

# Response to reviewers: *Modeling the marine chromium cycle: New constraints on global-scale processes*

We are grateful to all four reviewers for evaluating our work, and the particularly valuable and constructive comments that have helped to substantially improve the manuscript. We have thus endeavored to incorporate the suggested changes in the revised manuscript as detailed below in our point-by-point response.

The original reviewer comments are in black and our responses are colored blue. Line references correspond to the revised manuscript without tracked changes.

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## Reviewer#1

This paper is within the scope of the journal and I suggest publication after a minor revision addressing the comments in the attached PDF file.

Reply#1: We thank the reviewer for the positive assessment of our work and the important comments that have helped to clarify the manuscript.

In the following, we have highlighted the reviewer comments that are not of typographical or grammatical nature and demand a more detailed answer by us. The remaining comments (that is typographical and grammatical ones) have been amended in the revised manuscript, if not otherwise noted below.

Abstract

Reply#2: We now included the word suggestions by the reviewer. The reviewer further suggested to change the entire abstract to past tense. However, we feel that this is only a matter of style, and we thus prefer to keep it as is, i.e., in present tense.

L27: more appropriate references are suggested to be cited here.

Reply#3: We now additionally cite the studies by Ellis et al. (2002), Joe-Wong et al. (2019), and Wanner & Sonnenthal (2013) which investigated Cr isotope fractionation during redox transformations in detail.

L36: Wei et al., 2018, CG, is suggested to be cited here.

Reply#4: Reference added.

L58: Although submarine groundwater discharge and hydrothermal fluid may contribute a small fluxes to the oceanic Cr, I think you should discuss it in the text.

Reply#5: We added a sentence to the main text (lines 61-63), indicating that we neglected these two sources due to their expected very small contribution to the marine Cr budget.

L80: provide references.

Reply#6: We now added the reference to Köhler et al. (2017).

L110: Please provide references for supplementary data 1.

Reply#7: We now added references to the data in supplementary table 1.

L113: Sun et al. (2019) suggested that Cr was lost from particles to solution, when transitioning from brackish to salt water in the Connecticut River estuary. Please add discussions on this.

Reply#8: We now added a statement that some studies even indicate an increase of the total dissolved Cr concentration with salinity as found by Sun et al. (2019) at the Connecticut River estuary (line 117).

L150: I think Fe (II) is mainly produced in pore waters. How about organic matters?

Reply#9: In the here presented simulations a sediment module was not coupled to the Bern3D model. Pore water processes are thus not considered here.

L235: Bonnand et al. (2013) didn't estimate the oceanic residence time of Cr; add citations of Wei et al. (2018) and Reinhard et al. (2013) here.

Reply#10: Amended as suggested by the reviewer.

L344: What does "improving" mean?

Reply#11: We changed this section title to: *"Improving the representation of Cr reduction in OMZs"*, in order to clarify this.

L387: I think it is better to discuss the implication of this study for the application of Cr isotopes as a paleo-redox proxy.

Reply#12: Since this is the very first implementation of Cr in an Earth system model, we feel that it is more important here to discuss the performance of the model and the limitations of simulating Cr, than to already discuss the application of Cr isotopes as a paleo-redox proxy. Yet, we note that we intend to investigate the latter in a future study, which will allow for a much more in depth discussion of this aspect.

L427: Please rephrase this long sentence.

Reply#13: We split this sentence into two to increase readability.

L444: I think it should be "for the biogeochemical cycle of Cr and its tight interconnection with past oceanic and atmospheric oxygenation". In addition, as you said, marine Cr cycle is also associated with biological productivity.

Reply#14: Changed as suggested by the reviewer.

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## Reviewer#2 (Catherine Jeandel)

The authors propose a simulation of the Cr and Cr isotopes cycles at a global oceanic scale using the Bern3D EMIC. Despite a limited data set, they propose a well argued discussion of the sources, transformation and sink of this oceanic tracer including its redox forms (CrIII and CrVI). Although the limited set of data is narrowing the interpretation fields, leading to somehow hypothetical discussions (eg on the OMZ CrIII behavior and the Arctic specific case), the consistency between the modeled and observed data give confidence about the scientific approach. The manuscript is well written and illustrated. This work deserves publication in Biogeosciences with minor revisions as listed below.

