

We would like to thank both Reviewers for the detailed and valuable comments which allowed us to improve this manuscript. Implementation of reviewers' suggestions added a lot of quality to the manuscript.

Review 1 of revised manuscript version bg-2019-367

Some specific comments on the response to the author document:

5 • In the 'Author response' they do state that there is no protocol they could have used ('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'), however, if the whole aim of your study is to compare such a wide range of elements in different shells, maybe some method development should have taken place before. Even (relatively) simple comparison of shell fragments of a single shell with different cleaning treatment (versus no cleaning) applied, could have made
10 their dataset more robust. I highly suggest that for future work cleaning methods as well as the impact of organics should be investigated!

We did not have an opportunity to implement this approach at this stage, but we agree that organic matter is an important factor in biogeochemical research and we will make every effort to improve the methodology in our future research.

15 Authors: In the revised version of the manuscript, we emphasise that the contribution of the organic matter to the elemental variation is likely to be relatively minor considering that bivalve and barnacle shells contain, in general, less than 5% organic matter (Bourget, 1987; Marin and Luquet, 2004; Rueda and Smaal, 2004)
20 • Reviewer: 5% in weight? Is there any idea about the concentration of certain elements in this organic matter? Even if it is 5% of the total weight, if the concentration of e.g. Na is very high, this still leads to a biased E/Ca for the CaCO₃. Also, you refer to Takesue et al., 2008, who found e.g. 19% organic matter.

We agree that even a small amount of the organic content of a shell can affect its chemical composition. According to literature data, the organic content of the studied organisms ranges up to about 5% in weight (e.g. Wolowicz and Gouilletquer, 1999). Unfortunately, we are not able to determine what proportion of the examined elements comes from the organic matter and this is our task for the future research. In the presented manuscript, we noted that the entire skeletons were analyzed and we tried to highlight it in the discussion of the results. One of the references we refer to is Takesue et al. (2008) and in fact the authors studied shells there by up to 19% of organic matter. But the trends of metal accumulation were similar to many other researchers, which was widely discussed in this publication, therefore we decided include this work in our manuscript.

25 • After comments by both me and the other reviewer, I still do not see any discussion on the fact that larger (and thus older) shells have also experienced more time, and more environmental fluctuations. Can the authors comment on this directly?
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Please look at the fragment in Lines 398 – 412, where we discussed this issue.

Minor comments:

(General comment) The manuscript is incredibly dense in information. Of course, it is great to have numerous references and explanations for observed patterns, but also makes it sometimes difficult to absorb the main take home messages. Be careful for repetition, for instance, please check overlap between paragraph 2.2 and 4.3. *In the reviewed version of the manuscript, we tried to limit the overlapping information, for example on paragraph 2.2.*

- Line 17: please add clearly you work on bulk material. *This was added*
- Line 27: "Moreover, the elemental concentrations tend to be lower in larger than in smaller shells." This is confusing, suggesting to change to something like "lower in the large size class compared to the smaller size class. *Improved*.
- Line 41-43: changes in font size. *Corrected*.
- Line 44: consider changing metals to trace metals or trace elements. *Corrected*.
- Line 45: consider rephrasing, you mean the pathways of trace metals into the CaCO₃? What do you mean with multistage process? Do the organisms form their shell through meta-stable phases of CaCO₃? *We meant that elements taken from the environment are transported to the skeleton through the body, so biological processes can affect their final concentration in the skeletons. The sentence was worded ambiguously, so we corrected it but chose to put it elsewhere, in Lines 94 – 96.*
- Line 124: remove 'it'. *Corrected*.
- Line 124-125: I disagree. You demonstrate the study area is highly fluctuating, so the older specimens will have experienced different environmental conditions. Change e.g. to '.. we can try to disentangle...'. *Corrected*.
- Line 135: renumber your figures, this should be fig. 1, since it is the first figure you reference). Check full manuscript. Line 169: So this is then Fig. 2. *Corrected*.
- Paragraph 2.3 As requested before, please add the sample time(month) in the manuscript, not only in the table. *Corrected*.
- Line 259: Is this 20% error propagated into the SD/values reported in Table 3? *No, the SDs in Table 3 reflect the spread of concentrations between individual specimens, not the analytical error. In most, if not all cases, the spread is much higher than the estimate of the analytical error anyway.*
- Line 221: change to 'based on the size'. *Corrected*.
- Line 235-238: Samples were split and measured by both ICP-OES and ICP-MS? *Both methods of analysis are solution-based. From an aliquot of homogenized powder, a single solution was prepared, which was then split and diluted as necessary for both the ICP-OES and ICP-MS analyses.*
- Line 254: What was the precision (%) compared to the reference values? *The estimated analytical uncertainty based on the reference values is given in Lines 255 – 258: "Based on the analyses of CRMs and matrix-matched solutions, the maximum analytical error for the typical 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 10% for all other elements." If by "precision" one understands repeatability, it is similar or smaller than the uncertainty of the reference values, see Table 1 in Piwoni-Piorewicz et al. (2017). The measurements in this work were done using the same technique, equipment and analysts and gave very similar results for the standards we decided not to include the tabulated data for the standards in this work, but refer the reader to our previous work: Lines 258 – 259: "More details on method validation were reported previously (Piwoni-Piorewicz et al 2017)."*

75 • Line 272-274: "However, the concentrations of given metals were different between shells of Cerastoderma glaucum, Mya arenaria, Limecola balthica, Mytilus trossulus and Amphibalanus improvisus, showing high variability (Table 3, Fig. 3)." This sentence is confusion, please clarify the meaning. The variability was within a species, or between species? *Corrected*.

80 • Lin 367: change 'contained'. *Changed into "produced"*.

85 • Line 364: in inorganic precipitated carbonate, precipitation rate is inversely correlated to Mn incorporation (i.e. higher precipitation equals less Mn, Lorens, 1981). Why is the opposite suggested for organic carbonates? *The inorganic calcite precipitation experiments have shown a negative relationship between precipitation rate and the Mn partition coefficient (e.g. Lorens, 1981). However, the relationship between the growth rate of organism and shell Mn/Ca was revealed to be positive. This indicates that Mn concentration in shells is not directly controlled by a kinetic calcium carbonate precipitation rate, but must reflect other processes, likely physiological in origin (e.g. Carré et al., 2006; Freiras et al., 2016). We discussed this issue in lines 445 – 448.*

90 • Line 368: change to 'is in some degree regulating' Line 382: trace metal, not trace metals. *Corrected*.

95 • Line 394-395: Please look into these sentences and your references. Takesue et al., 2008 showed actually the organic content was 19% for their studied species, and say aragonitic shells have 'large component of non-lattice-bound Mg and Mn'. This is actually suggesting the opposite: at least Mg and Mn might be impacted by % organic matter. Line 394: separate ref for Sr? if not, remove. *These sentences were improved and the role of organic matrix in the total concentration of metals in CaCO₃ skeletons was highlighted.*

100 • Line 399-401. I totally agree, and believe this should also be mentioned in the abstract. (e.g. line 28: add composition and contribution of organic material). *Improved*.

105 • Discussion: Please also include organic material as a factor contributing to difference in (at least) Mg and Mn. *This was included in Lines 394 – 398.*

• Line 410-4111: I do not follow this logic. The larger shells (adults) still experienced a full year of environmental fluctuations. *Yes, but we believe that the long-lived shells additionally experienced environmental variability between years, and consequently elemental variability in shells of barnacles with lifespan of ~1 year might be lower.*

• Line 571 factors instead of features? Also, precipitation rate is a biological control? I would leave it at growth rate. *Corrected*.

• 581-583: It does not connect to the previous sentence, maybe rephrase or remove? This will never be possible from field samples, since it is impossible to know the biological impacts (growth, feed rate etc.). *The sentence was removed.*

• Table 2. Typo for size class I of Mytilus (should be 6-15)? *Corrected*.

• Figure 3. Consider also adding a symbols/column with values from other studies on the same species, maybe as a supplementary figure, if Figure 2 becomes to information dense. I see the authors added Table 4, but I would strongly advise to change this to a graphical presentation. *Such a figure would indeed be too information-dense. We still believe that the data in Table 4 are better in a tabular form so that other researchers can use it for reference, but we agree that this table can go to the Supplement if needed.*

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- Line 18: 'shells are discussed' Line 26: '...Cd) are more variable'. *Corrected*.
- Line 30: do you refer to your different sites? This should be 'sampling sites within the Gulf', if this refers to the comparison to literature data then this should be specified. *Corrected*.
- 115 • Line 36: 'mainly polymers,' comma missing Line 41: different font sizes, please correct. *Corrected*.
- Line 49: I would suggest to move the brackets after chemical factors, i.e. as follows '...chemical factors (e.g. metal...; Blackmore and Wang, 2002)'. *Corrected*.
- Line 52: I do not think this is correct, they are important, but I think dissolved C in the ocean is the largest C reservoir? *We agree that this is an imprecise statement and this was corrected*.
- 120 • Line 117: 'carbonate skeleton'. *Amended*.
Line 135: this is the figure to appear so should be Figure 1. *Corrected*.
- Line 156: delete 'and' i.e. 'that is, lower Ca²⁺'. *Corrected*.
- Line 158-159: The equation for omega is incorrect, K*_{sp} is the solubility product calcite or aragonite (depending on the in situ conditions). The citation is not necessary as this is basic thermodynamics, but I see 125 Kawahata et al., 2019 present a nice overview so could be put as 'e.g. Kawahata et al., 2019'. *Corrected*.
- Line 214-215: There is something wrong with this sentence, it is said that 'Three species were found at MA...' but in the brackets there is only one given, and then for following stations M2 and MW it is again one each. *Corrected*.
- Line 234: Subheading space formatting – above and below not same as for the other headings. *Corrected*.
- 130 • Line 234: 'uncertainty (2.5 SD)' please be more specific, 2.5 of what? *The uncertainty of the recommended values (Imai, 1996)*.
- Line 259: '4-10 % for all other elements' I would suggest to provide the details for each, unless it is always assumed that the uncertainty is not better than 10%, but then please mention it. *Changed to 10%*.
- Line 260: 'et al. 2017'. *Corrected*.
- 135 • Line 275: Should not be '316,000'? Please check the comma positions. *Corrected*.
- Line 276: Should not be '363,000'? *Yes, this was corrected*.
- Line 283: 'Both Sr and Mg were...' *Corrected*.
- Line 296: 'Shells' which ones you refer to? *Corrected*. Line 300: Two spaces missing, should be 'H ='. *Corrected*. Line 310: 'Shells' which ones? *Improved*.
- 140 • Line 370: better 'increased incorporation'? *Corrected*.
- Line 372: comma missing after 'in our study'. *Corrected*. Line 376: 'while larger Pb radii are favoured in aragonite structure'? *Corrected*.
- Line 379: 'determine their concentrations'. *Corrected*.
- Line 385: improvement of the data'. *Corrected*.
- 145 • Line 405: 'life spans'. *Corrected*.
- Line 409: 'drive its biogeochemical cycles'. *Corrected*.
- Line 411: commas missing ' to some extent'. *Corrected*. Line 413-416: Please rephrase this sentence (seems convoluted). *Improved*.
- Line 429: 'if a significant'. *Corrected*.

150 • Line 431: ' while size class effects were less pronounced in clams?' Also 'the varied elements' please rephrase.
Improved.

