features, but it is not so.

It should be made clear that in the mercury model for water the state variables are only dissolved Hg species, while adsorption to particles is calculated externally and introduced in the Hg model only as a sink for dissolved Hg species in water. In this regard, it appears misleading to state that the Hg module for water is “coupled” or “integrated” with a Nutrient-Phytoplankton (NP) model and with a model for contaminants bioconcentration in phytoplankton (Phytoplankton MERLIN-Expo Model), as plankton is not included in the equation of the Hg model (HR3DHG model).

Likewise, in the sediment module of the HR3DHG model, the concentrations of  $Hg_T$  do not have any source term, thus they are not simulated but used as a mercury source for pore water. This is not clear from the text, I think the model description must be improved explaining clearly that: a) the evolution of  $Hg_T$  in sediment is driven by exponential decay and not dynamically simulated; b) the processes driving Hg species exchanges at the water-sediment interface are only the molecular diffusion and the release of pore water driven by sediment motion, while sediment deposition/resuspension are not included.

The model is developed with a 3D water column, but the processes occurring in the vertical dimension are not discussed, and vertical profiles of Hg and MeHg are not shown in comparison to available observations. An “excellent” or “good” agreement with the data is claimed in the text but not proven or shown, probably because even the visual agreement provided only in the Supplement (Figures S3 and S4) is far from

being good. In general, the outcomes of the model are not critically discussed, and a quantitative approach is missing.

It is not clear why the model has been run for 250 years without varying the forcings. The conclusion drawn is that Hg concentrations in the ecosystem will decrease with time, but from my understanding this is a consequence of the model construction, assuming exponential decay of Hg in sediments, along with a low value of atmospheric deposition as the only input to the system. The dynamics of methylmercury, which is known to be the most worrisome mercury species, are not discussed. Overall, I found the focus of this work to be blurry.

In my opinion, this paper must undergo a major revision encompassing: the review of processes and parameterizations to include in the model, the run of new simulations and sensitivity simulations with the updated code, as well as a significant rewriting of the text addressing the concerns arose in general, specific and technical comments. I would be pleased to revise the manuscript again once it has been improved.

### Specific comments

**L4-5:** why is the sediment module presented as two different models?

**L5:** an adsorption/desorption model would need an adsorption and desorption rate constants, while here do you have a desorption rate constant combined with the  $K_d$ . I am concerned about this approach, given that the  $K_d$  represents the ratio between adsorption and desorption rate constants at the equilibrium. Can you provide a theoretical background for the parameterization chosen?

**L5-7** *“the spatio-temporal variability of dissolved and total mercury concentration both in seawater ( $[HgD]$  and  $[HgT]$ ) and first layers of bottom sediments ( $[HgsedD]$  and  $[HgsedT]$ ), and the Hg fluxes at the boundaries of the 3D model domain have been theoretically reproduced, showing an excellent agreement with the experimental data”.*

This sentence is not clear and misleading. It should be said what is simulated with the

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biogeochemical model (HgD) and what is estimated with other methods (HgT). Avoid claiming excellent agreement that is not supported by facts.

**L8-9** “*The mass-balance of the different Hg species in seawater has been calculated for the Augusta Harbor, improving previous estimations*” I only found the budget for HgT, not for other Hg species.

**L10-11** “*The HR3DHG 10 model includes modules that can be implemented for specific and detailed exploration of the effects of climate change on the spatio-temporal distribution of Hg in highly contaminated coastal-marine areas.*” This is never shown or discussed in the manuscript, except for a couple of similar mentions at the end of the Introduction and Discussion, so I do not find it relevant nor true.

**L18:** why sophisticated?

**L20:** Among the references cited to support this sentence, only the work Melaku Canu et al., (2015) is based on the WASP model. Zhang et al., (2014) do not use a box model, but a 3D ocean tracer model (OFFTRAC) coupled with a general circulation model. Ciffroy et al., (2015) use the MERLIN-Expo model, as explained just below by the authors. Other works based on the WASP model are Canu and Rosati (2017) and Rosati et al., (2018). There are also other applications of biogeochemical models specific for mercury in water (and thus more relevant here than the MERLIN-Expo model) that are never mentioned. I suggest modifying the paragraph and correcting the references after carrying out a more systematic review.