Reply#15: We thank the reviewer for the positive evaluation of our work as well as the thoughtful comments that helped to improve the manuscript.

- Riverine inputs: the authors adopt a simplified parametrization to the CrVI and CrIII removal rates in the estuaries. Although the respective values of 20% and 80% are consistent with the known behavior of these tracers, the reader is missing argument justifying this choice. In addition, the sensitivity of the model to this input term was not tested, it would have been interesting to explain why.

Reply#16: As we discuss in the main text (lines 114-118) investigations of the fraction of Cr removal in estuaries do not yet yield consistent values. In our simplified approach we therefore chose these values to be in general agreement with these investigations as well as the overall chemical behavior of the two redox states. We tried to now make this more clear in the manuscript. Since there are further many uncertainties associated with the riverine source, such as the limited dataset of riverine Cr concentrations, anthropogenic contamination, or the initial redox speciation during weathering, we feel that it is too early to test the sensitivity of the model to this input term.

- The same manner, what are the arguments justifying the increase of the OMZ reduction rates to 20 and then 30 nmol/m<sup>3</sup>/y? The way it's written looks like the authors played to the lottery which I don't think it's the case!

Reply#17: As we discuss in section 3.2 our parameter tuning did not substantially help to constrain the OMZ reduction rate, since direct [Cr(III)] and [Cr(VI)] measurements of OMZs are extremely sparse. Yet, from the understanding of the Cr redox behavior we know that Cr(III) concentrations should be strongly elevated in OMZs, which was not the case for our control simulation. As such, we wanted to explore the impacts of substantially higher OMZ Cr reduction rates. The values of 20 and 30 nmol/m<sup>3</sup>/yr fulfill this requirement, but are indeed somewhat arbitrarily chosen. With new direct measurements of Cr(III) and Cr(VI) concentrations from OMZs, we may be able to more strongly constrain the OMZ Cr reduction rate in the future.

- The observation data base: although provided in the annex, a map representing the locations of the available (and selected) data is missing. I strongly recommend to propose a figures compiling all the stations used in this work (if I am not wrong, only few Topogulf stations are represented while the whole set of published data is listed in the excel file in annex)

Reply#18: We now added a global map with all stations of the data compilation indicated in the supplement as Figure S1. All data presented in supplementary tables are also used throughout the study. Yet, for instance, for Fig. 5 only data close to the transect ( $\pm 15^\circ$ ) are shown, as is noted in the caption. Thus, it is possible that not all stations of the respective basins are depicted in this figure.

- Finally, I was slightly disappointed to read that the discussion on the Med Sea results was skipped since I analyzed 3 profiles, quite homogeneous with depth and that could be compared to the North Atlantic ones: this semi-enclosed sea is a good place to test the relative influence of dust vs sediment sources.

Reply#19: We agree with the reviewer that a discussion on the Mediterranean Sea would have been interesting due to the comparatively good data coverage. However, due to the coarse resolution of the Bern3D model, the Mediterranean Sea is only poorly spatially resolved (only few grid cells) that cannot represent the complex dynamics of this basin. We are therefore not able to confidently interpret simulated Cr in the Mediterranean Sea. For such task, a higher resolved Earth system or regional climate model is required.

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## Reviewer#3 (Roger Francois)

In view of the resurgence of interest in the marine Cr cycle in recent years, this is a timely study which highlights crucial gaps in knowledge and provides an important framework to guide further research. I recommend publication after considering the minor points I am raising below.

Reply#20: We thank the reviewer for the detailed and constructive evaluation of our work, which we highly appreciate.

General comment:

One of the main conclusions derived from this study is that sediments are the most important source of Cr to the ocean. Since this source was previously considered to be minor, this is a very important finding. I think, however, that the significance of this finding could be further discussed.

First, it would be interesting to contrast the Cr mass balance and residence time obtained from this study and previous estimates. I note that while the residence estimated by the authors is in the lower range of previous estimates, it is still within this range. How come? Since a major new source has been identified in this study, shouldn't the resulting residence time be lower than the previously estimated range?