• Line 451: 'activity of an organism'. *Corrected.*

155 • Line 488: Mg/Ca in many marine calcifiers has been used a temperature proxy, and known to be positively correlated with temperature. At the same time, Mg incorporation into the lattice is strongly dependent on growth rate, with more Mg incorporated under decreased precipitation rates. In addition, and in contrast to some other elements like Sr for example, Mg is thought to be transported by different pathways, and is strongly physiologically relevant. Growth increments are also lined with very high Mg contents, potentially linked to increased organics. Some organisms, like low-Mg brachiopods for example, actively discriminate against Mg. In summary, there are many known controls over Mg, but from the data in Figure 3 it is clear that in the studied samples it is the mineralogy (and especially on such larger orders). *We totally agree with this and all was included in the different sections of our discussion.*

160 • Line 530: 'in a shallow zone'. *Corrected.*

• Line 544: 'most likely caused'. *Corrected.* Line 545: 'as the trace elements'? *Corrected.* Line 6002: 'Mytilus' should be in italics. *Corrected.* Table 1: First row in the table 'in situ' should be in italics. *Corrected.*

165 • Table 3: Is the SD the standard deviation between all specimens of a species, please specify. Also please include sample size n along with the SDs and SEs. *Yes, this is the SD between all specimens. This is now explained in the table. The sample size is also given in the table.*

• Table 4: I think there is something wrong with the formatting, some cells have hyphens that appear out of place, please check. *Improved.*

170 • Supplement: 'Table S1' (not Tabke S1). *Corrected.*

A couple of suggestions for the authors to consider that could be of aid to their future work:

I assume that the difference in the dissolution procedures between standards and samples should not significantly affect the final results of the study, however, for the future I urge the authors to treat samples and standards exactly the same. They should also consider finding more appropriate standards for biologic samples. A potential easy 175 solution would be the making of an in-house standard by homogenising several individuals of a species, and cross-checking the different dissolution procedures on it. If an accepted international standard is not available for routine measurements, the authors could at least request small aliquots from the community or colleagues, cross check their in-house standard against it, and include it to the routine of running the limestone and dolomite standards. This would make their data and analytical procure more convincing from the start and overcome some of the 180 misunderstandings.

For the future, I would like to advise the authors to also collect and consider measuring water samples alongside the calcifiers. Such information would be very valuable and of great interest to the field. Widely accepted protocols for water sampling for trace element analyses are available from GEOTRACES.

We are very grateful for your comments, we will definitely use these suggestions in our future work.

185 • Line 1084: *We changed the photos 2, 4 and 5 in Figure 2 as the new ones, in our opinion, represent species better.*

References:

Carré, M., Bentaleb, I., Bruguier, O., Ordinola, E., Barrett, N. T., and Fontugne, M.: Calcification rate influence on trace element concentrations in aragonitic bivalve shells: Evidences and mechanisms, *Geochim. Cosmochim. Acta*, 70, 4906–4920, <https://doi.org/10.1016/j.gca.2006.07.019>, 2006.

190 Freitas, P. S., Clarke, L. J., Kennedy, H., Richardson, C. A., and Abrantes, F.: Environmental and biological controls on elemental (Mg/Ca, Sr/Ca and Mn/Ca) ratios in shells of the king scallop *Pecten maximus*, *Geochim. Cosmochim. Acta*, 70, 5119–5133, <https://doi.org/10.1016/j.gca.2006.07.029>, 2006

195 Imai, N., Terashima, S., Itoh, S. and Ando, A.: Compilation of analytical data on nine GSJ geochemical reference samples, *Sedimentary rock series, Geostand. Newslet.*, 20(2), 165–216, <https://doi.org/10.1111/j.1751-908X.1996.tb00184.x>, 1996.

Lorens, R. B., Bender, M. L., and Island, R.: The impact of solution chemistry on *Mytilus edulis* calcite and aragonite, *Geochim. Cosmochim. Acta*, 44, 1265–1278, [https://doi.org/10.1016/0016-7037\(80\)90087-3](https://doi.org/10.1016/0016-7037(80)90087-3), 1980.

200 Piwoni-Piórewicz, A., Kukliński, P., Strekopytov, S., Humphreys-Williams, E., Najorka, J., and Iglikowska, A.: Size effect on the mineralogy and chemistry of *Mytilus trossulus* shells from the southern Baltic Sea: implications for environmental monitoring, *Environ. Monit. Assess.*, 189, 197, <https://doi.org/10.1007/s10661-017-5901-y>, 2017.

Wolowicz, M. and Gouletquer, P.: The shell organic content in the energy budget of *Mytilus trossulus* from the South Baltic, *Haliotis*, 28, 1–10, 1999.

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220 **The patterns of elemental concentration (Ca, Na, Sr, Mg, Mn,
Ba, Cu, Pb, V, Y, U and Cd) in shells of invertebrates
representing different CaCO₃ polymorphs: a case study from
the brackish Gulf of Gdańsk (the Baltic Sea)**

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235 **Abstract.** The shells of calcitic arthropod *Amphibalanus improvisus*, aragonitic bivalve *Cerastoderma glaucum*, *Limecola balthica*, *Mya arenaria* and bimimetic bivalve *Mytilus trossulus* were collected in the brackish waters of the southern Baltic Sea in order to study patterns of bulk elemental concentration (Ca, Na, Sr, Mg, Ba, Mn, Cu, Pb, V, Y, U and Cd) in shells composed of different crystal lattices (calcite and aragonite). The factors controlling the elemental composition of shells are discussed in the context of crystal lattice properties, size classes of organisms and potential environmental differences between locations.

240 The study indicates that the elemental composition of studied species is a result of many biotic and abiotic factors acting on elemental incorporation mechanisms in a species-specific way. The incorporation of the main elements Ca, Na, Sr, Mg is mostly related to the crystal lattice properties of calcite and aragonite. Clams that precipitate fully aragonitic shells have a clear predominance of Sr over Mg in shells, contrary to dominant Mg accumulation over Sr in calcitic shells of barnacles. However, the barnacle calcite shell contains higher Sr concentration than bivalve aragonite. The elemental variability between size-grouped shells is different for each
245 studied species and the elemental concentrations tend to be lower in the large size classes compared to the smaller
size classes. Biological differences between and within species, such as growth rate, feeding strategy, including feeding rate and assimilation efficiency or composition and contribution of organic material seem to be important factors determining the elemental accumulation in shells. Because specimens used in this study were obtained from different sampling sites within the gulf, the impact of local environmental factors associated with sampling location, such as sediment type, cannot be excluded.

250 **1 Introduction**

255 Marine invertebrates such as molluscs, brachiopods, corals, echinoderms, bryozoans and some groups of protozoa (foraminifera) are able to use naturally occurring trace elements to form their skeletons. The combination of inorganic CaCO₃ crystals with incorporated elemental impurities and organic compounds with a characteristic and ordered structure, mainly polymers, create a composite strengthening material. As a result of long-term adaptation, calcifiers are armed with hard protective internal and external body parts such as shells, tubes, walls or plates with

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various components, colours, shapes and functions. The biogenic CaCO_3 is deposited mainly in the form of two polymorphs, calcite and aragonite, which are commonly found co-existing in the same specimens and appear to be precipitated in the same environment (Cusack and Freer, 2008; Morse et al., 2007; Taylor et al., 2008; Stanley et al., 2008). The bulk elemental composition of carbonate skeletons is determined by both CaCO_3 crystal lattice and proteins (C, O, H, N, S, P). Furthermore, various other trace elements, especially those forming divalent ions – mainly Mg and Sr, as well as e.g. Mn, Br, Cd, Cu, Pb, V – are present as impurities in skeletons. The major sources of trace elements for organisms during the calcification process are aquatic soluble phases and the food base that may consist of suspended and/or sedimented particles (Newman and Unger, 2003; Rainbow, 1995; Rainbow and Phillips, 1993). However, the bioavailability of trace elements depends on a complex of environmental (e.g. salinity, pH, sediment type, oxygen conditions) and chemical factors (e.g. element-particle binding strength, the composition of particle, presence of other trace elements and compounds, Blackmore and Wang, 2002).

Biological carbonates determine a very important component of the hydrosphere's carbon reservoir, and the biogenic production of CaCO_3 has a strong interdependence on the ocean composition, biogeochemistry and the carbon cycle (Cohen and McConaughey, 2003). In the last few decades, increasing attention has been paid to the relationship between the composition of shells and external environmental factors. It has been repeatedly observed that the mineral type and accumulated trace element concentrations in CaCO_3 shells of marine invertebrates are integrated records of environmental conditions (Marchitto et al., 2000; Rodland et al., 2006). The elemental composition of the carbonate skeleton can provide records of seawater chemistry and has a significant potential for the fields of palaeoceanography and palaeoclimatology (Freitas et al., 2006; Gillikin et al., 2006; Khim et al., 2003; Ponnurangam et al., 2016; Vander Putten et al., 2000). However, as recent studies have indicated (Dove, 2010), the influence of environmental parameters on shell precipitation could be very complex. The mineralogy and chemistry of shells are likely to be both linked to environmental conditions and controlled by the organism itself. Even a single population or closely related species within the same habitat may exhibit different accumulation strategies (Rainbow et al., 2000).

Calcite and aragonite differ in structure, symmetry and properties. The calcium ion has 9-fold coordination in aragonite and 6-fold coordination in calcite, and its coordination creates hexagonal and cubic packing (Putnis, 1992). Due to the spatial structure, aragonite shows preferential substitution with larger cations, such as Sr, while smaller cations, such as Mg, are energetically favoured in calcite. In natural systems, calcite commonly incorporates Mg (Morse et al., 2007; Reeder, 1983; Wang and Xu, 2001), and the solubility of Mg-containing calcite is known to increase with increasing Mg substitution (Kuklinski and Taylor, 2009; Smith et al., 2006). At the temperatures and pressures of the Earth's surface, low-Mg calcite is the most stable form of CaCO_3 (de Boer, 1977). Nevertheless, in many marine organisms, aragonite and high-Mg calcite are the dominant phases precipitated from seawater (Dickson, 2004). The solution chemistry (Cusack and Freer, 2008), temperature (Balthasar and Cusack, 2015), pressure (Allison et al., 2001), CaCO_3 saturation state (Watson et al., 2012), pCO_2 (Lee and Morse, 2010) and phylogenesis (Kuklinski and Taylor, 2009; Smith et al., 1998; Smith and Girvan, 2010) are known to influence shell mineralogy. The main driving force controlling the mineralogy of precipitated CaCO_3 is the ratio of Mg to Ca ions in seawater (Cusack and Freer, 2008; Morse et al., 2007). A Mg/Ca ratio > 2 favours the precipitation of aragonite and high-Mg calcite. At high Mg/Ca ratios, such as those in modern seawater (Mg/Ca = 5.2), calcitic structures incorporate Mg, which is observed to inhibit calcite nucleation and growth, whereas

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- **usunięto:** trace elements
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- **usunięto:** Metals incorporated into skeletons originate in the environment, yet as some of them are the components of enzymes or body fluids, the metal pathway to skeleton can be a multistage process (Cubadda et al., 2001; Luoma and Rainbow, 2008).
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330 aragonite nucleation is not affected by Mg in solution (De Choudens-Sanchez and Gonzalez, 2009; Morse et al., 2007). Most taxa producing low-Mg calcite are known to actively control the amount of incorporated Mg (Bentov and Erez, 2005; De Nooijer et al., 2014). Several studies of organisms that secrete calcareous skeletons have shown that lower seawater temperatures are correlated with the secretion of calcite skeletons with low Mg contents, rather than more soluble high-Mg calcite or aragonite skeletons (Taylor and Reid, 1990). The mineralogy of many calcareous structures changes with latitude, likely as a result of the temperature gradient from the poles to the equator (Kuklinski and Taylor, 2009; Loxton et al., 2014; Taylor et al., 2014). However, this is not an absolute rule (Cairns and Macintyre, 1992). Thermodynamics predicts that aragonite is the stable phase at pressures higher 335 than 5000 hPa (roughly 40 m depth), and calcite is the stable phase at lower pressures. However, aragonite is still the major constituent of shells or pearls, indicating its metastable formation in shallow waters (Sunagawa et al., 2007). The incorporation of Sr was suggested to play a significant role in the biomimetic precipitation of aragonite (Allison et al., 2001). Many studies have demonstrated a clear correlation between the concentration of 340 Sr in the hard parts and precipitation of the aragonite layer (Iglińska et al., 2016; Reeder, 1983). The ionic radius of Sr is larger than that of Ca; thus, Sr is more likely to form 9-fold coordination, which triggers metastable aragonite nucleation (Sunagawa et al., 2007).