**L21:** As before, the citation “Zhang et al., (2014)” is unrelated to the sentence.

**L21:** I suggest to change ‘WASP-based approach’ with box model approach.

**L22-25:** “*Similarly, a box-model approach has been adopted by the River MERLIN-Expo model (Ciffroy, 2015), which has been used to reproduce the spatio-temporal distribution of inorganic and organic contaminants in the abiotic compartments of rivers, and to calculate [Hg] mass balance for each of them.*” The reference here provided

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“Ciffroy et al., (2015)” seems to be the model documentation <https://merlin-expo.eu/wp-content/uploads/2015/10/Documentation-River-V2.1.pdf> I could not find any case study for Hg in the reference provided.

**L25-27:** *“Although the River model is able to describe many of the physical and chemical processes involved in freshwater and sediment, corresponding this model specifically targets environments characterized by (i) nearly-homogeneous water bodies and (ii) limited variations in landscape geometry.”* The Introduction begins stating the importance of “biogeochemical dynamics of Hg species in the marine environment”, and then it goes on with the WASP model that is specific for Hg. Why does it now go back to a general model for contaminants in freshwater and sediment and neglect other existing models?

**L27-28:** *“In general, models based on zero dimensional boxes do not deliver reliable concentration values of contaminants in highly heterogeneous environments.”* I suggest rewording this sentence. Zero dimensional boxes models can provide reliable concentrations as much as other models. Box models can be less or more accurate than other models depending on the parameterizations used and on the spatial resolution, which however could be very fine.

**L28-34:** *“[. . .] in more recent works (Yakushev et al., 2017; Pakhomova et al., 2018) the biochemistry of Hg in aquatic ecosystems has been studied using a 1D advection reaction-diffusion model: the Bottom RedOx Model (BROM) has been used to reproduce the vertical dynamics of the total dissolved Hg and MeHg in the marine coastal areas of the Etang de Berre lagoon (France) (Pakhomova et al., 2018). However, even the BROM includes some criticalities in the estimation of mercury dynamics [. . .]”* Why should a 1D model be better than a box model for highly heterogeneous environments? Also, the reference “Yakushev et al., 2017” refers to the original BROM model formulation for water and sediment biogeochemistry but not Hg, I think it doesn’t need to be here.

**L35-38:** “*All these approaches forego the complete representation of the spatial variability by approximating the model domain as a set of interconnected boxes or by detailing only the vertical dynamics of the investigated chemical species. In the present work we report on results obtained using a 3D advection-diffusion-reaction biogeochemical model for three Hg species in seawater (Hg<sub>0</sub>, Hg<sub>II</sub>, and MeHg), coupled with a diffusion-reaction model in sediments and connected pore water.*”. This part needs rewording. No model can achieve a “*complete representation of the spatial variability*”. Even within this manuscript, you conclude that (L385-386) “*only some specific differences [between model and observations] are observed in some of the most contaminated areas, where concentration hot spots are hard to capture given the resolution grid used in the present work.*”, and that (L390) “*The differences (larger than 3.2 ng/l) can be mainly explained by the significant distance between the sampling sites and the model calculation grid nodes*”.

**L43:** has the model been validated? Where is this explained in the text?

**L46:** how exactly can this model be useful “*to explore the effects of sorption-desorption dynamics*”?

**L47:** how can this model addresses the “*role played by the spatio-temporal behavior of phytoplankton and the potential mechanism responsible for the uptake of Hg within the cells*”?

**L58-61:** here I would like to read something more informative such as the paper aim.

**L88-95:** I suggest to use this part to better explain the general architecture of the work, explaining with a figure how the various part of the model(s) interact with each other.

**L90** why eukaryotes? You mean phytoplankton here (see comment on S4)

**L91-92:** too many references

**L93:** what is this reference “*Radomyski and Ciffroy 2015*”?

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**L93:** here is the first mention to Supplement material, with no section specified, which after a long search I found to be S5, at the end of the document, and part of S1.3. This issue occurs throughout the manuscript and must be fixed.

**L98:** the reference “*Melaku Canu et al., 2015*” is not necessary here.

**L102-103:** “*By solving the model equations, we obtain the spatio-temporal distributions of  $Hg_0(x,y,z, t)$ ,  $Hg_{II}(x,y,z, t)$ , and  $MeHg(x,y,z, t)$ .*” Redundant with the previous lines.

