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Interactive comment on "Elemental composition of invertebrates shells composed of different $CaCO_3$ polymorphs at different ontogenetic stages: a case study from the brackish Gulf of Gdansk (the Baltic Sea)" *by* Anna Piwoni-Piórewicz et al.

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We are grateful for the review, that will help to improve our manuscript. We carefully read the comments and tried to answer all questions in a clear and concise manner.

Comment: Fundamental information regarding the measurements and concentration calculations is missing or unclear, and the analytical uncertainties and repeatability based on appropriate reference materials are also lacking. In addition, in my opinion,

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Discussion paper

the sample preparation and pre-cleaning procedures are questionable. The authors must prove the validity and explain their analytical procedures, and take into account analytical uncertainties when presenting or interpreting their data.

Response: The analytical details will be discussed in full in the revised version of MS; also see the specific comments below.

Comment: Furthermore, as detailed below, I have problems understanding how whole shell bulk measurements may be used to assess the role of ontogeny or even environmental variations. By using entire shells, the authors 'average' the composition of the growth lines precipitated during earlier and later stages of life, as well as the composition of growth lines built during different seasons or under different environmental conditions. Thus, I am not sure that by comparing bulk values from smaller vs. bigger (younger vs. older) individuals it is possible to determine whether environmental or ontogenetic controls drive the composition of the shell. Simply, the differences between the mean bulk values would depend on the elemental variability encompassed in the shell, which would depend on individuals' growth and environmental conditions experienced. The mean bulk values from older individuals integrate large intra-shell variabilities, while in younger individuals smaller intra-shell variabilities, but I think that with this design it is difficult to disentangle the underlying controls on the elemental composition of the carbonates. Moreover, the problem of using bulk also limits the interpretation of the data when it comes to the different polymorphs, and particularly this is the case for the bimineralic bivalve. Here, the authors may only conclude whether the composition of the mixture is different to other species building pure calcite vs. aragonite. However, it does not answer the question whether the composition of the calcitic part or aragonitic part within fundamentally differs and how much, which I think is the relevant question here. When discussing the composition of the bimeralic bivalves the authors could, at least, attempt to estimate the contribution from each polymorph to the mixture, and discuss the implications. Moreover, I am wondering why the entire shells were crushed? Surely, >100 mg is not required for the analyses, as concentration mea-

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Discussion paper

surements are typically done on <mg level. Why did the authors decide to measure the entire shell instead of e.g. a profile across the shell or different growth bands? Such approach, I believe, would be much better for defining an ontogenetic trend, and could also provide some insights into the intra-shell variability. The intra-shell variability, in particular, would be very meaningful to assess before any mean bulk values are used for interpretation of ontogenetic or environmental signals – i.e. how heterogenous are the shells, what is the driver, is it random or not, how big is the variation and what it reflects? I think it is really a shame this was not considered beforehand as a great amount of information from the shells is lost when measuring the whole shells rather than specific parts=-. Furthermore, I am not convinced that comparison of bulk large vs. small individuals, in this case, answers the question whether ontogenetic trend drives the elemental variability. For numerous calcifiers group, the partioning of elements between seawater and the carbonate is within a certain range band 'baseline' which is principally determined by their calcification mechanisms and mineralogy, and then this variability of the 'baseline' may be driven by environmental factors. In such case, simply by a probability, larger individuals would have lived longer vs. smaller individuals and thus likely witnessed during their life time more environmental fluctuations (e.g. temperature, nutrients, pH, O2, etc.). Thus, when using an average of an entire shell, it is reasonable to assume that the mean of the shell integrates larger intra-shell and therefore elemental variations in the older individuals in contrast to the younger, simply because they experienced more changes over their life. I believe that this is also quite apparent in Fig. 3. How may one, therefore, discriminate between ontogeny vs. environmental variability?