345 Many studies have demonstrated that the biological control of shell composition is often more important than the environmental control (Carré et al., 2006; Freitas et al., 2005, 2006; Gillikin et al., 2005b). Elements incorporated into skeletons originate from the environment, yet as some of them are the components of enzymes or body fluids, the trace element pathway to skeleton can be altered by biological processes of the body (Cubadda et al., 2001; Luoma and Rainbow, 2008), which can affect the relationship between the concentrations of a given trace element between skeleton and environment. In biologically controlled mineralization, the organism drives the process of nucleation and growth of the minerals independently from the environmental conditions. Endogenous factors manifest themselves through co-regulation of all the structures and functions of the organism, including its sex, growth rate, metabolism, and feeding strategy (Lowenstam and Weiner, 1989). The main 350 physiological processes involved in element accumulation are ingestion, assimilation, elimination and growth (Wang and Fisher, 1997). Throughout the lifespan, the biological system experiences ontogenetic trends and seasonal variations in physiology, determining metabolic expenses based on life's needs. Biological effects have been repeatedly used to explain shifts of elemental concentrations in shells from a theoretical equilibrium (Davis et al., 2000; Roger et al., 2017; Watson et al., 1995). Ontogenetic fluctuations of the growth rate and metabolic 355 activity affect the intensity of the element uptake (Lee et al., 1998). Vander Putten et al. (2000) concluded that the seasonality of the accumulation of Mg, Sr and Pb in *Mytilus edulis* shells shows significant similarity across individuals, with a maximum during spring and early summer, and the elemental profiles cannot be explained by seasonal variations in the seawater composition. Carré et al. (2006) developed a model of ion transport in bivalve shells that shows that Ca^{2+} channels are less ion-selective when Ca^{2+} fluxes are higher. Other studies have found 360 that the rate of trace element uptake increases as mussel filtration rate increases (Janssen and Scholtz, 1979).

365 It is still difficult to separate the degree to which the organism itself controls the composition of the carbonate skeletons and how much this process is affected by the environment (Casella et al., 2017; Schöne and Krause, 2016; Weiner et al., 2001). Although calcareous parts serve as a powerful tool for the interpretation of environmental conditions, a detailed insight into the different factors controlling the composition of carbonate skeletons is critical. Tracking potential sources of variation within calcifying organisms of many species with

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380 diverse mineralogy should provide valuable insight into the patterns driving the biominerization process (Smith et al., 1998).

The aim of this study is to assess the patterns of elemental variability (Ca, Na, Sr, Mg, Mn, Ba, Cu, Pb, V, Y, U and Cd) in shells of mussels and barnacles representing three possible mineralogical forms. The selected species were clams: aragonitic *Cerastoderma glaucum*, *Mya arenaria*, and *Limecola balthica*, bimimetic mussels *Mytilus trossulus*, and barnacle *Amphibalanus improvisus* with a fully calcitic shell, from the low-salinity environment of the southern Baltic Sea. A comparison of elemental concentration levels between size classes is also performed. Assuming the larger specimens are older than the smaller specimens of the same species, we assess how different ontogenetical stages influence elemental accumulation. The potential influence of biological control and local environmental conditions on the observed elements concentrations in shells is briefly discussed. The study area offers the variety of fluctuating factors, giving the opportunity to increase our understanding of 385 elemental variation patterns of skeletons formed in the area. Brackish waters affect the activity and speciation of elements, enhancing their bioavailability (Fritioff et al., 2005). The seasonal changes (e.g. surface temperature, primary production and freshwater inflow) determine the element sources and drive the physiological processes 390 of living organisms (Urey et al., 1951).

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2 Material and methods

395 2.1 Study area

The study area is located in the Gulf of Gdańsk in the southern Baltic Sea, more precisely, in the outer Puck Bay and central Gulf of Gdańsk (Fig. 1). The gulf is partially sheltered from the northwest by the Hel Peninsula and from the west and south by the coastline (Kruk-Dowgiałło and Szaniawska, 2008; Rainbow et al., 2004). This location makes the seawater the most turbulent in January and the calmest in June, with weak bottom currents and 400 minimal tidal amplitudes. The hydrophysical parameters of the gulf are mostly driven by the temperate climate and the following seasonal changes. Differences in air temperature and water mixing cause seasonal fluctuations of the surface water temperature, ranging from approximately 4 to 22°C (Uścinowicz, 2011). The Gulf of Gdańsk is a low-salinity system under the influence of brackish water from the open southern Baltic Sea and fresh waters from rivers, mainly the Vistula River; the Vistula is the largest river in Poland and has an average annual inflow 405 in the estuary of 1080 m³ s⁻¹, which varies seasonally from 250 to 8000 m³ s⁻¹ and has a maximum in spring (Cyberski et al., 2006). Thus, the average water salinity in the gulf is 7, varying from approximately 5.5 in summer to 8.4 in winter (Bulnheim and Gosling, 1988; Szefer, 2002).

The Gulf of Gdańsk is an area highly influenced by human activities. This is due to intensive usage of its 410 resources and to anthropogenic emissions originating from various coastal sources, river inflows and atmospheric deposition. The most significant input of industrial and municipal pollution into the gulf is derived from the Vistula River, which transports pollutants from a catchment area of 194,000 km² (Pruszak et al., 2005). Both the water discharge and sediment load into the gulf are strongly seasonally dependent. The maximum river flow typically occurs in spring, with the minimum in autumn and winter, mainly due to periods of snow and ice melting (Cyberski et al., 2006; Pruszak et al., 2005; Szefer et al., 1996). Winter storms cause re-deposition of sediments further into 415 the Gulf of Gdańsk (Damrat et al., 2013). Because of the local conditions, mainly the limited water exchange,

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river-borne contaminants remain in the ecosystem for decades, accumulating in the sediments and in living organisms (Glasby et al., 2004; Szumiło-Pilarska et al., 2016).

425 Most regions of the Baltic Sea have lower salinity and alkalinity (that is, lower Ca^{2+} and CO_3^{2-} concentrations) than oceanic surface waters (Beldowski et al., 2010; Cai et al., 2010; Findlay et al., 2008). Due to the seasonality of temperature and biogeochemical cycle, the amplitude of CaCO_3 saturation state ($\Omega = \frac{[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]}{K_{\text{sp}}^*}$, K_{sp}^* is the a solubility product of calcite or aragonite at situ conditions; e.g. Kawahata et al., 2019) in the Baltic Sea is high in comparison to saline waters. It alternates between approximately 1 to 5 for calcite and 0.5 to 2.5 for aragonite (Findlay et al., 2008).

430 The community of calcifiers from the Gulf of Gdańsk is characterized by the dominance of benthic filter feeders and deposit feeders (Kruk-Dowgialło and Dubrawski, 1998). These organisms exploit their growth potential during the productive seasons of the year when the availability of suspended matter, mainly phytoplankton is the highest (Piersceniak et al., 2010; Staniszewska et al., 2016).

2.2 Species

The clam *Cerastoderma glaucum* (Mollusca, Bivalvia; Fig. 2.1), commonly known as the lagoon cockle, is a saltwater organism found along the coasts of Europe and North Africa, including in the Mediterranean and Black Seas, the Caspian Lake, and the low-salinity Baltic Sea. It is a euryhaline species living in salinities between 4 and 440 84. *C. glaucum* can tolerate habitats with wide range of temperatures, from periodically freezing to above 30°C. It is a filter feeder that actively lives near the sediment surface, acting as a biodiffuser (Urban-Malinga et al., 2013). The clam is surrounded by a ribbed aragonite shell, which is externally yellowish to greenish brown (Jelnes et al., 1971). In the brackish environment of the Gulf of Gdańsk, *C. glaucum* spawns in May-July and typically lives up to 4 years, achieving a height of 27 mm (Żmudziński, 1990).

445 The soft-shell clam *Mya arenaria* (Mollusca, Bivalvia; Fig. 2.2) is a marine invasive species introduced into European waters from the Atlantic coasts of North America (Behrends et al., 2005). It has a wide global distribution, mainly due to its adaptability to varying environments with salinities between 4 and 35 and temperatures between -2 and 28°C (Gofas, 2004; Strasser et al., 1999). *M. arenaria* is a filter feeder, filtering organic particles and microinvertebrates using long fused siphons, and a deposit feeder. In the Gulf of Gdańsk, *M. arenaria* is a common inhabitant of shallow waters down to a depth of 30 m. It spawns once or twice a year in spring or summer, at temperatures of 10 – 15°C. Individuals live 10 – 12 years. They have aragonitic shells and grow up to 70 mm (Żmudziński, 1990).

450 The clam *Limicola balthica* (Mollusca, Bivalvia, Fig. 2.3) lives in the northern parts of the Atlantic and Pacific oceans, in Subarctic and European waters from southern France to the White Sea and Pechora Sea, 455 including the Baltic Sea (Strelkov et al., 2007). It is a euryhaline clam capable of living in a wide range of water salinities from 3 to 40 and at temperatures from -2°C to above 30°C (Sartori and Gofas, 2016). *L. balthica* is a filter feeder and deposit feeder, has a semi-sessile lifestyle, with the ability to undertake periodic migrations (Hiddink et al., 2002). In the Baltic Sea, *L. balthica* lives at depths down to 40 m and grows to 24 mm. Adults 460 reproduce in spring when the water temperature reaches 10°C and live 12 years (Żmudziński, 1990). They have aragonitic shells varying in colour between individuals and locations, mainly exhibiting white, pink, yellow and orange (Sartori and Gofas, 2016).

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The mussel *Mytilus trossulus* (Mollusca, Bivalvia; Fig. 2.4) is one of three closely related taxa in the *Mytilus edulis* complex of blue mussels, which, collectively, are widely distributed in the temperate and cold-water coasts of the Northern Hemisphere and are often dominant organisms on hard substrates of shallow nearshore habitats (Rainbow et al., 1999; Wenne et al., 2016). Generally, *M. trossulus* has a life span of approximately 12 years and grows to 100 mm, yet in the estuarine environment of the Gulf of Gdańsk, it reaches a maximum length of approximately 50 mm (Gofas, 2004; Źmudziński, 1990). Mussels are sessile filter feeders, mainly depending on phytoplankton. They reproduce from late spring to early autumn, depending on the temperature and food abundance (Larsson et al., 2017; Lauritsen et al., 2014; Rainbow et al., 2004). The shell of *M. trossulus* is bimimetic and consists of two calcium carbonate layers: an outer calcite and inner aragonite layer in variable proportions between individuals (Dalbeck, 2008; Piwoni-Piórewicz et al., 2017).

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The barnacle *Amphibalanus improvisus* (Arthropoda, Maxillopoda; Fig. 2.5), commonly named the bay barnacle, is a small sessile crustacean that typically exists in shallow coastal zones that are less than 10 m deep. It is widespread around the Atlantic and has been dispersed by shipping to many parts of the world, now having a worldwide distribution. It is a euryhaline and eurythermal species that is absent only from the Arctic and Antarctic seas (Kerckhof, 2002). *A. improvisus* is a filter feeder that inhabits hard substrates. In the Baltic Sea, the reproduction of barnacles starts in spring with temperatures over 10°C and ends in autumn. The species grows to approximately 10 mm in diameter with a maximum height of approximately 6 mm, and generally, it has longevity of one year (Źmudziński, 1990). It has a conical shell composed of six fused calcite plates (Weidema, 2000).

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2.3 Sample collection and preparation

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Samples of shells were gathered by a Van Veen grab sampler from four stations: GN (May 2013), MA, M2 and MW (June 2014), located in the Gulf of Gdańsk (Table 1, Fig. 1). One species was found at stations MA (*Mya arenaria*), M2 (*Cerastoderma glaucum*) and MW (*Limecola balthica*), while two species were collected at station GN (*Mytilus trossulus*, *Amphibalanus improvisus*; Table 1). To ensure that the samples were not contaminated or modified by solutions of preservatives, the collected material was transported alive in tanks filled with seawater to the laboratory, where sample preparation took place.