**L119:** “*As initial conditions, we assumed an uniformly distributed concentration of  $HgD$  and  $HgT$ , set to 1.9 ng/l corresponding to the experimental detection limit*”. This part should be moved to the “Model and simulation setup” section. I am not sure to understand it well, is it  $HgT(t_0)=HgD(t_0)=1.9$ ? It should be specified “experimental detection limit for  $HgT$  in our dataset (reference)” or something similar, as 1.9 ng/l (about 9.5 pM) is very high as a detection limit. See for comparison (Mason et al. 1999; Horvat et al. 2003; Han et al. 2007; Monperrus et al. 2007; Hammerschmidt and Bowman 2012; Lamborg et al. 2012) who have detection limits well below 1 pM. What about initial conditions for MeHg?

**L126-138:** a crucial process such as biotic demethylation is missing. The description of photo demethylation is inconsistent with Figure 2.

**L132:** the sentence “*All data to estimate the rate constants of the redox reactions are derived from remote sensing (see Supplement).*” should be moved to the Model setup section, along with similar sentences appearing below in the text (I listed some but not all of them) and the reference to the Supplement must be more specific.

**L142-144:** “*The vertical turbulent diffusivity is calibrated according with experimental data, which indicate highly stratified water column conditions during the whole year*”. So is there oxygen depletion in the water column? If so, it should be discussed in the paper. The value given for vertical diffusivity in Table S1 is not representative of stratified conditions, and the reference provided in the table is missing in the bibliography.

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(This part should be moved to model setup section)

**L148:** there are eight references for one model implementation, is confusing.

**L152:** it is not clear to me how are “*the dynamics of the dissolved HgII and MeHg species [estimated], considering effects due to (i) the adsorption by SPM (scavenging process)*”. Your equations 2 and 3 contain the terms for Hg and MeHg scavenging ( $S_{SPM}^{II}$  e  $S_{SPM}^{MeHg}$ ). These terms, adopted from the work of Zhang (2014) and described in the Supplemental do not include SPM:

$$S_{SPM}^{II} = -\frac{\delta}{\delta z} \left[ NPP \cdot pe - ratio \cdot \left( \frac{z}{z_o} \right)^{0.9} \cdot \left( \frac{k_D}{forg} \right) \cdot Hg^{II}(z) \right]$$

The equation should be moved to the main text.

**L153-154:** How is “*the scavenging process for both HgD species regulated by the gradient of mercury concentration along the water column*”?

**L155:** this is a repetition of L90-92, please mention explicitly which parameter or variable you extract from which model and where it has been used in the Hg model, choose for each parameter one or two references that actually refer to the model implementation you used.

**L172-176:** I don't think there is any wet deposition for Hg0, please provide one reference for each process and parameterization selected/excluded. It should be stated explicitly that dry deposition and MeHg deposition are neglected. Somewhere should be also mentioned that Me<sub>2</sub>Hg is not explicitly considered.

**L175-176:** the boundary conditions describing the diffusion of HgII and MeHg at the sediment-water interface are very important in your model, as they represent the only connection between the water and the sediment, but they are not explained. Saying that you simulate “*the exchange of HgII and MeHg at the seawater-sediment interface due to particulate matter deposition and re-suspension mechanisms*” is extremely



misleading because the reader will likely understand that you simulate deposition and resuspension fluxes of particulate Hg species, while this is not the case. I suggest to separate these equations from atmospheric boundary conditions and spend more words to explain well how they are implemented.

**L182-196:** maybe the equations can be distributed within the text describing them, or at least they must be recalled in the text when being described.

**L207:** references?

**L212-214:** *“the mass transfer coefficients ( $MTC^{II}_{sed-water}$  and  $MTC^{MM}_{sed-water}$ ) at the water-sediment interface are calculated in order to fit the experimental findings and according to previous works (Schulz and Zabel, 2006; Ciffroy, 2015) (see Supplement).”* I think that the equations for these MTC should stay in the main text. The fact that they are adjusted to fit experimental findings should be said in the Model setup section. The reference “Schultz and Zabel 2006” is incomplete, and so is “Ciffroy 2015”.