Response: In this study, individuals were collected in a wide range of sizes from each station, representing different ages and various periods of time, living under the influence of seasonal changes. The idea was to find any patterns related with the biological effect of organisms. This part of the discussion should include more detailed environmental dataset, which we will introduce (based on literature data; more details below) to draw more certain conclusions about the biological effect. Our strategy of investi-

gating the whole shells was based on the resignation of small-scale analyzes at the expense of analyzing many individuals of different species. We presented data on the level of 12 metals in shells of mussels and barnacles from the Baltic populations, which has not been available until now. Thanks to this, we found patterns of biological and environmental control over for the concentration of metals in shells. Removal of organics without mobilisation of any trace elements associated with CaCO3 is not a task that is easy to achieve. There are good studies on this subject, e.g., Barker et al (2003), Holcomb et al (2015), see also Loxton et al (2017) for further discussion of this issue. However, we do not believe there is a single accepted protocol for bivalve shells that is tested and validated for a large range of trace elements. We, therefore, have opted for the analysis of the bulk composition instead of trying to analyse selectively the CaCO3 phases. We will make it more obvious and discuss further in the revised version of the manuscript. In the revised version of the manuscript we will emphasise that the variation observed could also be due to the presence of organic material within the carbonate structure. This contribution should be minor relative to the major influence of the carbonate shell, while bivalve and barnacle shells contain in general up to 5% organic matter (Bourget; 1987; Rueda and Smaal, 2004), yet some patterns were found eg. for Mg and Sr (Walls et al., 1977; Lorens and Bender, 1980; Takesue and van Geen, 2004).

Comment: In my opinion, the authors need take into account these problems, before any interpretations can be made. While a great deal of information is unfortunately lost by using average values, and I think the authors really have to reconsider the interpretations that can be made from this data and discuss their limits, I do acknowledge the authors' efforts for measuring numerous individuals, which I do not think is often done, and perhaps a point to that could be better taken advantage of. Just as a suggestion, maybe, this could be of use for defining the 'typical range' for each element for each species in the Gulf of Gdansk, which could be then compared to literature values from same / similar species in other parts of the world with very different settings. If possible, I think it would be interesting to see how the general elemental concentrations and

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Discussion paper

variability compares between regions or not, and could be of use when constraining environmental influences on the biomineral composition. In addition, I would also like to see a comparison between the different sampling sites within the Gulf of Gdansk. While on one hand it could be perhaps assumed that the differences between the sites are negligible, this is a very dynamic environment, and it might be that spatio-temporal variations account, at least partially, for some of the observed variabilities.

Response: These interpretations will be made clearer in the revised version of MS; many of the points we explain in the specific comments below. The suggestion about a 'typical range' for each element for each species in the Gulf of Gdansk, which could be then compared to literature values from same/similar species in other parts of the world with very different settings is very valuable and will be also discussed. We will establish a table will average values (and ranges) for each element in each species as a baseline value for the species in this region, that other researchers may use in the further studies.

Comment: One thing that has surprised me the most about this study is that, despite the careful organism sampling strategy, the authors did not consider collecting and measuring water samples. In my opinion, this should come first in this kind of studies, and something I was expecting to see, and thus a real shame it was not done, especially since the authors had the opportunity to do so (and elemental analyses on water samples are relatively more straightforward that on carbonates). Data on seawater chemistry is critical for the calculation of partitioning coefficients, which could ease the interpretation of the results from different sites (in the case that the chemistry at the different sites strongly varies). While it may be a tall task to ask for the measurements at this stage, the authors should, at least, compile the available information on local concentrations of elements in seawater (including additional physico-chemical characteristics), and estimate the partitioning coefficients for each element for the different species.

Response: Because we did not measure the concentration of elements in the environ-

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Discussion paper

ment, the discussion about its impact on the composition of the shell is challenging, yet very valuable. We should definitely place more emphasis on the environmental characteristics based on literature data. The sediment type, feeding strategy and environmental sources of metals are important factors affecting the concentration of metals in shells and should be discussed. In the revised version of the manuscript, this subject will be improved. We will add information about sediment type in study area in the context of metal bioavailability. In sandy sediments elemental concentrations are even several orders of magnitude lower than in silty sediments (Kim et al., 2004). There is literature data regarding the concentration of some studied metals (mainly in sediments) around the study area (such as Rainbow at al. 2000; Rainbow at al., 2004; Szefer at al. 2002) and we will include this into the manuscript.

Specific comments:

Comment: Line 1-2: I would suggest to reconsider the title language – 'composition' and 'com- posed', as well as 'different' twice in the same sentence, this is not orderly.