Reply#21: Previous estimates for the marine Cr residence time at the lower range are indeed similar to the one found here, even though these studies did not include a benthic source (e.g., McClain and Maher, 2016). However, we note that we excluded rivers from our database for which exceedingly high Cr concentrations, and thus total fluxes to the ocean, were reported that are contaminated by anthropogenic sources (e.g., the Panuco River; McClain and Maher, 2016). These rivers were instead included in the calculations of the marine Cr residence time in these previous studies, which consequently yielded lower values than we get without considering the benthic source. We now also expand on this in the section 3.1 of the main text.

Second, when reporting residence times in a reservoir, we must define and justify the boundaries of this reservoir, and I think this is particularly important here. The residence time calculated in this study is based on the assumption that pore waters are a source of “new” Cr, similar to that added by rivers and dust. However, it is possible (likely?) that much of the pore water Cr diffusing to bottom water was scavenged from the water column and is being recycled. In which case it may be more appropriate to calculate residence time based on river/dust input only, which would match the burial rate of Cr in sediments. On the other hand, if much of the pore water Cr is derived from dissolution of lithogenics in sediments, then pore waters would be a source of new Cr, and the residence time calculated in this study would be unambiguously correct. At this point, we know little about the source of Cr in pore water, so this distinction is still difficult to make. However, I think it is important to bring this up in the discussion, considering that there has been a slow paradigm shift in recent years regarding the importance of lithogenic dissolution in sediments as a source of elements to the ocean (in particular for Nd (e.g. Abbott et al., GCA 154, 186, 2015) but also other elements (e.g. Jeandel and Oelkers, Chem Geol 395, 50, 2015)). Whether pore water Cr is “new” or “recycled” can be assessed from the shape of the pore water profiles. Pore water Cr concentration would gradually increase with depth in the sediment if the Cr is “new”. Recycled Cr would produce

a surficial or subsurface pore water Cr maximum. Clearly, the pore water profile reported by Janssen et al (2021) is of the latter type, and so are the pore water profiles from the California Borderland reported by Shaw et al (1990) [which I think should also be brought in the discussion; GCA, 54, 1233]. However, these pore water profiles generate fluxes that are much higher than needed to match model results with the existing water column profiles, and therefore cannot be representative of the whole ocean, as indicated by the authors. Whether the needed lower Cr fluxes reflect the slow dissolution of lithogenics producing pore water profile of the former type (i.e. gradually increasing with depth) over large area of the ocean floor (presumably in low productivity regions) is an open question, which could be asked explicitly in this paper.

Reply#22: We fully agree with the reviewer that it is important to define how the residence time is calculated (as we do in lines 142-143) and that it makes a difference for the conceptual understanding of the Cr cycle whether the benthic Cr is “new” or recycled. However, in our model we are currently unable to differentiate between these two processes, because we do not employ a sediment module that explicitly calculates the Cr pore water chemistry. Thus, in the model the benthic Cr is technically always new Cr, but we can in fact say nothing about its true origin.

The reviewer further mentioned that the pore water depth profile for Cr that is solely of lithogenic origin should produce increasing concentrations with depth, which is not observed by Janssen et al. (2021). Instead, these profiles show a subsurface maximum. However, similar subsurface pore water enrichments are also observed for neodymium (Abbott et al., 2015a), and it is assumed that pore water Nd is mainly of lithogenic origin as indicated by isotopic data (Abbott et al., 2015b) and REE patterns (Abbott et al., 2015a). It thus appears that one cannot unequivocally deduce the origin of the trace metal from its pore water profile.

Nevertheless, we agree with the reviewer that these are important points worth mentioning in the manuscript. As such, we added a brief discussion on the origin of benthic Cr and the implication on the residence time to section 3.1.

#### Detailed comments

Line 44: “Cr(III) accounts for the majority of total dissolved Cr in OMZ..” vs line 47-48 “subsurface Cr(III) concentrations are substantially lower than Cr(VI) concentrations typically ranging 0 and 0.3 nM”. These two statement are not consistent.

Reply#23: We now specified that subsurface Cr(III) concentrations are only substantially lower than Cr(VI) concentrations away from OMZs, where the converse may occur.

Line 110: “..rivers showing strong anthropogenic contamination were removed (supplementary data 1)” It is not clear how the selection was done from this spreadsheet.