**L214-218:** *“The dynamics of the mercury benthic fluxes ( $\phi_{res}$ ) caused by particulate matter deposition and resuspension mechanisms (Neumeier et al., 2008; Ferrarin et al., 2008) is obtained by considering both the spatial distribution of sediment porosity and the spatio-temporal behavior of removed/settled sediment thickness at the seawater-sediment interface. The sediment exchanges at the water-bottom interfase are obtained from the application of the hydrodynamic model, which accounts for sediment transport processes induced by currents (see Supplement).”* This part seems very confusing to me. The equation for  $\phi_{res}$  and  $Er$  should be defined in the main text and should be probably given different names. Moreover, the hydrodynamic SHYFEM model can not provide fluxes of sediment, if the SEDTRANS model or any other Sediment model has been run with SHYFEM to obtain sediment fluxes in the Augusta Bay, it should be described in detail in the Supplement (including the parameters used). Also, if you had run a sediment model, why did you adopt experimentally measured SPM concentrations for your eq. 13? If you had not run a sediment model, explain where

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the sediment fluxes come from and make it more evident throughout the text that they are not transporting particulate mercury. In Figure 2 there are thick arrows with an “R” that looks like resuspension, which is misleading.

**L219-220:** repetition

**L221:** this should appear before in the section

**L223:** same KD for Hg and MeHg? No units for the terms of this equation?

**L225-227:** please change “in very good agreement with” with “within the range of”

**L228-229:** is then SPM kept constant in time? If so, it should be stated

**L230-242:** This part should be elsewhere, is not part of the model.

**L242:** Figure 2 should be mentioned before in the text, and used to help the reader in the model description. The caption does not explain the figure.

**L245:** please recall the equations where needed, not in this aggregated form

**L249:** Please motivate this choice. This is a strong assumption that I have never seen before.

**L259-260:** This is already mentioned in the section for the water model. I think features are common to the water and sediment modules for Hg might be explained just once at the beginning of section 3 (same for L265-266, L278-279).

**L284-285:** diffusion coefficients are not constant in time in Melaku Canu et al., (2015)

**L290, L291:** while I understand the use of MeHg fraction ( $k_{MeHg}$ ) in setting the initial conditions, I do not understand why it is used in the partial difference equations that also include Hg methylation and demethylation (eq.16 and 17). Can you explain the parameterization in the text? I suggest changing  $k_{MeHg}$  with  $f_{MeHg}$  so it is more intuitive.

**L296 and L301:** I’ve never seen this approach based on a desorption rate () in mercury

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modeling. In this way, your sediment HgT decrease with time by assumption, as there are no source terms. By adopting a *reductio ad absurdum* logic, if your simulation would start in 1900 or before, which initial conditions HgT(0) would you need to achieve observed HgT concentrations for 2005? Can you provide any theoretical background for this parameterization? Also, you state “*The desorption rate is fixed to a low value to fit the slow mercury release from the sediment particles to pore water according to experimental observations*” but in Table S1 “no data” is given as a reference for the parameter .

**L298** “*The spatial distribution of the fraction of methylmercury in the sediments is that obtained by field observations, while the two sediment-pore water distribution coefficients are calibrated, according to previous work (Oliveri et al., 2016)*” move to model setup, provide a reference for the data/publication from where you derived the fraction of methylmercury and mention how much is this fraction.

**L306** why is the MTC parameterization not included in the boundary conditions for sediment? Are you assuming only one-way fluxes toward the water?

**L338-339, L342:** this is different from what is said in L142-144.

**L338-344:** please do not go back and forth from vertical to horizontal diffusivity, discuss one at a time and select a reference that is consistent with that given in Table S1.

**L351:** it is not clear to me why you chose to run 250 years of simulation without varying the forcings.

**L357-361:** this part should not be in the Results section, Table S1 must be introduced much before in the text.

**Figure 3:** you must show modeled vertical profiles against observations when available. I do not find useful or interesting what is currently shown in Figure 3.

**L364:** please provide the values of these ratios and values for comparison to prove this excellent agreement (this applies to most of the Results section, show the numbers).

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**L368-369:** “*In general, the mercury concentration is maximal at the seawater-sediment interface, where the main sources of HgII and MeHg are localized.*”. Do you mean in general in your model? While from your budget I see that diffusion flux appears to be the first HgT source, what supports this statement for MeHg? Especially in this model configuration without biological demethylation in the water column, I would expect water column methylation to be significant. Is the increase of Hg species at the bottom of the water column in agreement with your dataset? Please show and discuss it.