Response: Based on the reviews received and the changes that will take place in the manuscript, the title will be changed to: Patterns of metals concentration in invertebrates shells built of different CaCO3 polymorphs: a case study from the brackish Gulf of Gdansk (the Baltic Sea)

Comment: Line 32: 'Mg > Sr > Na' this needs a written definition first.

Response: This will be improved.

Comment: Line 195-197: Here, it would be particularly useful to provide concrete numbers on the local carbonate chemistry (other than Ω). Ideally, this should have been measured upon the collection of the specimens from in situ water samples, however, if this is not available the authors could at least summarize the information from the literature. An overview table with the physico-chemical characteristics of the local waters (including temperature and salinity trends etc., carbonate chemistry as well as the

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Discussion paper

elemental composition), would be particularly useful.

Response: As mentioned above, available literature data about environment will be included in the revised MS.

Comment: Line 267: Why no water samples were collected?

Response: We agree that environmental research would be very useful in the discussion, yet unfortunately we do not have them. Therefore, we will use data available in the literature for the discussion of the results.

Comment: Line 282-286: I have difficulties following this protocol and serious doubts on its effectivity and validity. Previously, the authors state that the periostracum was first physically removed. This is good and indeed important as it constitutes a large amount of organic material, which is difficult to treat chemically without having an impact on the carbonate. However, organic rests might still be present on the inside of the shell for example from the mantle, and foremostly in the pore spaces. Thus, physical cleaning is insufficient, and at least at a powder stage it is a generally established routine to apply a cleaning protocol step, consisting of oxidation of organics by buffered hydrogen peroxide (Barker et al., 2003 G3 4, 8407). As far as I am aware, this protocol or close adaptations are commonly applied to a wide range of calcifiers from forams to corals, bivalves and even brachiopods. In this sentence the authors indeed mention the use of H2O2, but only after the dissolution of the sample, which logic I cannot follow. All in all, I do not think that this is the correct way to treat carbonates samples, and would strongly recommend to first demonstrate the validity of this protocol (if the authors insist on using it, or follow a more broadly used protocol such as that of Barker et al., 2003).

Response: We are well aware of the presence of the organic matter and are going to discuss it in more details in the revised MS. However, we do believe, as Inoue et al (2004) did that “plausible pre-treatment method [for the removal of organics] is yet to be established”. With full appreciation of the importance of the protocols discussed and tested by Barker et al (2004) we believe that the benefits of any chemical treatment still

remain controversial, see, for example, discussion in Holcomb et al (2015) and Loxton et al (2017). We will aim to discuss the potential contribution of organic matter in detail in the revised MS.

Comment: Also, when it comes to ontogenetic trends, let's take for example bivalves and specifically Mytilus, as far as I am aware, broadly speaking their shell growth follows von Bertalanffy growth curve (see e.g. ig. 3; Steffani & Branch, 2003; Mar Ecol Prog Ser 246, 197-209), which is common for many calcifiers. This means that during the very early shell formation the carbonate precipitation is relatively faster, which for the incorporation of numerous elements translates into kinetic effects. It is thus the geochemical composition of the umbo and the first growth lines vs. the latter growth lines (the ones at the growth 'plateau') that form the greater part of the valve that is commonly at- tributed to being driven by ontogeny. Potentially, in the case of the very small and thus very young individuals, their geochemical composition may reflect one environmental condition e.g. certain season and one ontogenetic stage i.e. the one dominated by kinetic factors, but I am not sure this can be directly compared to older individuals which mean elemental composition then reflects different ontogenetic stages (with potentially different contribution of each to the bulk), and broad range of seasons. Or am I missing something?

Response: As mentioned earlier, this part of the discussion will be based on a more accurate environmental background, which will strengthen the inference of potential biological control on metal concentration in shells. Despite the influence of many factors, some patterns of metals concentration were found and presented.

Comment: Line 294: What type of solutions? What do you mean by matrix-matched – one solution for each carbonate polymorph? Please provide more details.

Response: Calibration of the ICP-OES analysis was performed using solutions that were matrix-matched to the high calcium concentrations in the samples at a ratio of 49:1 calcium to magnesium.