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By measuring the shell heights of clams and shell diameters of barnacles using a calliper with an accuracy of ± 1 mm, the shells were classified into four size classes. The division into size classes was performed based on the size reached by each species in the southern Baltic Sea environment (Table 2). Forty shells (ten in each class) were selected for *A. improvisus*, *C. glaucum*, *M. arenaria* and *L. balthica*. For *M. trossulus*, 20 shells were selected, with five in each class, while the results for the rest were obtained from Piwoni-Piórewicz et al. (2017). After the removal of soft tissues, each shell was viewed under a stereoscopic microscope to examine the epibiotic flora and fauna, which could contaminate the sample and bias the chemical analysis. If any organisms were present on the shell, they were carefully removed. To remove the biofilm, the periostracum was scraped with a scalpel, and pre-cleaned shells were placed in an ultrasonic bath (InterSonic IS-7S) in ultra-pure water for 30 minutes and then dried at 70°C for 24 hours. The shells were then crushed and ground into a fine powder with an agate mortar and pestle. Aliquots (2.8 – 849 mg, mean = 132 mg) of the powdered samples were weighed using a 5-digit analytical balance, placed into a 15 ml plastic tube (Sarstedt®) and dissolved in a mixture of 1.5 ml concentrated nitric acid (HNO_3 , Sigma Aldrich®, Trace SELECT for trace analysis), 1.5 ml ultra-pure water and 0.3 ml 30% hydrogen

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525 peroxide (H_2O_2 , Merck® Suprapure grade). After 24 hours at 70°C, the liquid samples were diluted to c. 15 ml by weight with ultra-pure water.

2.4 Elemental analysis

Concentrations of chemical elements in the digested samples were determined at the Natural History Museum, London, using a Thermo iCap 6500 Duo inductively coupled plasma optical emission spectrometer (ICP-OES) for 530 Ca, Na, Sr and Mg and an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) for Mn, Ba, Cu, Pb, V, Y, U and Cd. Calibration of the ICP-OES analysis was performed using solutions containing 1–50 mg ^{40}Ca , 0.01–5 mg ^{23}Na , and 0.001–0.5 mg ^{87}Sr and Mg in 0.8 M HNO_3 . Na, Mg and Sr calibration solutions all contained Ca at one hundred times the Mg concentration, to account for the effects on other wavelengths by high Ca contents in the samples and standards. Multiple wavelengths for each element were recorded, and line 535 selection was performed by accounting for the suitability of the wavelength to the concentrations in the samples and accounting for any potential spectral interferences. The accuracy and reproducibility of the analyses were checked using two calcium-rich certified reference materials (CRMs), JLs-1 Limestone and JD-1 Dolomite (both from the Geological Survey of Japan). The reference materials were diluted to match the concentrations of Ca in the sample solutions. Ca, Mg and Sr concentrations were found to be within $\pm 1 SD$ of the reported values (Imai 540 et al. 1996).

The limits of quantification (LOQ) of the ICP-MS analysis were generally determined as the concentration corresponding to ten times the standard deviation of the signal obtained by analysing 0.8 M HNO_3 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 elements (V, Mn, Cu, Y and Cd) to minimize the molecular interference from plasma and 545 solution components and Ca from the samples.

The accuracy and reproducibility were checked by analyses of JLs-1 and JD-1 before and after every batch of samples. The results obtained for all elements were within $\pm 2.5 SD$ of the recommended values (Imai et 550 al. 1996). 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 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 10% for all other elements. More details on method validation were reported previously (Piwon- 555 Piórewicz et al. 2017).

2.5 Statistical analyses

To evaluate the effect of the shell size (ontogenesis stage) on the concentrations of trace elements in calcareous 555 parts of *A. improvisus*, *C. glaucum*, *M. arenaria* L. *balthica* and *M. trossulus*, the concentrations of Ca, Na, Sr, Mg, Mn, Ba, Cu, Pb, V, Y, U and Cd were examined in the four size classes separately for each species. The data were not normally distributed (Shapiro-Wilk test); therefore, significant differences between the mean concentrations of the selected trace elements in the size classes were identified by one-way Kruskal-Wallis 560 nonparametric ANOVA (p -value = 0.05) and post-hoc Dunn's tests for multiple independent groups. Statistical computing and graphical visualizations were performed in RStudio.

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3 Results

The concentrations of trace elements in studied individuals can be found in Table S1 in the Supplement. The mean concentrations in all studied organisms decreased, being the highest for Ca and the lowest for Cd, in the following order Ca>Na>Sr>Mg>Mn>Ba>Cu>Pb>V>Y>U>Cd. However, the concentrations of given elements were different for Cerastoderma glaucum, Mya arenaria, L. balthica, M. trossulus and A. improvisus, showing high variability both between and within species (Table 3, Fig. 3).

There is a pattern of the highest concentration of Ca in all individuals, that ranges from $316,000 \pm 26,000 \mu\text{g g}^{-1}$ (mean \pm standard deviation) in *A. improvisus* to $363,000 \pm 18,000 \mu\text{g g}^{-1}$ in *M. arenaria*. The rest of elements had mean concentrations in shells below $4,000 \mu\text{g g}^{-1}$. In mussels most concentrated were Na>Sr>Mg, while in barnacles Mg>Na>Sr. The concentration of Na ranged, on average, from $2,000 \pm 300 \mu\text{g g}^{-1}$ in *M. trossulus* to $3,200 \pm 200 \mu\text{g g}^{-1}$ in *C. glaucum*. In *A. improvisus*, Mg ($3,940 \pm 320 \mu\text{g g}^{-1}$) was the dominant after Ca ($3,940 \pm 320 \mu\text{g g}^{-1}$), while mean concentration of Sr ($2,250 \pm 1,900 \mu\text{g g}^{-1}$) was lower than Na ($2,850 \pm 470 \mu\text{g g}^{-1}$). Clams *C. glaucum* (Mg: $80 \pm 30 \mu\text{g g}^{-1}$, Sr: $1,700 \pm 140 \mu\text{g g}^{-1}$, Na: $3,220 \pm 210 \mu\text{g g}^{-1}$), *M. arenaria* (Mg: $150 \pm 20 \mu\text{g g}^{-1}$, Sr: $2,160 \pm 280 \mu\text{g g}^{-1}$, Na: $3,080 \pm 210 \mu\text{g g}^{-1}$) and *L. balthica* (Mg: $80 \pm 30 \mu\text{g g}^{-1}$, Sr: $1,770 \pm 210 \mu\text{g g}^{-1}$, Na: $3,100 \pm 300 \mu\text{g g}^{-1}$) had concentrations of Sr over 15 times higher than those of Mg. Both Mg and Sr were concentrated in shells of clams less than Na. Mussels *M. trossulus* were characterized by concentrations of Mg and Sr, reaching $1,060 \pm 170 \mu\text{g g}^{-1}$ and $1,170 \pm 100 \mu\text{g g}^{-1}$, respectively. This species also was characterized by concentration of Na ($2,010 \pm 310 \mu\text{g g}^{-1}$) higher than Mg and Sr (Table 3, Fig. 3).

The trace elements (Mn, Ba, Cu, Pb, V, Y, U, Cd) exhibit a general trend of highest concentrations in *A. improvisus* and *M. trossulus*, lower in *C. glaucum* and *L. balthica* and the lowest in *M. arenaria*. Mn was the most variable element and increased from $1.4 \pm 1.0 \mu\text{g g}^{-1}$ in *M. arenaria* to $620 \pm 155 \mu\text{g g}^{-1}$ in *A. improvisus* (Table 3, Fig. 3).

The results of the Kruskal-Wallis nonparametric ANOVA test, which was used to compare the element concentrations between the four size classes in each species, revealed the lack of variability within *M. arenaria*. The smallest variability was found in *L. balthica*. Only the concentration of Na ($H = 10.586, p = 0.014$) decreased with shell growth for this clam. The third clam species, *C. glaucum*, showed high variability of the four trace elements. Shells of C. glaucum had increased concentrations of Sr ($H = 14.584, p = 0.002$), which was contrary to the decreasing concentration of Na ($H = 10.529, p = 0.015$), Mn ($H = 10.658, p = 0.014$) and Cd ($H = 11.655, p = 0.009$). Similarly, shells of *A. improvisus* also showed variability of four trace elements between size classes, namely, Mg ($H = 11.996, p = 0.007$), V ($H = 11.206, p = 0.011$), Cu ($H = 9.146, p = 0.027$) and Pb ($H = 13.308, p = 0.004$). However, in this case, the sequences of the changes were not straightforward but, rather, had a tendency to fluctuate between the smallest and the largest individuals. The highest variability was found within the bimimetic shells of *M. trossulus*. The size classes differed in terms of five trace elements. The incorporation of V ($H = 22.595, p < 0.001$), Cu ($H = 26.18, p < 0.001$), Y ($H = 10.819, p = 0.013$), Cd ($H = 15.353, p = 0.002$) and U ($H = 18.202, p < 0.001$) into shells decreased in larger mussels (Fig. 4).

Detailed analyses of the differences in the studied elements between the size classes based on post-hoc Dunn's tests for multiple independent groups indicated that the significant variations were not linear (Fig. 4). In *L. balthica*, Na concentration decreased in larger shells, showing differences between the size classes I and III and I and IV. In the shells of *C. glaucum*, Sr concentration increased gradually, reaching a peak in the size class IV,

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while statistically significant differences were observed between the size classes I and IV and the III and IV. An inverse pattern was observed for Na, yet its concentration differed only between the smallest and largest clams.

625 Shells of *C. glaucum* were also characterized by a common trend of the Mn and Cd, which decreased from I size class and later reached a plateau. In shells of *A. improvisus*, the concentrations of Mg, V, Cu and Pb decreased in larger individuals. The levels of Mg in shells statically differed between the size classes III and IV; likewise, shells from the size class III had the highest concentrations. The elements V and Pb occurred at the highest concentrations in shells of the smallest individuals, and later, they oscillated around a similar mean value. Cu decreased in growing shells of barnacles, reaching the minimum in the size class III. There were no statistically significant differences between the classes III and IV, and the oldest half of the group maintained the downward trend. However, it is worth noting that Cu concentrations in many of the oldest shells are several times higher. Shells of *M. trossulus* were characterized by the highest variability of trace element concentrations between size classes. The trend of decreasing concentrations was clearly marked for V, Cu, Cd and U. The concentration of Y decreased in larger shells, but the oldest shells showed an upward trend; therefore, significant differences were found between the size classes I and III (Fig. 5).

The comparison of elemental concentrations in shells of mussels and barnacles from different regions, based on literature data is presented in Table 4.

4 Discussion

640 4.1 CaCO_3 polymorph type and elemental concentrations

The Ca concentration of all species collected in the Baltic Sea was found to be $343,200 \mu\text{g g}^{-1}$ (Table 3), which corresponds to c. 86% weight per weight (w/w) of pure CaCO_3 . For comparison, same species or congeners from different regions contain between 310,000 and 420,000 $\mu\text{g g}^{-1}$ of Ca in shell (Table 4), the results above 400,000 $\mu\text{g g}^{-1}$ probably being caused by analytical bias.