**L369:** I don't think (x,y) is useful here.

**L370-371:** “[...] *peaks of mercury concentration occur at mid-depth of the water column possibly due to the effects of the velocity field of marine currents and the bathymetric features of Augusta basin.*”. I do not understand this explanation.

**L372:** specify “in our model”

**L375-377:** please support this “*good agreement*” with statistical and visual tools. There is no comparison of modeled and observed vertical profiles of Hg and MeHg, which would be interesting to see and discuss, especially considering the emphasis put in the 3D model domain.

**L377-378:** “*This result is probably due to the overestimation of the MeHg benthic fluxes in these two stations.*” Can you support this statement? Other reasons would be possible as well.

**L379-81:** I think it must be highlighted that HgD is modeled while HgT is estimated assuming a linear correlation with modeled HgD concentrations and SPM through equation 13 (which might be not representative of processes occurring in the field).

**L383-384:** same comment as for L375-377

**L387:** same comment as for L375-377 and 383-384

**L391-395:** the reader knows nothing about your modeled concentrations and spatial

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distribution of SPM since they are not shown.

**L399-400:** “*The model reliably reproduces the high benthic mercury fluxes also in the part of the south-east sector close to the inlets of the Augusta Bay, where intensive ship traffic and the relatively high velocity field of the marine currents cause sediment re-suspension and intensive transport of SPM.* is the high sediment resuspension induced by ship traffic considered in your model? How does it relate to your modeled benthic fluxes? From figure 4, I find modeled fluxes to be one order of magnitude higher than fluxes reported by (Salvagio Manta et al. 2016). Please explain what I am missing or what is going on.

**Figure 4:** probably you don't need to show fluxes for both inorganic Hg and HgT, as they look the same. Why available data are not shown on the map, or in another figure?

**L407-409:** “*In general, the theoretical distribution of the mercury evasion fluxes is in a very good agreement with the experimental results for the investigated periods*”. Same comment as for L375-377, 383-384 and 387. From figure 5, I see that modeled evasion (up to 100 ug/m2d) is about 100 times as high as evasion modeled by Bagnato et al. 2013.

**L416-419:** “*The modeled HgD benthic fluxes (...) are significantly larger than those estimated for both sampling periods on the basis of the field observations (...) (Salvagio Manta et al., 2016).*” Why do you go back to benthic fluxes, which are already discussed from L396 to L404, contradicting your previous statements (L399 and 403)?

**L419-420:** “*This probably depends on the limited number of sampling sites available in the experimental work with a consequent extremely coarse capacity to capture reliable estimates of benthic fluxes.*” Six sites for measuring benthic fluxes within the Augusta Bay is a lot. Other work of this kind I came across only had 2-3 sampling stations for larger study areas, I thus disagree with the statement that they provide an “extremely coarse representation”.

**L421-423:** I do not follow why this should ensure that your model results for a specific period are better than values experimentally detected under conditions that are representative of that period.

**L424-429:** you have already discussed evasion fluxes before, so the two parts should go together. Be careful of the references.

**L439-440:** “*The model results for the annual recycled mercury flux are shown in Fig.6d. In this case, values calculated (2.45 kmol y<sup>-1</sup> for the year 2011 and 2.41 kmol y<sup>-1</sup> for the year 2012) are larger and more realistic than those estimated in Salvaggio Manta et al. (2016) by simple linear subtraction of the available fluxes in the mass-balance equation (0.84 kmol y<sup>-1</sup>).*”. How do you support this statement that your estimate is more realistic? Isn't the mercury recycling calculated by subtraction also in this work (equation 14)? How do you argue the significant gap that is shown in Figure 6d between the “Total recycled” and the “Scavenged recycled”? How large is your estimated HgT reservoir in the water and sediment of Augusta Bay?

**L447:** 50 cm is not shallow for sediment. Why did you choose to represent about 2 m of sediment with a coarse resolution (10 cm layers)?