Printer-friendly version

Discussion paper

Comment: Line 300: Why were the standards not treated the same way as samples? First, I do not think it is acceptable that the authors do not process the standards and the samples in the same way, and second, I do not think that the standards are representative and should be compared to these samples. The authors need to provide the measured absolute values (as well the relative standard deviation over the analysis period at least) of comparable biogenic standards such as JCp-1 or JCt-1, or similar internationally accepted alternatives.

Response: The authors appreciate that using biogenic standards would potentially be preferable; however, those standards were not available to the authors at the time of analysis. On the other hand, complete digestion eliminates potential uncertainty that might originate from potentially incomplete conversion of organic matter typically performed when digesting by HNO3 only (Inoue et al 2004). The use of reference limestone and dolomite for the control of the analysis (without considering the digestion step) is fully justified for the digestion protocol used (HF+HNO3 with evaporation and matrix modification to HNO3 solution of the same concentration). The digestion step includes HNO3+H2O2 mixture, which is perceived to be suitable for digesting CaCO3-based materials with low amount of non-refractory organic material. For comparison, a well-cited paper on the composition of JCp-1 or JCt-1 standards (Inoue et al 2004) employed a milder treatment of HNO3 only at room temperature. We agree that a full method validation employing homogenized samples of clams containing high level of organic matter (in addition to biogenic reference materials, which potentially do not cover the natural range in terms of organic matter content/reactivity) would be desirable, but this must be a subject of a separate study.

Comment: Also, regarding the methodology, I am wondering how were the obtained counts converted into concentrations; e.g. did the authors use a calibration line for this or standard-bracketing?

Response: Calibration was performed typically using 5 points covering the range of concentrations.

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Discussion paper

Comment: Did you normalise all measurements to a stable concentration of a selected element, e.g. Ca?

Response: We did not normalize measurements to Ca.

Comment: What was the precision of the individual analyses, and the long-term reproducibility? How many times was each sample measured? Line 305 'most trace elements' – which elements were measured in He mode and which not? The authors must provide these details with rigour. Line 307 'periodic analyses' do you mean the standards were not measured along with the samples in a sequence? I have serious doubts on these analytical protocols, and especially do not consider it a good practice to not include standards along with samples in a run.

Response: ICP-OES: The accuracy and reproducibility of the analyses were checked using two calcium carbonate-rich certified reference materials (CRMs): JLs-1 Limestone and JDo-1 Dolomite (both from the Geological Survey of Japan) prepared by total digestion method (using hydrofluoric acid). The reference materials were diluted to match the concentrations of Ca in sample solutions. Ca, Mg and Sr concentrations were found to be within the uncertainty (1 standard deviation) of the reported values (Imai et al. 1996). Limits of quantification (LOQ) in solution for ICP-MS were generally determined as a concentration corresponding to ten times standard deviation of the signal obtained by analysing 5% HNO3 solution (6–7 times) in each individual run. ICP-MS was run in helium (He) mode (5 ml min−1 He, 99.9995% purity) for lighter trace elements (V, Mn, Cu, Y and Cd) to minimize the molecular interferences from plasma and solution components and Ca from samples. The accuracy and reproducibility was checked by analyses of JLs-1 and JDo-1 before and after every batch of samples. The results obtained for all elements were within the uncertainty (2.5 SD) of the recommended values. Accuracy of Pb determination cannot be checked using these CRMs because of the large spread of reference values probably due to insufficient homogeneity of Pb distribution in these samples. Based on the analyses of CRMs and matrix-matched solutions, the maximum analytical error for the typical

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Discussion paper

range of concentrations in the shells can be estimated (in relative percentage) as 1.5% for Ca, Mg and Sr; 3% for Ba; 20% for Cu and U; and 4–10%for all other elements.

Comment: Line 311: I would really welcome some visual representation for this – i.e. pictures of the different species, maybe with the different ontogenetic stages for each. It is really shame this is not provided; the authors study various interesting species, which offers an opportunity to include visually appealing picture figures, which is not used. Perhaps this is too much to ask, but given that the species build very different carbonate types and I assume microstructures, scanning electron microscope images could also be very relevant and interesting here.

Response: Unfortunately, we did not have the possibility to make scanning electron microscope images, but we will include macroscopic images presenting the studied species.