645 Among shell impurities, the most concentrated elements were Na, Sr, Mg in all studied CaCO_3 polymorphs (Fig. 3). These compositions are considered to be typical in calcareous skeletons of marine invertebrates, as those elements are energetically favoured in CaCO_3 crystal lattice, substituting for Ca (Allison et al., 2001; Iglikowska et al., 2016; Reeder, 1983; Sugawara and Kato, 2000; Wang and Xu, 2001, see also Table 4). The main elemental constituents of the Baltic shells showed generally uniform distribution in collected samples, 650 and within the ranges typical for a given species. Clams, that precipitate fully aragonitic shells and bimimetic mussels were characterized by the following order of accumulated concentrations: Na>Sr>Mg, while in barnacles this order was different: Mg>Na>Sr (Fig. 3). The most evident observation was that the aragonitic shells of *C. glaucum*, *M. arenaria* and *L. balthica* contained over 15 times more Sr than Mg. In the calcitic *A. improvisus*, Mg was 1.8 times more concentrated than Sr, while the bimimetic shells of *M. trossulus* containing layers of calcite and aragonite, were distinguished by equalized concentrations of Mg and Sr in shells (Table 3, Fig. 3). Such pattern of Mg and Sr is observed in number of calcareous species including bivalves and barnacles (Table 4; Dalbeck, 2008; Iglikowska et al., 2016; Wang and Xu, 2001; Zhao et al., 2017). However, by comparing species, it is evident that the calcite of barnacles *A. improvisus* deviated from this general trend. Out of the species studied in this work, both Mg and Sr concentrations were higher in calcitic barnacles than in aragonitic clams (Table 3, Fig. 3). Kinetic and biological effects influence the partitioning of Sr between the shell and seawater (Urey et al., 1951), and Sr in

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665 shells is known to significantly exceed its concentration expected at the thermodynamic equilibrium (Schöne et al., 2010). Furthermore, previous studies revealed that barnacles have significantly higher Sr shell concentration (up to 2,300 $\mu\text{g g}^{-1}$) than other marine invertebrates (Carpenter and Kyger, 1992; Ullmann et al., 2018). The concentration of Sr in shells of *A. improvisus* from this study ($2,250 \pm 190 \mu\text{g g}^{-1}$) supports these findings, suggesting that barnacle precipitation process differs from other marine organisms. Carpenter and Kyger (1992) 670 concluded that Sr is a sensitive indicator of precipitation rate this may explain the elevated Sr concentrations in barnacles. The shell increment in barnacles is rapid (15 – 30 mm per year, Milliman, 1974) due to their relatively short lifespan (approximately one year). Consequently, the observed Sr concentration of *A. improvisus* may be caused by higher precipitation rate of barnacle calcite in comparison with the precipitation rate of aragonite in long-lived bivalves (Tables 3 and 4, Fig. 3). Crystal lattice distortions in barnacle calcite induced by rapid 675 incorporation of impurities (Pokroy et al., 2006) may allow for even higher Sr incorporation and support the high Sr concentration in *A. improvisus* shell. This indicates that Mg and Sr concentration in shell are controlled by CaCO_3 lattice properties, yet in a strongly species-specific way (Skinner and Elderfield, 2005).

The concentrations of Mn and Ba are several orders of magnitude higher in the calcitic shells of barnacle *A. improvisus* than in other species (Table 3, Fig. 3). Based on the ionic radii of Mn and Ba, it is expected that aragonite shells would incorporate Ba more intensively than would calcitic shells (Findlater et al., 2014; Gillikin et al., 2006), yet this trend is not observed in this study, indicating Ba as not clearly related to the crystal lattice orientation. Furthermore, barnacles appear to have a stronger capacity for Mn incorporation into shells than other benthic calcifiers (Pilkey and Harris, 1966), even *A. improvisus* collected at the same location (GN, Fig. 1), possibly due to the species-specific biological factors (Bourget, 1974). Yet, as both species with highest concentration of Mn produced calcite (Table 3, Fig. 3), we should not rule out that the polymorph type of CaCO_3 to some degree regulates the level of shell Mn in low salinity environment.

680 It was observed that an increased incorporation of Mg and Sr into shell can contribute to distortion of CaCO_3 crystal lattice and results in parallel increased incorporation of trace elements into the shells (Harris, 1965; Davis et al., 2000; Finch and Allison, 2007; Dalbeck, 2008). In our study, shell lattices of mussels and barnacles 685 could be changed through the concentration of Mg and Sr higher than in clams. Therefore, the concentration of Cu, V, Cd, Y and U seems to be driven to some degree by crystal lattice properties having the highest values in species containing calcite in their shells (Fig. 3). It is also important to note that the smaller ionic radii of V, Cd, Y, U and Cu are energetically favoured in calcite, while larger Pb radius is favored in aragonite structure (Morse et al., 1997; Reeder, 1983; Wang and Xu, 2001). However, trace elements, Cu, V, Cd, Y were present at the highest 690 levels in bimimetic *M. trossulus*, while only U, as well as Pb, in calcitic *A. improvisus* (Table 3), which suggests that additional factors, other than the crystal lattice effects, determine those concentrations. Furthermore, this study likewise revealed inconsistent variability of trace element concentrations between aragonitic clams. Out of the three species of clams, *M. arenaria* was characterized by the lowest concentration of all trace elements (Table 3). This also indicates that factors other than mineral properties co-regulate trace elements accumulation in shells.

700 This study considers element concentrations in shells that were not subjected to chemical removal of organic matter prior to the dissolution of the carbonate matrix. Chemical cleaning of carbonate skeletons prior to chemical analysis and both improvement of the data quality and potential artefacts associated with this are widely discussed in the literature (Barker et al., 2003; Holcomb et al., 2015; Loxton et al., 2017), but the plausible pre-treatment method for the removal of organics still needs to be found (Inoue et al., 2004). Mannella et al. (2020)

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showed that the suitability of chemical pre-treatments for organic matter removal from carbonate matrices should be evaluated on a case-by-case basis and, in case of relatively low organic content, should be avoided. In addition to CaCO_3 crystal lattice, shells of barnacles and bivalves usually contain up to 5.0 wt% of organic matter (Bourget, 1987; Wolowicz and Gouilletquer, 1999; Marin and Luquet, 2004; Rueda and Smaal, 2004). However, the specific features and composition of given organic matrix might be a cause of the inter-species and inter-individual variability of elemental concentration in shells (Fig. 3, Table 3; Takesue and van Geen, 2004). The organic fraction was found to be generally not associated with significant level of trace elements (Lingard et al., 1992; Takesue et al., 2008), which are strongly incorporated into the crystal phase. Yet, many authors found correlations, especially for Mg and Mn, associated with the shell organic matrix (Bourget, 1974; Walls et al., 1977; Lorens et al., 1980; Rosenberg et al., 2001; Takesue and van Geen, 2004). Despite replacing with Ca in shell lattice, these elements are biologically essential (Bellotto and Miekeley, 2007), and inter-species variability of Mg and Mn between barnacles, mussels and clams (Fig. 3) could be enhanced by specific properties of organic phases.

4.2 Size classes and potential biological impact on elemental concentrations

The recorded concentrations of trace elements in all populations exhibited marked variability among individuals (Table 3, Fig. 3), a feature previously recorded by several authors (Gillikin et al., 2005a; Vander Putten et al., 2000). In this study, individuals were collected over a wide range of sizes (Table 2), representing different ages and life spans. Bivalves are long-living organisms, and these of the Gulf of Gdańsk have life expectancy of 4–12 years (Gofas, 2004; Żmudziński, 1990), contrary to barnacles with the relatively short lifespan of approximately one year (Bornhold and Milliman, 1973). The southern Baltic Sea is driven by cyclical environmental dynamics, which evoke physiological stress, determine the food base and drive its biogeochemical cycles (Elder and Collins, 1991). Shells of *A. improvisus* experienced one-year variability of environmental factors, while bivalves represent long-term variability. Thus, the life span to some extent, may explain the lowest variability of trace elements in barnacles (Fig. 3). However, this relation is not noticeable in mussels, for which the inter-individual variability of trace elements in the youngest individuals (size class I) was not lower than in the oldest ones (size class IV, Fig. 4). Thébault et al. (2009) revealed low inter-individual elemental variability in bivalves and on this basis indicated the environment as a factor controlling their incorporation within shells. Therefore, the heterogeneous elemental concentrations between individuals from the brackish Gulf of Gdańsk may to some extent be caused by biological factors, that could led to a deviation from, what is expected with purely environmental control. The biological influence on the shell chemistry in the southern Baltic Sea could be reinforced by unfavourable conditions for calcification. The low salinity (~7) and alkalinity, which is typical for the studied area of the Gulf of Gdańsk, cause a reduced CaCO_3 saturation state (Beldowski et al., 2010; Cai et al., 2010; Findlay et al., 2008). Ions of Ca^{2+} and CO_3^{2-} are essential components for the crystal formation, and when their concentrations in seawater are low, calcifying organisms exert selective Ca^{2+} channels to enable an active ion capture from solution (Sather and McCleskey, 2003). The required higher contribution of Ca^{2+} active pumping results in greater degree of biological control over the calcification process (Sather and McCleskey, 2003; Waldbusser et al., 2016) and shells are not produced in equilibrium with environmental conditions when it comes to an elemental concentration.

Within species, organisms from juveniles to adults experience morphological and functional changes related to sex, metabolic rate or reproductive stage, which complicate the biomineralization process (Carré et al., 2006; Freitas et al., 2006; Gillikin et al., 2005b; Schöne et al., 2010, 2011; Warter et al., 2018). The size-related

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elemental patterns in shells of *A. improvisus*, *C. glaucum*, *M. arenaria*, *L. balthica* and *M. trossulus* from the Gulf of Gdańsk indicate that if a significant variability exists, it is specifically expressed in trace element concentrations. 810 The studied mussel *M. trossulus* and barnacle *A. improvisus* showed the greatest variability between size classes, while the size class effects were less pronounced in clams (Fig. 4). However, the variability of trace elements were not uniform for *M. trossulus* and *A. improvisus*, even though the organisms came from one location (Table 1). The size-related trend was observed for V, Cu, Y, Cd and U in molluscs, and Mg, V, Cu and Pb in barnacles (Fig. 3). 815 Among clams, we found the lack of size-dependent changes within *M. arenaria*. In *L. balthica* only the concentration of Na decreased with shell growth, while *C. glaucum* showed variability of Sr, Na, Mn and Cd (Fig. 4). Different patterns of elemental accumulation for species in the same habitat were observed before (Rainbow, 2002, 1995). Rainbow et al. (2000) tested *A. improvisus* and *M. trossulus* from the Gulf of Gdańsk as 820 environmental biomonitor by measuring the concentrations of Co, Zn, Fe, Cd, Pb, Mn and Ni in soft tissues. They found that mussels and barnacles occurring at the same location did not show the same variation in elemental bioavailabilities, probably because barnacles were particularly strong accumulators of trace elements (Rainbow, 2002, 1998). This shows that biological differences between species, such as growth rate, feeding rate, assimilation efficiency (Luoma and Rainbow, 2005), route and degrees of element uptake (Rainbow and Wang, 2001) are significant factors determining the elemental accumulation in shells.

In this study, it was generally observed that, when statistical differences between size classes were recorded, the concentrations of trace elements decreased with the shell size. The reverse was found only for Sr in the shells of *C. glaucum*, in which the concentration of Sr increased with size (Figs. 4 and 5). Large mussels pump less water per unit of the body weight, and their uptake of trace elements is lower than that in smaller individuals. When the concentrations of trace elements decrease with increasing shell size (Fig. 4), the incorporation might depend on the growth rate. The younger specimens could have a greater growth rate and shell precipitation rate, 830 resulting in a greater uptake of trace elements (Dalbeck, 2008; Szefer et al., 2002). Rosenberg and Hughes (1991) suggested that areas of higher shell curvature, such as the umbo, require greater metabolic expenditure, resulting in an increase of element uptake. When the metabolic activity of an organism decreases, the ionic flux likewise decreases, increasing the tendency of Ca^{2+} to block other ions fluxes (Carré et al., 2006; Friel and Tsien, 1989). Therefore, in a low salinity environment of the Gulf of Gdańsk, metabolic fluctuations of organisms can have an 835 exceptionally strong effect on elemental variability, which was high among studied individuals (Table 3, Fig. 3). The surface-to-volume ratio decreases with size and affects the contribution of the adsorbed element content to the bulk concentration (Azizi et al., 2018). Therefore, the negative correlation between the bulk elemental concentration and shell size (Fig. 4), noted in some previous studies (Martincic et al., 1992; Piwoni-Piórewicz et al., 2017; Ritz et al., 1982), could have been caused by a greater potential of surface adsorption in smaller 840 individuals. This is most pronounced for a few trace elements, the concentrations of which decreased across the four size classes in shells of *A. improvisus* (V, Cu, Pb), *M. trossulus* (V, Cu, Y, Cd, U) and *C. glaucum* (Mn, Cd, Figs. 4 and 5). Catsiki et al. (1994) suggested that, apart from metabolic processes, an active detoxification mechanism in tissues is responsible for this trend, and its efficiency is higher in older and larger individuals.