Reply#24: Generally, we included all available data for riverine Cr concentrations, which are based on the compilation by McClain and Maher (2016) updated with data from Guinoiseau et al. (2016), Skarbøvik et al. (2015), and Wei et al. (2018). We now further added the data we excluded, due to anthropogenic contamination, to supplementary data 1 and reference the study that describes the contamination.

Line 120/130; equation (5)/(7): What is  $V(\theta,\varphi)/V(\theta,\varphi,z)$ ? Is this the volume of the grid in the model receiving the river inflow and pore water efflux? (also, for the sake of non-modelers like me, indicate somewhere that  $(\theta,\varphi)$  simply represents latitude and longitude)

Reply#25: Yes,  $V(\theta,\varphi)$  and  $V(\theta,\varphi,z)$  are the volumina of the grid cells where the sources enter the ocean. We clarified this now in line 125. We further now note in line 81 that  $(\theta,\varphi)$  are latitude and longitude.

Table 1 Caption: Indicate that references/justifications for the values given to these variables are discussed (mostly) in the text. Make sure that you justify or reference all of them. Also, adding references in this table would help.

Reply#26: We added to the caption of the table that the references and justifications are described in the text.

Line 240; Fig. 2: It would help the reader if you use a different color to highlight the runs with the best fit, which are associated with benthic fluxes of 0.1 – 0.2 nmol/cm<sup>2</sup>.y and residence times of 5 – 8 kyrs. It must be obvious to the authors but it took me a while to figure out what I was supposed to look at in Fig. 2.

Reply#27: We slightly expanded the caption of Figure 2 to clarify that we determined the model performance with the cost function of the mean absolute error (MAE) and that simulations yielding a smaller MAE indicate a better model performance. We additionally marked the simulations with the best model performance in the figure.

Line 293: It is probably a simple wording issue, but what “deficit” are we talking about here? The model overestimates Cr concentration in the Arctic.

Reply#28: We here mean a model inadequacy, which we now changed accordingly in the manuscript.

First reference in the text to Fig. 6 is on line 426, after Fig. 7 and 8 have been referred to.

Reply#29: Figure 6 is first mentioned in line 329 of the manuscript, before Figures 7 and 8.

Line 345: the actual Cr sink is the sediment in contact with the OMZ, right? Not the OMZ in the water column. Cr(III) produced in the OMZ could be scavenged and re-oxidized deeper in the water column.

Reply#30: Yes, the reviewer is correct, the sink is the sediment not the OMZ itself. We therefore rephrased this sentence as follows: “*Oxygen minimum zones are thought to represent important regions where Cr is removed from the ocean and deposited in the underlying sediments.*”

Line 347: Probably another wording issue. “below the OMZ” to me means in water deeper than the OMZ, but I think the authors mean Cr removal happens in the sediment in contact with (“below”) the OMZ.

Reply#31: We here indeed mean all sediments below OMZs and not only in direct contact with them. Thus, Cr(III) can in fact re-oxidize in the oxygenated water below the OMZ itself, and therefore not be deposited in the underlying sediments.

Line 348: “Cr(III) concentration are partly in disagreement with observed Cr(III)” How is the reader supposed to see this? Can you add a figure or provide the concentrations in the model vs observations? I find this entire paragraph difficult to follow.

Reply#32: We now added the values for simulated and observed Cr(III) concentrations to this sentence. Further, we split long sentences of this paragraph into two, which together with the additional information provided as mentioned in replies#30 and 31 should improve the readability.

Line 371: Again, give the value or range of values observed.

Reply#33: Added.

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## Reviewer#4 (Edward Boyle)

Review of “Modeling the marine chromium cycle: New constraints on global scale Processes” by Pöppelmeier, Janssen, Jaccard, and Stocker (bg2021-0106)

The paper serves a useful purpose as a first-stab model for Cr in the global ocean. The model itself is well documented, and for many purposes, of sufficient complexity that many processes can be included. It makes estimates of things that are poorly known (most notably, the benthic flux of Cr), which gives observationalists targets to aim at. And if anyone disagrees with some of the model assumptions, then they are free to make their own model. Hence I recommend publication of a revised version of the manuscript.

Reply#34: We thank the reviewer for the positive assessment of our work and for sharing his insight in the geochemical cycling of Cr.