Comment: Line 321: Throughout the Results section the figures are referred to very sporadically only, and there are several instances that a value is given and a statement is made, however the figure is not referred to afterwards. Foremostly, all individual panels of the figures need sub-categories (e.g. a, b, c, etc. please check the Biogeosciences format style), and need to be mentioned where the individuals results are being discussed.

Response: This will be improved in the revised version of MS.

Comment: Line 322: I am not sure what the authors mean here, please rephrase.

Response: The species exhibited the highest concentration of Na, Sr and Mg and the lowest concentrations of U and Cd in shells. The levels of incorporated metals are similar between species, contrary to their bulk concentrations (Table 3, Fig. 2).

Comment: Line 327: I would say it is more appropriate to use μg/g rather than mg/kg.

Response: This will be improved in the revised version of MS.

Comment: Line 328: When concluding that some elements were ‘generally present at higher concentration’ or lower please also provide the concrete numbers in the text, here, but also in further parts of this section it is missing.

Response: This will be improved in the revised version of MS.

Comment: Line 334: What do you mean by ‘lack of ontogenetic tren’?

Response: The lack of patterns related with the size classes

Comment: Line 371: The entire Discussion section needs major revision, and foremostly substantial reorganisation in order to make it more suitable to the readers and a wider audience. I am aware that dealing with many different variables like several elements, size classes, species and carbonate polymorphs is not easy, but the authors really need to find a better way for presenting their findings and extracting their ‘main mes- sage points’ to the audience. At the moment I find the Discussion very broad and, to me, it does not provide clear answers to the research questions. I am afraid that often problems are addressed that cannot be resolved by the present dataset. I would say that it is better if one or two key points are discussed in-depth rather than touching on the surface many (these may still be mentioned, but the in a more concise form, with focus on the key points). The structuring is also relevant for the other parts of the manuscript and especially the Results section. I would start with ensuring that were possible, the geochemical data is presented in a more systematic manner. The Discussion could benefit from being divided into different subsections, where different aspects are being discussed. The data quality and limitations need discussing, as well each of the different factors controlling the incorporation of the elements into the carbonate (preferably in different subsections), a comparison to other studies, and the implications of the presented findings (for e.g. biomineralisation, application as recorders of environmental conditions). At this stage, it is difficult for me to make a concrete suggestion on how to subdivide this, the authors need to see what works best when structuring the Discussion and the message they would like to convey. I would

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Discussion paper

also suggest to separate the Results section, perhaps by species could work well for this part.

Response: The manuscript will present the trace element concentrations in calcitic, aragonitic and bimineralic shells to assess the patterns governing bioaccumulation of metals in shells. To make the manuscript more accessible for readers, the revised version will more clearly present the trace element concentrations in calcitic, aragonitic and bimineralic shells and patterns governing bioaccumulation of trace elements in shells. The discussion will be divided into the three parts to make reading easier. Due to the large number of factors potentially controlling the metal concentrations in skeletons, the discussion will be first focused on the polymorphic form of calcium carbonate (with the context of the shell organic matter); then on potential environmental factors (based on literature data); and finally on a potential biological response based on tracking metal variability in shell size classes. The discussion will be focused on finding patterns of inter-species and inter-individual variations in the concentration of metals in studied shells. There is literature data regarding the concentration of some studied metals (mainly in sediments) around the study area (such as Rainbow at al. 2000; Rainbow at al., 2004; Szefer at al. 2002) and we will include this into the manuscript.

Comment: Line 372: There are numerous studies on Mg and Sr in carbonate, which uses and incorporation mechanisms, potential proxy-applications etc. need a better summary. Same for all other elements, the discussion of each element should be opened by the factors that control its incorporation into the carbonate. Also, as these are often not similar for calcite and aragonite, and especially since this study is focused on the incorporation of elements into different polymorphs, these two should be treated separately.

Response: This will be improved in the revised version of MS. We will put more attention on factors that control the incorporation of metals.

Comment: Line 375: The statistics should be provided in brackets. Also, please be

specific, how much?

Response: This will be improved in the revised version of MS.

Comment: Line 378: 'Mg was the dominant impurity', please rephrase, what do you mean?

Response: This will be improved in the revised version of MS.

Comment: Line 383: Please be specific, what species?

Response: This will be improved in the revised version of MS.

Comment: Line 397: What is the origin of the high Sr in barnacles?