Nevertheless, many of the trace elements studied herein showed a lack of statistically significant 845 relationships between the shell sizes. Few trace elements in the shells of *A. improvisus* (Y, U and Cd), *M. trossulus* (Pb), *C. glaucum* (V, Cu, Y, Pb and U) and all trace elements in the shells of *L. balthica* and *M. arenaria* (V, Cu, Y, Pb, U and Cd) showed no significant variability related to the size of organisms (Figs. 4 and 5). This is not an

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unusual pattern for marine invertebrates, which has been shown by a number of studies. Saavedra et al. (2004) observed no differences between Cd, Pb, Cr, Ni, As, Cu and Zn concentrations for different shell lengths of the raft *Mytilus galloprovincialis* separated into four size classes. Protasowicki et al. (2008) similarly found that the concentrations of Hg, Pb, Cd, Cu, Zn, Cr, Ni, Fe, Mn, V, Li and Al in the shells of the mussel *Mytilus edulis* from the Polish coast of the Baltic Sea did not vary between shell sizes. This inconsistent relationship shows that trace elements concentration in shells of different sizes might be under influence of a number of factors including species-specific biological mechanisms (e.g. metabolic rate). ▶

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4.3 Environmental factors and elemental concentrations

Organisms derive trace elements in dissolved and particulate forms primarily from surrounding water, sediments and their food base (Freitas et al., 2006; Gillikin and Dehairs, 2005; Poulain et al., 2015). The concentration of basic macro elements Na, Mg and Sr in surrounding seawater is generally proportional to salinity (Beldowski et al., 2010; Cai et al., 2010; Findlater et al., 2014; Wit et al., 2013), therefore the environmental level of these elements should be rather homogenous in the study area (salinity range 6.9–7.3, Table 1). And indeed, our analysis has shown low variability of the concentrations of Na ($2,010 \pm 310 \mu\text{g g}^{-1}$ – $3,220 \pm 210 \mu\text{g g}^{-1}$) and Sr ($1,170 \pm 100 \mu\text{g g}^{-1}$ – $2,250 \pm 190 \mu\text{g g}^{-1}$, Table 3) in the shells of studied species, which might reflect environmental stability. However, the concentration of Mg in shells as this element was highly variable ($3,940 \pm 320 \mu\text{g g}^{-1}$ – $80 \pm 30 \mu\text{g g}^{-1}$, Table 3, Fig. 3). Although salinity was indicated as the factor controlling the concentration of Na, Sr and Mg in environment and skeletons built there (Elderfield and Ganssen, 2000; Rosenheim et al., 2004), the range of surface salinity in the study region was unlikely to explain the observed range of Mg concentrations. Mg is the most energetically preferred skeletal element (Allison et al., 2001; Wang and Xu, 2001), is associated with the shell organic matrix (Bourget, 1974) and its concentrations has been found to depend on seawater temperature (Freitas et al., 2005; Dalbeck, 2008; Schöne et al., 2011). Vander Putten et al. (2000) observed that the skeletal Mg/Ca variations in *M. edulis* could not be interpreted solely based on variations in the seawater Mg, while Dodd and Crisp (1982) showed that the Mg/Ca ratios of most estuarine waters only differ significantly from the open-ocean ratios at salinities below 10. Therefore, the variations in the shell Mg concentration must be the combination of many biological and environmental factors.

Among trace elements (Mn, Ba, Cu, Pb, V, Y, U and Cd), Mn and Ba were definitely the most concentrated in shells (Fig. 3), as previously reported for bivalves (Lazareth et al., 2003; Vander Putten et al., 2000). Such high concentrations of Mn and Ba are usually associated with freshwater inputs to estuarine systems, which likewise causes phytoplankton blooms (Gillikin et al., 2006; Vander Putten et al., 2000; Thébault et al., 2009). Consequently, Ba and Mn may be taken up by calcifiers through ingestion of phytoplankton (Stecher et al., 1996) or decaying algal flocs (Brannon and Rao, 1979; Stecher et al., 1996). The elemental incorporation into shell has been shown to correlate at species level with changes in primary production and phytoplankton blooms (Freitas et al., 2006; Lazareth et al., 2003; Vander Putten et al., 2000). Therefore, the food base and elemental transport in the trophic chain might cause the spatial and species-specific elemental variability in shells (Fig. 3). This pattern is generally confirmed in different regions by the contents of Mn and Ba relative to other trace elements (Fig. 4).

Seawater trace element concentrations in the study area depend on seasonality and human activity, but elemental concentrations in sediments represent long-term chemical background. In coastal regions, trace elements

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915 discharged from various sources, such as atmosphere, rivers, and plankton blooms, can be rapidly transported from the water column to the bottom sediments (Bendell-Young et al., 2002; Szefer et al., 1995). In this study, samples were collected in two regions of the Gulf of Gdańsk: the outer part of the Puck Bay (stations MA, M2 and MW) and central part of the Gulf of Gdańsk (station GN, Fig. 1). The shells of clams collected in the outer Puck Bay, with sandy sediment (Szefer et al., 1998; Szefer and Grembecka, 2009; Uścinowicz, 2011), were depleted in trace elements. On the other hand, mussels and barnacles from the central Gulf of Gdańsk, with sandy mud, were characterized by higher elemental concentrations than clams (Fig. 3). On this basis we can assume that the concentrations of trace elements Mn, Ba, Cu, Pb, V, Y, U and Cd in shells might be related to sediment

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920 granulometry and increase from sandy to silty type (Góral et al., 2009; Uścinowicz, 2011). The maximum concentration of trace elements within a given region is commonly associated with the finest sediment fraction ($<2 \mu\text{m}$) as compared to the sandy fraction (Kim et al., 2004; Szefer et al., 1998). In addition, the formation of Mn-Fe oxyhydroxides in the surface sediments (Glasby and Szefer, 1998; Szefer et al., 2002) has a particular role in absorbing trace elements in the fine sediments (Pruyters et al., 1991; Szefer et al., 1995; Tessier et al., 1979). It has been previously shown that for mussel *M. trossulus*, clam *L. balthica* and barnacle *A. improvisus* from the central part of the Gulf of Gdańsk (near the GN station), elemental concentrations in shells (Szefer and Szefer, 1985) and tissues (Rainbow et al., 2000, 2004; Sokolowski et al., 2001) were similar to that in the Vistula River plume and higher than trace elements concentration in macrozoobenthos from the outer Puck Bay.

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925 However, the studied trace elements exhibited variations in accumulated concentrations between species, both within the Puck Bay (M2: *C. glaucum*, MA: *M. arenaria*, MW: *L. balthica*) and within the central Gulf of Gdańsk (GN station: *M. trossulus* and *A. improvisus*, Fig. 3). The highest concentration of trace elements in *C. glaucum* (M2: 10 m) and *L. balthica* (MW: 31 m) within clams from the sandy Puck Bay could be driven by 930 elevated amounts of trace elements in oxygenated zones where Fe-Mn oxyhydroxides accumulate. At the Mn(II)/Mn(IV) redox interface manganese oxides may predominantly precipitate on the periostracum of molluscs comparing to inorganic surfaces (Strekopytov et al., 2005), which may, in turn, influence the incorporation of trace elements into shells. *M. arenaria* likewise was collected in a shallow zone (MA: 10 m), but had, nevertheless, the 935 lowest concentrations of all studied trace elements (Fig. 3). This bivalve mainly spends life buried 20–30 cm in a sediment (Żmudziński, 1990). Szefer et al. (1998) reported that in the Gulf of Gdańsk the enrichment factors for Cu, Zn, Ag, Cd and Pb are highest in the $<2 \mu\text{m}$ fraction and decrease with increasing both fraction size and depth of the sediment. This may be a reason why *C. glaucum* and *L. balthica* have similar patterns of elemental accumulation, while *M. arenaria* was characterized by the lowest values (Fig. 3). Such dependence indicates that 940 the sediment properties belong to factors controlling concentration of trace elements in the shells.

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945 Mussels *M. trossulus* and barnacles *A. improvisus* from the same location (Fig. 1, Table 1) showed greater chemical differentiation than clams. This relationship is most evident for Mn and Ba. Much lower concentrations of Mn and Ba were found in the shells of molluscs (Mn: $54.0 \pm 15.0 \mu\text{g g}^{-1}$, Ba: $17.0 \pm 6.70 \mu\text{g g}^{-1}$) than in barnacles (Mn: $625 \pm 160 \mu\text{g g}^{-1}$, Ba: $73.0 \pm 20.1 \mu\text{g g}^{-1}$, Table 3). A similar relationship was found in the soft tissues of *M. trossulus* and *A. improvisus* collected from different locations in the Gulf of Gdańsk in May 1998 (Rainbow et al., 2000). The range of Mn in the soft tissues of *M. trossulus* varied from 19.0 to $41.0 \mu\text{g g}^{-1}$, while that in *A. improvisus* ranged from 187 to $307 \mu\text{g g}^{-1}$ and was interpreted as species-specific accumulation efficiency. The concentration of Mn has been repeatedly reported to be influenced by phytoplankton blooms (Vander Putten et al., 2000; Gillikin et al., 2006; Zhao et al., 2017), thus the diet seems to affect the shell Mn

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concentration. Due to size of the organism, the diet of *A. improvisus* depends more on Mn-rich phytoplankton than larger *M. trossulus* that easily picks zooplankton. The lower proportion of zooplankton in the barnacle diet could have hereby add to a higher Mn concentration in their shells (Fig. 3). This suggests that the Mn concentration in shell is highly species dependent.

Some studies have investigated trace element concentrations in shells (but many more have concentrated on the soft tissues) of marine invertebrates as a tool to assess trace **elements** contamination of the aquatic environment. The concentrations of trace elements Mn, Ba, Cu, Pb, Cd and U in the shells of a studied organism in Gulf of Gdańsk and in other regions was found to be highly variable, even within a single taxon (Table 4). Therefore, the environmental conditions prevailing during biominerization are largely reflected in the trace element concentrations of the shells; nevertheless, their interpretation requires consideration of biological factors specific to the species.

5. Conclusions

The shells of calcitic *Amphibalanus improvisus*, aragonitic *Cerastoderma glaucum*, *Limecola balthica*, *Mya arenaria* and bimimetic *Mytilus trossulus* from the Gulf of Gdańsk are accumulators of a wide spectrum of **trace** elements from the surrounding environment. The elemental concentration levels in studied species are not only determined by their bioavailability in the environment. Many biotic and abiotic factors are acting on the shell incorporation mechanism and their effect is likely to be species-specific.

By determining Ca, Na, Sr, Mg, Mn, Ba, Cu, Pb, V, Y, U and Cd in the shells of given species we found some patterns of **elemental** accumulation. At a local scale of the Gulf of Gdańsk, the main elements Na, Sr and Mg are mostly dependent on crystal lattice properties of calcite and aragonite. Clams that precipitate fully aragonitic shells have a clear preference for accumulating Sr over Mg in shells, contrary to dominant Mg content over Sr in barnacle shell calcite. It is energetically more favourable for larger cations such as Na and Sr to enter the aragonite lattice with smaller cations (e.g. Mg) favouring calcite. However, this relationship breaks down when comparing shells of different species or genera. For example, the barnacle calcite contains higher Sr concentration than the bivalve aragonite. The level of main elements, especially Sr and Mg, seems to be determined by specific biological **factors**, such as growth rate.

In case of trace **elements** Mn, Ba, Cu, Pb, V, Y, U and Cd, factors other than given crystal lattice presence, seem to determine their concentrations. The elemental variability between size-grouped shells indicates that trace elements were more variable than Na, Sr, Mg, but this varies between species. Moreover, there is a trend of the elemental concentrations being lower in larger than in smaller shells. Biological differences between and within species, such as feeding including its rate and assimilation efficiency related to age of organisms (size of the shell), are potentially important factors determining the elemental accumulation in shells.

Given that the specimens were obtained from two regions of the Gulf of Gdańsk: the outer part of the Puck Bay and central part of the Gulf of Gdańsk, an impact of local environmental factors, such as the sediment type and the food base cannot be excluded as factors controlling concentration of trace elements in shells.