**L459:** you should make it clear which data are used for calibration and which are used for validation.

**L465-466:** “*This “integrated” model, which allows to give a description of the mercury dynamics in the whole system (seawater, pore water, and particulate phase of the sediment), represents an absolute novelty in the landscape of the mathematical modeling of spatio-temporal dynamics in a biogeochemical context*”. This is not true, as you can realize with a thorough review of the mercury modeling at the state of the art. Besides, the parameterization chosen in your model for Hg species dynamics in water and sediment is overall questionable and not well supported by theoretical knowledge at the state of the art. Even correcting major oversights mentioned in other comments, this model still neglects the dynamics of Hg in the particulate phase. It thus does not pro-

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vide a “description of the mercury dynamics in the whole system”, and is probably less advanced than other existing models.

**L480-482:** “the different approach used in the WASP models and River MERLIN-Expo model allowed neither to reproduce the dynamics of the vertical profiles of mercury concentration in the seawater compartment, nor to obtain the spatio-temporal behavior of mercury concentration in the sediments”. Again, the River MERLIN model does not seem to be relevant here, and it is not true that the previous approaches could not reproduce the vertical dynamics nor the spatio-temporal evolution of Hg species. For example in Rosati et al., (2018) the WASP model has been used to simulate the vertical profile of Hg and MeHg in the water column and sediments of the Black Sea; this has been done in 1D but it could have been done in 3D as well. Soerensen et al., (2016) also implemented a 1D model for Hg species in the water and sediments of the Arctic Sea. As for the spatio-temporal evolution of Hg and MeHg in water and sediment, an example can be found in Canu and Rosati (2017).

**L484:** “In general, no forecast about the mercury depletion time in the sediment compartment of Augusta Bay was possible by other models.” See Canu and Rosati, 2017.

**L486-490:** “Finally, the biogeochemical models introduced in previous publications included neither the Nutrient-Phytoplankton model (Dutkiewicz et al., 2009; Morozov et al., 2010; Valenti et al., 2012; Denaro et al., 2013a, c, b; Valenti et al., 2015, 2016a, b, c, 2017) nor the Phytoplankton MERLIN-Expo model for the mercury content in eukaryotes cells (Pickhardt and Fischer, 2007; Radomyski and Ciffroy, 2015). All the aforementioned aspects are therefore an element of novelty in the context of 3D biogeochemical modeling.” The model here presented do not include a plankton model, the two tools are used together but not integrated. Moreover, there has been previous work integrating phyto- and zooplankton in a biogeochemical model for marine Hg cycle (e.g. Soerensen et al., 2016).

**L491-492** “The HR3DHG model considers the effects of the seasonal changes of the

*environmental variables on the mercury outflows towards the atmosphere and the open sea, and this also is a new feature in biogeochemical model. The seasonal effects are never discussed in the manuscript, and anyways this is clearly not a new feature.*

**L495** *“Firstly, the mass transfer coefficients at the water-sediment interface are highly sensitive to the layer thickness above the sediment and their variation could cause significant changes of mercury benthic fluxes.”* Why is this relevant? Which are the environmental implications?

**L497** *“Sensitivity analysis performed on the sediment compartment indicates that the spatio-temporal dynamics of the benthic mercury flux strongly depends on the spatial distribution of the sediment porosity and of the initial total mercury concentration in the top-sediments”.* Sensitivity analysis is never discussed in the manuscript but should be.

**L500** *“Sensitivity analysis performed on the environmental parameters and variables used in the seawater compartment indicates that the spatio-temporal dynamics of [HgT] and [HgD] primarily depends on the velocity field of the marine currents obtained from the hydrodynamic model (Burchard and Petersen, 1999; Umgiesser et al., 2004; Umgiesser, 2009; Umgiesser et al., 2014; Ferrarin et al., 2014; Cucco et al., 2016a, b, 2019), even if the role played by the vertical and horizontal diffusivities (Pacanowski and Philander, 1981; Massel, 1999; Katz et al., 1979; Denman and Gargett, 1983; Peters et al., 1988; Valenti et al., 2015, 2017)”.* How did you perform sensitivity analysis on HgT that is not modeled but assumed to be linearly correlated to HgD (eq.13)? From my experience, HgD and HgT dynamics are likely to have different drivers. If sensitivity analysis has been carried out, it should be described. There are too many references.

**L508** if both data and model suggest Hg is mostly in the particulate phase, why is your model designed around the dynamics of dissolved Hg species?

**L510** *“the amount of mercury dissolved in pore water is negligible with respect to the total amount in the sediments”* this is not a finding of this work.