Response: Unfortunately, so far, we have not been able to reach data on this issue. We will put in an effort to find the answer.

Comment: Line 405: The concentrations are sometimes given in mg/kg and sometimes in wt%, which is confusing. Please be consistent throughout the manuscript in figures, and this should be preferably μg/g.

Response: This will be improved in the revised version of MS.

Comment: Line 414: Please explain, what do you mean?

Response: The idea was that we found no patterns in metals concentration in shells at inter-individual and inter-species level. This will be improved in the revised version of MS.

Comment: Line 478: I wonder how would the data look if the metal concentrations are plotted as a function of the distance to the Vistula River mouth? Can you conclude that it is the contamination that controls the trace metal composition? A comparison to the species from non-contaminated water might help.

Response: This will be improved in the revised version of MS.

Comment: Line 481: Yes, and it is really necessary to add that the whole shells were measured. Therefore the mean values integrate these variations.

Response: This will be improved in the revised version of MS.

Comment: Line 486-489: Please rephrase. Also, of course, they varied but it is difficult to determine why.

Response: In the revised version of MS, the variability of elemental concentrations will be discussed with new details, and the discussion will have a new structure. The enrichment of environmental data will facilitate the inference of biological contribution to metals concentration in shells. We will not be able to recognize exactly what biological factor is responsible for variability, but we will present implications whether the inclusion of a given metal in the shell depends on the environment.

Comment: Line 497: 'chemical profiles' please rephrase, as far as I am aware no chemical profiles were made.

Response: 'Chemical profiles' will be replaced by 'obtained results'.

Comment: Line 479-509: This sections contains many redundant parts, and the discussion could be sharpened.

Response: This will be improved in the revised version of MS.

Comment: Line 510: In addition to relative increase or decrease in concentrations, also the variability in the elemental concentration for a size class should be considered (although I am not sure if the differences between size classes will be significant).

Response: This will be improved in the revised version of MS.

Comment: Line 520: Please be specific, which trace elements (please provide in brackets; similar cases can also be found in other parts of manuscript).

Response: This will be improved in the revised version of MS.

Printer-friendly version

Discussion paper

Comment: Line 527: Yes, but as mentioned I doubt this has anything to do with the size/age.

Response: This will be discussed with more details in the revised version of MS.

Comment: Figure 1: Please provide the full site names in the figure caption to abbreviations. What are the grey lines in the big panel (bathymetry?), please specify in caption as well.

Response: This will be improved in the revised version of MS. Yes, bathymetry.

Comment: Figure 2: This figure needs error bars. The analytical uncertainty should be shown here, as well as the variation of the mean i.e. the 2SD of the mean for each group and the respective n should be provided too. Also, what size classes were used for this? Is this the mean of a certain size class or the mean of all individuals, this needs definition in the caption. It may be more appropriate, too, instead of the mean of all individuals to depict the mean and the variation of each size class. I would also include information on the different polymorphs of each species. In general, I have no problems with the figures being black-and white only, but personally, I would try to improve the visual representation. In this case, maybe increasing the figure size to double and placing the legend within the top right corner could help separate a bit more out the different elements. Also, this is a detail, but to make it more intuitive, the grey filled symbols could be the aragonitic species, empty symbols the calcitic and half-filled for example bimineralic.

Response: These comments will be taken into account and the figure will be improved.

Comment: Figure 3: What is the x-axis? Please make the y-axis similar where possible, this is really difficult to read for me. Also, the information on the differences between size classes should be removed as at the moment there is too much information in this figure. The individual panels are missing sub-headings that should be also referred to in the manuscript text.

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Response: This figure will be simplified and more easy to read.

Comment: Figure 4: Please appropriately label all panels as ‘a,b,c, etc.’ What do you mean by ‘raw data as black dots’? (I see blue dots.) Please include polymorphs, analytical uncertainty, indicate the sizes for each category. Maybe better to put each species in a separate row. Why some size classes have values in between the size class number categories?

Response: These comments will be taken into account and the figure will be improved.

Comment: Figure 5: I find this figure difficult to follow, maybe there is a better way to illustrate the message? Should be ‘dashed line’ instead of ‘broken line’. Why are some panels darker? Please specify in the caption.

Response: These comments will be taken into account and the figure will be improved.

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