Author contribution. APP and PK designed and led the study. SS and EHW conducted elemental analysis. APP prepared the original draft, which was reviewed and edited by all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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- **usunięto:** and the trace elements deposited over time in the shells are determined by environmental and biological conditions. As this study was conducted in a highly dynamic coastal system, notable elemental variability between mussels and barnacles is associated with fluctuating environmental conditions. The *A. improvisus* shell is a record of annual variability only compared to the *M. trossulus* shell, which records many years of fluctuations of environmental parameters.⁴
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- **usunięto:** → On this basis, it can be emphasized that by analysing the species-specific biological factors in parallel with the elemental variability of shells within widely distributed species, it might be possible to separate the environmental and biological signals in the biominerization process.⁴

Data availability. The underlying research data can be accessed at Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland.

Supplement. The supplement related to this article will be available online.

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Tables and Figures

Table 1. Details of the sampling locations. Temperature (T) and salinity were measured near the bottom during sample collection.

Station	Coordinates	Collected species	Depth (m)	T (°C)		Sediment type ^a	Sampling date
				measured	in situ		
GN	54°32'N 18°48'E	<i>Amphibalanus improvisus</i>	36	3.1	7.3	Sandy mud, silty sand	May 2013
GN	54°32'N 18°48'E	<i>Mytilus trossulus</i>	36	3.1	7.3	Sandy mud, silty sand	May 2013
M2	54°38'N 18°33'E	<i>Cerastoderma glaucum</i>	10	16.9	6.9	Sand	June 2014
MA	54°37'N 18°32'E	<i>Mya arenaria</i>	10	19.8	6.9	Sand	June 2014
MW	54°37'N 18°37'E	<i>Limecola balthica</i>	31	4.7	7.0	Fine sand, sandy mud, silty sand	June 2014

1515 ^a Based on Uścinowicz (2011)

— sformatowano: Czcionka: Kursywa

Table 2. The range of shell sizes for each studied species within a given size class.

Species	Mineral type	Size classes (mm)				Maximum size in the Gulf of Gdańsk (mm) ^a
		I	II	III	IV	
<i>Amphibalanus improvisus</i>	Calcite	3–4	5–6	7–8	9–10	10
<i>Mytilus trossulus</i>	Bimineralic	6–15	16–25	26–35	36–44	50
<i>Cerastoderma glaucum</i>	Aragonite	4–8	9–12	12–16	16–20	27
<i>Mya arenaria</i>	Aragonite	10–20	20–30	30–40	40–49	70
<i>Limecola balthica</i>	Aragonite	4–7	8–11	12–15	15–18	24

^a Based on Źmudziński (1990)

1520 **Table 3.** Elemental concentrations in shells of studied organisms, presented in decreasing order of means for each species (SD = standard deviation between all specimens of a species).

— usunięto: , SE = standard error

Barnacle *Amphibalanus improvisus*: CALCITE

Element Sample size Mean conc. SD Weight ratio El/Ca Molar ratio El/Ca

(El)	n	[$\mu\text{g g}^{-1}$]		[arbitrary]	[mmol/mol]
Ca	37	316,000	26,000	1	1
Mg	37	3,940	320	0.012	20.5
Na	37	2,850	470	0.009	15.7
Sr	37	2,250	190	0.007	3.3
Mn	37	625	160	1.978	1438.4
Ba	37	73.6	20.1	0.231	67.3
Cu	37	3.90	2.2	0.012	7.7
Pb	37	1.34	0.79	0.0042	0.82
V	36	0.47	0.156	0.0015	1.16
Y	37	0.21	0.12	0.0007	0.30
U	37	0.11	0.043	0.0003	0.06
Cd	37	0.06	0.02	0.0002	0.07

— usunięto: N

— usunięto: ± 1

— usunięto:

Element Sample size Mean conc. SD Weight ratio El/Ca Molar ratio El/Ca

(El)	n	[$\mu\text{g g}^{-1}$]		[arbitrary]	[mmol/mol]
Ca	40	348,000	16,000	1	1
Na	40	3,220	210	0.009	16.1
Sr	40	1,700	140	0.005	2.2
Mg	40	80	30	0.0002	0.4
Ba	40	15.0	10	0.043	12.6
Mn	40	11.9	10.5	0.034	24.9
Cu	40	4.08	6.29	0.012	7.3
Pb	34	0.14	0.1	0.0004	0.08
U	40	0.10	0.084	0.0003	0.05
Y	40	0.07	0.074	0.0002	0.09
V	37	0.07	0.061	0.0002	0.16
Cd	37	0.01	0.009	0.00003	0.01

— usunięto: N

— usunięto: ± 1

— usunięto:

Element Sample size Mean conc. SD Weight ratio El/Ca Molar ratio El/Ca

(El)	n	[$\mu\text{g g}^{-1}$]		[arbitrary]	[mmol/mol]
Ca	40	345,000	17,000	1	1
Na	40	3,100	300	0.009	15.6
Sr	40	1,770	210	0.005	2.3
Mg	40	80	30	0.0002	0.4
Ba	40	13	10	0.038	11.0
Mn	40	7.9	7.1	0.023	16.7
Cu	40	3.0	3.4	0.009	5.43
Pb	39	0.14	0.16	0.0004	0.08
Y	40	0.08	0.11	0.0002	0.10
V	35	0.04	0.031	0.0001	0.08

— usunięto: N

— usunięto: ± 1

— usunięto:

Element	Sample size	Mean conc.	SD	Weight ratio El/Ca	Molar ratio El/Ca
(El)	n	[$\mu\text{g g}^{-1}$]		[arbitrary]	[mmol/mol]
U	40	0.03	0.024	0.0001	0.02
Cd	37	0.01	0.008	0.00002	0.01
Ca	40	363,000	18,159	1	1
Na	40	3,080	207	0.0085	14.8
Sr	40	2,160	280	0.0060	2.72
Mg	40	150	25	0.0004	0.68
Ba	40	2.60	1.6	0.00716	2.1
Mn	40	1.40	1	0.00386	2.8
Cu	40	0.031	0.024	0.00009	0.053
Y	40	0.020	0.018	0.00006	0.025
V	40	0.016	0.014	0.00004	0.035
Pb	40	0.015	0.014	0.00004	0.008
U	40	0.006	0.005	0.00002	0.003
Cd	37	0.002	0.003	0.00001	0.002
Element	Sample size	Mean conc.	SD	Weight ratio El/Ca	Molar ratio El/Ca
(El)	n	[$\mu\text{g g}^{-1}$]		[arbitrary]	[mmol/mol]
Ca	40	344,000	28,000	1	1
Na	21	2,010	310	0.006	10.2
Sr	41	1,170	100	0.003	1.6
Mg	40	1,060	170	0.003	5.1
Mn	35	54	15	0.157	114.16
Ba	38	17.0	6.7	0.049	14.40
Cu	40	14.0	10	0.041	25.44
Pb	32	1.00	1.4	0.003	0.56
V	40	0.78	0.52	0.002	1.78
Y	40	0.70	1.2	0.002	0.91
Cd	40	0.09	0.11	0.0003	0.09
U	40	0.05	0.033	0.0002	0.03

Table 4. Elemental concentrations in shells from different regions based on this study and literature data.

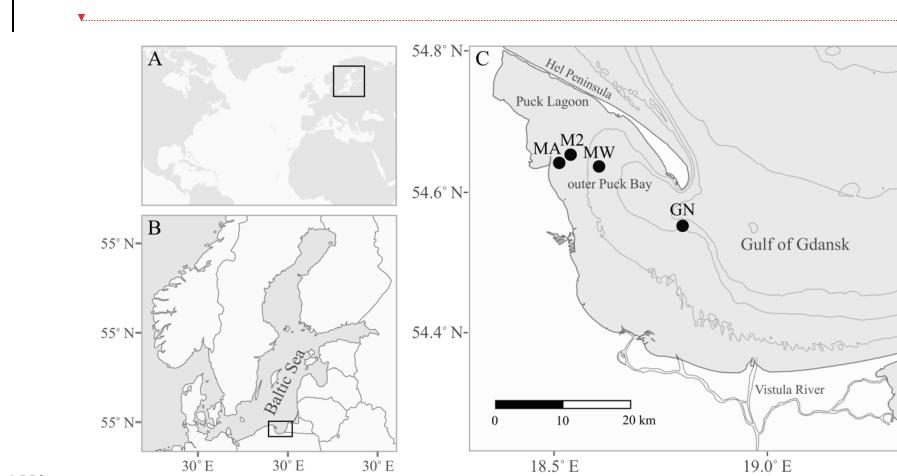
Element concentration in shell	Ca	Na	Sr	Mg	Mn	Ba	Cu	Pb	Cd	U
	[$\mu\text{g g}^{-1}$]				[$\mu\text{g g}^{-1}$]					
<i>Amphibalanus improvisus</i> ^a	316000	2850	2250	3940	625	73	3.90	1.34	0.11	0.06
<i>Balanus sp.</i> ^o		1600 –			80 –					
		5000			3800					
<i>Balanus sp.</i> ^z					39 –		<18.2	0 –	1.48	
<i>Balanus balanoides</i> ^d					313					
					77					

<i>Amphibalanus reticulatus</i> ^h												
<i>Cerastoderma glaucum</i> ^a	348000	3220	1700	80	11.9	15.0	4.08	0.140	0.011	0.096		Sformatowano: Do lewej
<i>Cerastoderma glaucum</i> ^g	400000			280	26		0.16	17	0.015	0.03		Sformatowano: Do lewej
<i>Cerastoderma edule</i> ^r							1.11 –			4.94		Sformatowano: Do lewej
<i>Limecola balthica</i> ^a	345000	3100	1770	80	7.9	13.0	3.0	0.14	0.007	0.034		Sformatowano: Do lewej
<i>Macoma (=Limecola) balthica</i> ^s							0.68					Sformatowano: Do lewej
<i>Mya arenaria</i> ^a	363000	3080	2160	150	1.40	2.60	0.031	0.015	0.002	0.006		Sformatowano: Do lewej
<i>Mya arenaria</i> ⁱ							9.5		0.05			Sformatowano: Do lewej
<i>Mytilus trossulus</i> ^a	344000	2010	1170	1060	54	17	14	1	0.091	0.050		Sformatowano: Do lewej
<i>Mytilus trossulus</i> ^j				1185								Sformatowano: Do lewej
<i>Mytilus trossulus</i> ^g	310000			1400	120		0.16	24	0.029			Sformatowano: Do lewej
<i>Mytilus trossulus</i> ^g	420000			1700	90		<0.02	5.2	0.009			Sformatowano: Do lewej
<i>Mytilus edulis</i> ^e			970	970	24.2	3.31	<dl	0.321		0.007		Sformatowano: Do lewej
<i>Mytilus edulis</i> ^x			862	856	0.13	0.26	<dl	0.385		0.0009		Sformatowano: Do lewej
<i>Mytilus edulis</i> ⁿ	398000											Sformatowano: Do lewej
<i>Mytilus galloprovincialis</i> ^v							9.54	1.19				Sformatowano: Do lewej
<i>Mytilus galloprovincialis</i> ⁱ							10	7.3				Sformatowano: Do lewej
<i>Mytilus galloprovincialis</i> ^b	360000	2500 – 4000	500 – 800	900 – 1400	<160	0 – 3.8	0 – 5.5	0 – 5.0	0 – 3.0			Sformatowano: Do lewej
<hr/>												
<i>Shell weight ratio element/Ca</i>			Na/Ca	Sr/Ca	Mg/Ca	Mn/Ca	Ba/Ca	Cu/Ca	Pb/Ca	Cd/Ca	U/Ca	
			[arbitrary]			[mg/g]						
<i>Amphibalanus improvisus</i> ^a	0.012	0.009	0.007			1.978	0.231	0.012	0.0042	0.0003	0.0002	Sformatowano: Do lewej
<i>Amphibalanus amphitrite</i> ^t		0.01										Sformatowano: Do lewej
<i>Balanus balanoides</i> ^u	0.009	0.009	0.01			0.0005						Sformatowano: Do lewej
<i>Balanus balanoides</i> ^u	0.010	0.007	0.01			0.001						Sformatowano: Do lewej
<i>Balanus balanoides</i> ^u	0.017	0.008	0.01			0.0003						Sformatowano: Do lewej
<hr/>												
<i>Shell molar ratio element/Ca</i>			Na/Ca	Sr/Ca	Mg/Ca	Mn/Ca	Ba/Ca	Cu/Ca	Pb/Ca	Cd/Ca	U/Ca	
			[mmol/mol]			[μmol/mol]						
<i>Amphibalanus improvisus</i> ^a	15.7	3.3	20.5	1438	67.3	7.71	0.82	0.070	0.057			Sformatowano: Do lewej
<i>Amphibalanus improvisus</i> ^p		4.20	20.55	0.71								Sformatowano: Do lewej
<i>Balanus balanus</i> ^c	20.49	3.85	14.83	0.077	0.055							Sformatowano: Do lewej
<i>Mya arenaria</i> ^a	14.8	2.72	0.68	2.80	2.09	0.053	0.008	0.002	0.003			Sformatowano: Do lewej
<i>Mya arenaria</i> ^m		2.1 – 2.45	1.0 – 1.9	0.06 – 0.14	1.7 – 3.7		0.002 – 0.005					Sformatowano: Do lewej
<i>Mytilus trossulus</i> ^a	10.16	1.55	5.07	114.16	14.40	25.44	0.56	0.094	0.026			Sformatowano: Do lewej
<i>Mytilus edulis</i> ^w				40 – 190								Sformatowano: Do lewej
<i>Mytilus edulis</i> ^l		1.1 – 1.6	2.5 – 6.0									Sformatowano: Do lewej
<i>Mytilus edulis</i> ^f		1.92	8.67									Sformatowano: Do lewej