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**L511-L512** *“In general, the concentration of the three mercury species dissolved in seawater decreases slowly as a function of time, whereas their concentration ratios remain approximately constant”* this happens due to the exponential decay of Hg parameterized for sediment and the absence of inputs in your system (except atmospheric deposition, which is set to be very low, ~3 times lower than observations in Bagnato et al. 2013).

**L526-528** *“the amount of mercury absorbed by the phytoplankton, and recycled in seawater, is negligible. In this last respect, it is however important to underscore that even a reduced amount of MeHg entering phytoplankton cells can be very dangerous for the health of human beings due to the bio-accumulation processes which occur throughout the food chain.”* this seems to be pointless in the discussion. Can you quantify the amount of Hg adsorbed and released?

**L529** *“The dynamics of the particulate matter deposition-resuspension process (Neumeier et al., 2008; Ferrarin et al., 2008) does not significantly modify the spatial distribution of the HgT recycled at the surface layer of the sediments”* the dynamics of particulate matter are not included in the Hg model, and never presented in the manuscript, so where does this statement come from? (see comments on L214-218)

**L530-533** *“Moreover, the theoretical results show that the recycled mercury flux in the Augusta Bay can only partially be described by the scavenging process of organic particles, which however needs further experimental investigations. In fact, improved knowledge of the scavenging process would be necessary to obtain a better estimation of the HgT removed from the water column”.* Which are other processes affecting the “recycled mercury”? I argue that here, rather than more experimental investigation, you would need a model that can reproduce particulate Hg dynamics.

**L537** I do not think is relevant talking about climate change here, at the very end of discussion.

**L551** why should this model be a promising tool to explore and predict the effects of

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climate changes on Hg dynamics?

## 0.1 Supplement Material

**S1.1** All the parts that are repetition of section 3.1 in the main text must be removed.

**L49** why is Net Primary Production obtained from satellite if you have a NP model run for the area?

**L51-52:** this seems to be a misunderstanding of the concept of euphotic layer. If equation S7 is not used must be removed.

**L54** why is chlorophyll concentrations obtained from measurements if you have a NP model run for the area? How should the reference Zhang be related to this sentence?

**S1.1.1**  $\phi_{dep} = \frac{Hg_{gas-atm} \cdot Pr}{\Delta t}$  is not dry+wet deposition of Hg, and is a questionable parameterization.

**S1.1.2** “*The lateral fluxes for all variables are set up equal to zero at the boundaries of Augusta basin (Valenti et al., 2017) except where inlets, rivers and sewerage are localized.*” In this work, only inlets are considered while inputs from rivers and sewerage are assumed to be negligible, but this is not mentioned in the text (it can only be seen from the equations S13 and S14).

**S1.2** equation S17 is already in the main text (eq.2). Equation S18 should be moved in the main text. In the definition of PHg should be specified that it is estimated externally with the plankton model and is not coupled with the Hg model. It should be explained that  $\eta$  is the nutrient recycling efficiency coefficient, which is assumed to be the same for mercury. Equation S19 should be also presented in the main text. The definition given for  $\eta$  is inconsistent. How are the units for  $S^{II}_{SPM}$ ? The name  $S^{II}_{SPM}$  is misleading, this is an estimate of Hg scavenged by phytoplankton, not SPM.

**S1.2.1** equation S21 is only for wet deposition, differently from what is stated.

**S1.2.2** The definition for  $\phi_{res}$  is misleading, why not keeping only the extended version of eq. S22 (which is eq. 7 in the main text)?

Is not  $Hg^{II}_{dis-water}$  the same as your modeled  $Hg^{II}$  with  $z=z_b$ ? Why using a different name?

**L212** Why do the values of the “boundary layer thickness above sediment” for Hg and MeHg differ in Table S1? Why are their values so low (0.009 cm for HgII and 0.03 cm for MeHg)? And why are they lower than the “boundary layer thickness below sediment” that is 0.01 for both Hg and MeHg?

Equations S22 and S25 is already given in the main text (eq. 16 and 18), refer to that. Equation S25 is not in agreement with Melaku Canu et al., 2015 as stated in L228.

**S1.2.3** is already in the main text (eq.15).

**S1.2.5** eq. S27 is eq. 9 in the main text. Equations S28-S29 are the same as S13-S14, and S42-S43, I think they can be written in a more general formula without repeating them for each Hg species, especially considering that they are set to 0 for your implementation.