That said, there are many things in here that I wouldn't have done if I were the one constructing the Cr assumptions. My major unhappiness is in the assumption of a (relatively large) globally uniform seafloor flux for Cr, although I would also have handled the OMZ assumptions differently. I think the manuscript bears some confusion on the ocean residence time of Cr. If the benthic flux of Cr comes from regenerated biogenic matter that removed it from the upper ocean, it doesn't shorten the residence time in the entire ocean-surface sediment system. I think that the river flux is the main constraint on that number, unless Cr release from aluminosilicates in sediments is significant. And there is no data upon which to know whether this happens.

Reply#35: We acknowledge that we had to make a number of (simplifying) assumptions in our implementation of the Cr cycle in the Bern3D model, largely due to missing observational constraints. However, we here want to seize the opportunity and further elaborate on the aspects mentioned by the reviewer. First, we consider a globally uniform benthic flux the only sensible parameterization with the current state of knowledge. For now, only a handful of pore-water profiles exist that characterize the nature of the benthic Cr flux and very little is known about the driving processes leading to the sedimentary release of Cr. As such, we feel that an implementation of a regionally variable benthic flux is premature at this point and could in fact create a false sense of precision that is not supported by the data. Further, we here want to emphasize that the strength of this benthic flux is a free parameter in our implementation that was tuned for the best model-data agreement. Indeed, our tuning ensemble also included runs with no benthic flux, which however produced worse model-data agreements than a moderate benthic flux of  $0.1-0.2 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ . The reviewer further mentions that our calculation of the ocean residence time bears some confusion, since it remains unclear whether the Cr associated with the benthic flux is recycled or new. We have already addressed this issue in response to a similar comment by reviewer#3 in reply#22. As such,

we now clearly state in the manuscript that the model cannot distinguish between recycled and new benthic Cr and that the ocean residence time may hence be larger dependent on the fraction of recycled Cr contributing to the benthic flux (see section 3.1).

As the authors note, the model's handling of oxygen deficient zones (ODZs, which should be distinguished from oxygen minimum zones (OMZs) is inadequate to represent them very well – even for simpler properties such as oxygen. Is there a companion paper on the nitrogen system in ODZs? I bet that it is similarly problematical. Probably someone needs to make a regional model that can do a decent job at representing ODZs before trying to include them in a global model.

Reply#36: We agree that the representation of OMZs (here defined as  $[O_2] < 5 \mu\text{mol/kg}$ ) is somewhat limited in the Bern3D model, which is primarily related to the coarse spatial resolution (see also line 376). Yet, we want to note that the representation of ODZs ( $5 \mu\text{mol/kg} < [O_2] < 80 \mu\text{mol/kg}$ ) is substantially better as characterized by Battaglia & Joos (2018) who investigated the impact of (de)nitrification in OMZs and ODZs on the nitrogen cycle in the Bern3D model. These authors further parameterized subgrid-scale processes that partly alleviated the issue of the somewhat poor representation of OMZs on the nitrogen system. With a better understanding of the processes driving the Cr redox behavior in OMZs, this may also be a possibility for the Cr implementation in the future. We discuss these model shortcomings and their potential alleviations in section 4.2.

The paper misses out on some significant references:

Lines 110-120: Shiller (1991) GCA 55:3241

Lines 120-129: Brumsack (1983) Mar.Chem. 14:89 and Shaw (1990) GCA 54:1233

Lines 180-185: Elderfield (1970) EPSL 9:10 and Shiller (1987) GCA 51:3273

Line 275: Sherrell (1988) DSR 35:1319

Reply#37: All suggested references are now added to the main text, except the last one (Sherrel & Boyle, 1988), which measured Cr in the Mediterranean Sea, a basin that we explicitly excluded from our interpretation, because it is only very poorly spatially resolved in the Bern3D model (please see also reply#19).

And I would also add for lines 285-290, Arctic surface Cr is influenced by Fe(II) oxidation by reduced Fe released from organic-rich Arctic shelf sediments, with Cr(III) formation and Fe oxide scavenging.

Reply#38: We now added the process suggested by the reviewer as an alternative/additional explanation for the low Cr(III) surface concentrations in the Arctic.

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## References

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