<i>Mytilus edulis</i> ^k	1.34 – 5.1 –	13 – 35							
	1.5 – 7.86								
<i>Mytilus edulis</i> ⁿ	0.7 – 2.5 –	100 – 20 –							
	1.5 – 12.0	450 – 70							
<i>Cerastoderma glaucum</i> ^a	16.1	2.23	0.378	24.9	12.6	7.3	0.078	0.011	0.046
<i>Cerastoderma edule</i> ^y	1.6	1.5		20 – 60	15		0.01		

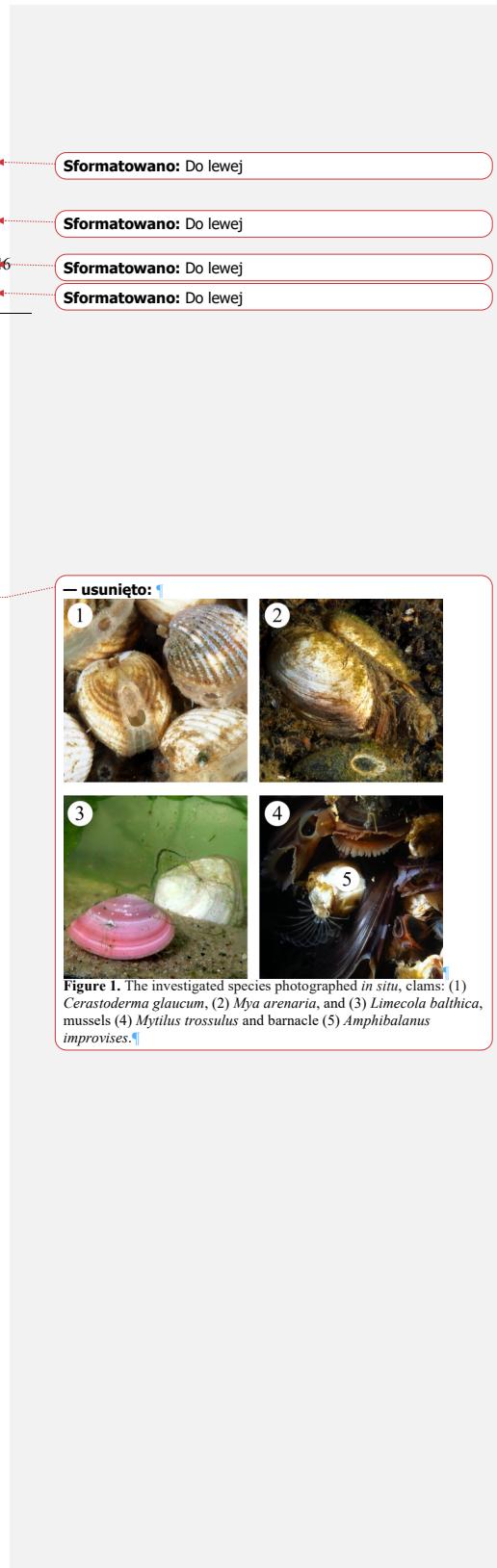
1540 [–] <dl – below the detection limit

^a Baltic Sea, Gulf of Gdańsk (this study), ^b Adriatic Sea, Croatia (Rončević et al., 2010), ^c Arctic (Iglikowska et al., 2018), ^d Atlantic, USA (Blanchard and Chasteen, 1976), ^e North Sea, Germany (Ponnurangam et al., 2018), ^f Baltic Sea, Germany (Heinemann et al., 2008), ^g Baltic Sea, Gulf of Gdańsk (Szefer and Szefer, 1985), ^h Bay of Bengal, India (Raman and Kumar, 2011), ⁱ Black Sea (Mititelu et al., 2014), ^j Canada (Klein et al., 1996), ^k Cultured (Freitas et al., 2009), ^l Cultured (Heinemann et al., 2011), ^m Cultured (Strasser et al., 2008), ⁿ Cultured (Vander Putten et al., 2000), ^o Cultured (Gordon et al., 1970), ^p Denmark (Ullmann et al., 2018), ^r England (Price and Pearce, 1997), ^s Canada, estuary (Thomas and Bendell-Young, 1998), ^t Hong Kong (Zhang et al., 2015), ^u Irish Sea, UK (Bourget, 1974), ^v Spain (Puente et al., 1996), ^w North Sea, UK (Freitas et al., 2016), ^x Portugal (Ponnurangam et al., 2018), ^y Portugal (Ricardo et al., 2015), ^z S-W coast of India (Ashraf et al., 2007)



1550

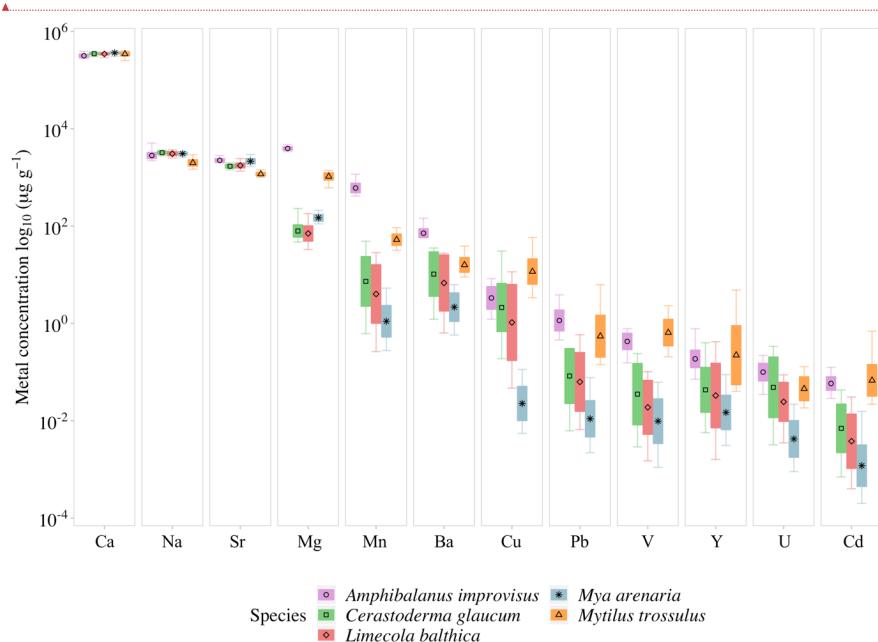
Figure 2. The location of the study area: the Baltic Sea (A) and the Gulf of Gdańsk (B) marked by black rectangles. Figure C shows the sampling stations as black circles (see Table 1 for station details). The grey lines indicate 20 m isobaths.





1560 **Figure 2.** The investigated species photographed *in situ*, clams: (1) *Cerastoderma glaucum*, (2) *Mya arenaria*, and (3) *Limecola balthica*, mussels (4) *Mytilus trossulus* and barnacle (5) *Amphibalanus improvisus*.

— **sformatowane:** Czcionka: 10 pkt, Nie Pogrubienie, Nie Kursywa



1565 **Figure 3.** The distribution of logarithmically transformed mean elemental concentrations in shells of studied species (grouped by colour). The boxplots represent standard deviations ($\pm 1\text{SD}$) around means, and whiskers indicate the minimum and maximum concentrations for each studied species.

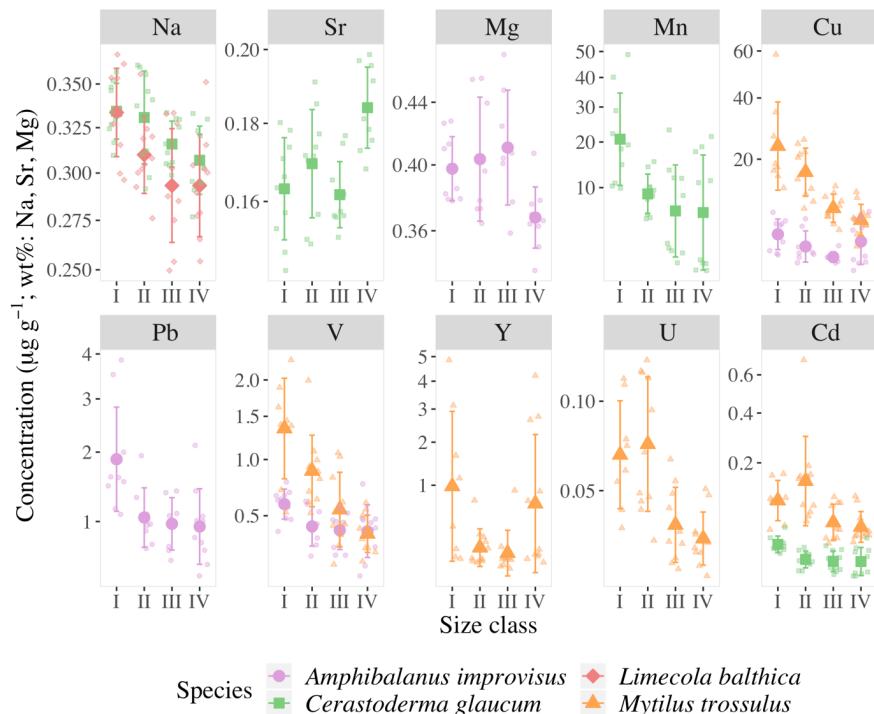
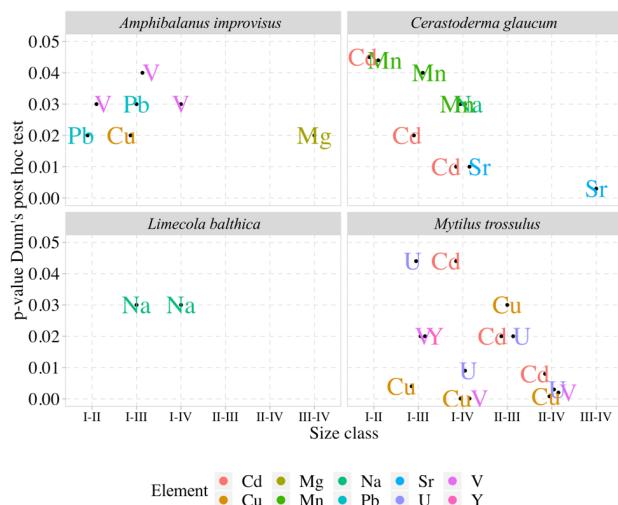


Figure 4. The mean concentrations of **elements** with statistically significant differences between the four size classes (for size class details see Table 2) in the shells of studies species, error bars indicate standard deviations ($\pm 1\text{SD}$). Concentrations of Mn, Cu, Pb, Cd, V and Y are presented in square root scale.

— **usunięto:** metals

◀ **Sformatowano:** Normalny



1575 **Figure 5.** Pairwise comparisons of elements in the shells of studied species with statistically significant differences ($p < 0.05$) between size classes (for size class details see Table 2). — **usunięto:** metals