**S1.3** Equation S32 is already in the main text (eq.3).

**L295-296** why all these references?

**L304-307** the text is already in the main text.

**L308** “The rate constant for the methylation of inorganic mercury is fixed according to Monperrus et al. (2007) (Batrakova et al.,2014; Monperrus et al., 2007b).” Why are references reported in this way? There are other cases.

**L311-317** same comments as for S1.2 (and it can be explained just once for both Hg and MeHg)

**S1.3** Almost the entire section is a repetition of information already given in the main

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text or in S1.2. The only difference with section S1.2 is the substitution of “HgII” with “MeHg”, there must be a better way.

**S1.3.1** MeHg atmospheric deposition is  $> 0$ , although low (e.g. Mason et al., 2012)

**S2** “*Since the direct loads of SPM (Ciffroy, 2015; Melaku Canu et al., 2015) for the Augusta basin were unknown, the SPM concentration dynamics could not be reproduced correctly. Therefore, we reproduced the spatial distribution of SPM concentration at the steady state by interpolating the experimental data observed in recent samplings (October 2017) performed in the site investigated.*” You obtained SPM values by interpolating observations and assume steady state conditions, thus why do you present a dynamic model for SPM that is not used (eq.S46)? What about the references? Besides, at a first and second reading is not clear why you need SPM if adsorption of particulate Hg species is based on NPP obtained from satellite data. At some point, I realized that this is only used in eq. 13 to estimate HgT.

**S2.1** the definition given for forg “*organic fraction of suspended particulate matter in dissolved-phase*” is meaningless.

**S3 and S3.1** These sections should present the site-specific implementation of SHYFEM model for Augusta Bay, rather than providing a general description of the model, which is available elsewhere in the literature. The reader should be able to understand how the hydrodynamic and sediment models have been run (add values used for parameters and coefficients, show the calibration). The title for S3.1 is incomplete.

**S4** Be aware that eukariotes are not a planktonic population, thus line 566 is meaningless. The term eukariotes is much broader than phytoplankton, which is what is actually simulated here; this must be corrected throughout the text.

The NP model is already described in many publications reported here and is not a central part of this work, so as for the hydrodynamic and sediment models I do not think the model theory should be explained in detail here. Probably a description of

the implementation for the Augusta Bay (linked to Table S3) clarifying which are site-specific parameters and which parameters are adopted from other areas, would be more useful. I would also like to see calibration, or a map of the output.

**Table S1** all parameters where “no data” is reported are set to 0. Is it possible to make assumptions and estimate them?

**Table S2** why is it separated from S1? The caption is the same. Do you have 0 porosity value?

**Table S9** It should be explained in the main text why your modeled value of atmospheric deposition is 2.5 lower than the deposition measured at your study site in 2011-2012 (Bagnato et al. 2013; Salvagio Manta et al. 2016). How would affect your results the increase atmospheric deposition to the observed rate? It should be also explained in the main text why all inputs different from atmospheric deposition are set to 0.

Why is the term “MeHg released from sediment” in this HgT budget? Here only the total is needed. Why is MeHg budget not estimated?

**Table S5-S6-S7-S8-S10.** To improve readability, I would move the station/longitude/latitude information for data and model in a separate table and keep here only Station | Period | Depth | Hg.

**Figure S3.** I don't see a good agreement here. I took the effort to copy your HgD data from Table S5 and found an average relative error of 86% (median 62%) between model and observations, this could even be fine if you acknowledge it and properly discuss it.

**Figure S4.** The scale (up to 140) is almost two time as high as the maximum value shown, so almost everything appears in blue.

### Technical comments

In general, I found this manuscript difficult to read for the following reasons:

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1. most of the time the authors refer to the “Supplement” without specifying the section, which makes it very difficult to follow since one has to dive into 47 pages of text, equations, and figures;
2. some sentences/equations/concepts are repeated several times in the main text and the Supplement, overwhelming the reader with redundant information while other parts of the work are barely mentioned in the main text (e.g. the way the water and sediment modules for Hg interact with each other and with the other models used, i.e. the Phytoplankton MERLIN-Expo and the Nutrient-Phytoplankton, or the terms of equations S22 and S36);
3. the equations are not recalled in the text where needed;
4. the language needs to be made more fluent and objective, thus a professional English editing service is recommended.

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