The patterns of elemental concentration (Ca, Na, Sr, Mg, Mn, Ba, Cu, Pb, V, Y, U and Cd) in shells of invertebrates representing different CaCO$_3$ polymorphs: a case study from the brackish Gulf of Gdańsk (the Baltic Sea)

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Abstract. The shells of calcitic arthropod *Amphibalanus improvisus*, aragonitic bivalve *Cerastoderma glaucum*, *Limecola balthica*, *Mya arenaria* and bimineralic 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.

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 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.

1 Introduction

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 CaCO$_3$ 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 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

40   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

45   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).

50   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 McConnaughey, 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

55   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

60   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

65   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 $CaCO_3$

70   (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 $CaCO_3$

75   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 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 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 biomineralogical precipitation of aragonite (Allison et al., 2001). Many studies have demonstrated a clear correlation between the concentration of Sr in the hard parts and precipitation of the aragonite layer (Iglikowska 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).

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 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 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 that the rate of trace element uptake increases as mussel filtration rate increases (Janssen and Scholtz, 1979).

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

120   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*, bimineralic 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

125   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 elemental variation patterns of skeletons formed in the area. Brackish waters affect the activity and speciation of

130   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 of living organisms (Urey et al., 1951).

2 Material and methods

2.1 Study area

135   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 minimal tidal amplitudes. The hydrophysical parameters of the gulf are mostly driven by the temperate climate

140   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 in the estuary of 1080 m³ s⁻¹, which varies seasonally from 250 to 8000 m³ s⁻¹ and has a maximum in spring

145   (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 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

150   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 the Gulf of Gdańsk (Damrat et al., 2013). Because of the local conditions, mainly the limited water exchange,

155   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).

       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 ($\Omega =$

160     $\frac{[Ca^{2+}] \times [CO_3^{2-}]}{K_{sp}^*}$, 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).

       The community of calcifiers from the Gulf of Gdańsk is characterized by the dominance of benthic filter feeders and deposit feeders (Kruk-Dowgiałło and Dubrawski, 1998). These organisms exploit their growth

165   potential during the productive seasons of the year when the availability of suspended matter, mainly phytoplankton is the highest (Pierscieniak 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

170   Seas, the Caspian Lake, and the low-salinity Baltic Sea. It is a euryhaline species living in salinities between 4 and 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

175   to 4 years, achieving a height of 27 mm (Żmudziński, 1990).

       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

180   organic particles and microinvertabrates 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).

       The clam *Limecola balthica* (Mollusca, Bivalvia, Fig. 2.3) lives in the northern parts of the Atlantic and

185   Pacific oceans, in Subarctic and European waters from southern France to the White Sea and Pechora Sea, 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

190   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).

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; Żmudziński, 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; Lauringson et al., 2014; Rainbow et al., 2004). The shell of *M. trossulus* is bimineralic 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).

The barnacle *Amphibalanus improvisus* (Arthopoda, 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 (Żmudziński, 1990). It has a conical shell composed of six fused calcite plates (Weidema, 2000).

2.3 Sample collection and preparation

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.

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-Piorewicz 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

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 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 l^{-1} Ca, 0.01 – 5 mg l^{-1} Na, and 0.001 – 0.5 mg l^{-1} 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 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 JDo-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 ± 1 SD of the reported values (Imai 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 solution components and Ca from the samples.

The accuracy and reproducibility were checked by analyses of JLs-1 and JDo-1 before and after every batch of samples. The results obtained for all elements were within ± 2.5 SD of the recommended values (Imai et 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 (Piwoni-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 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 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.

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*, *Limecola balthica*, *Mytilus trossulus* and *Amphibalanus 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 $316,000 \pm 26,000$ $\mu g\ g^{-1}$ (mean ± standard deviation) in *A. improvisus* to $363,000 \pm 18,000$ $\mu g\ g^{-1}$ in *M. arenaria*. The rest of elements had mean concentrations in shells below 4,000 $\mu g\ g^{-1}$. In mussels most concentrated were Na>Sr>Mg, while in barnacles Mg>Na>Sr. The concentration of Na ranged, on average, from $2,000 \pm 300$ $\mu g\ g^{-1}$ in *M. trossulus* to $3,200 \pm 200$ $\mu g\ g^{-1}$ in *C. glaucum*. In *A. improvisus,* Mg ($3,940 \pm 320$ $\mu g\ g^{-1}$) was the dominant after Ca ($3,940 \pm 320$ $\mu g\ g^{-1}$), while mean concentration of Sr ($2,250 \pm 1,900$ $\mu g\ g^{-1}$) was lower than Na ($2,850 \pm 470$ $\mu g\ g^{-1}$). Clams *C. glaucum* (Mg: 80 ± 30 $\mu g\ g^{-1}$, Sr: $1,700 \pm 140$ $\mu g\ g^{-1}$, Na: $3,220 \pm 210$ $\mu g\ g^{-1}$), *M. arenaria* (Mg: 150 ± 20 $\mu g\ g^{-1}$, Sr: $2,160 \pm 280$ $\mu g\ g^{-1}$, Na: $3,080 \pm 210$ $\mu g\ g^{-1}$) and *L. balthica* (Mg: 80 ± 30 $\mu g\ g^{-1}$, Sr: $1,770 \pm 210$ $\mu g\ g^{-1}$, Na: $3,100 \pm 300$ $\mu g\ g^{-1}$) 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 $1,060 \pm 170$ $\mu g\ g^{-1}$ and $1,170 \pm 100$ $\mu g\ g^{-1}$, respectively. This species also was characterized by concentration of Na ($2,010 \pm 310$ $\mu g\ g^{-1}$) 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 ± 1.0 $\mu g\ g^{-1}$ in *M. arenaria* to 620 ± 155 $\mu g\ g^{-1}$ 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 bimineralic 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,

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. 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

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 µg 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 µg g^{-1} of Ca in shell (Table 4), the results above 400,000 µg g^{-1} probably being caused by analytical bias.

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, and within the ranges typical for a given species. Clams, that precipitate fully aragonitic shells and bimineralic 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 bimineralic 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

345   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 $\mu g\ g^{-1}$) 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 ± 190 $\mu g\ g^{-1}$) supports these findings, suggesting that barnacle precipitation process differs from other marine organisms. Carpenter and Kyger (1992)

350   concluded that Sr is a sensitive indicator of precipitation rate this may explain the elevated Sr concentrations in barnacles. The shell increment in barnacles in 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

355   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

360   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

365   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.

        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 (Harriss, 1965; Davis et al., 2000; Finch and Allison, 2007; Dalbeck, 2008;). In our study, shell lattices of mussels and barnacles

370   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

375   levels in bimineralic *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.

380   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)

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 Goulletquer, 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

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. 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). 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 environmental biomonitors 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, 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 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 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 relationships between the shell sizes. Few trace elements in the shells of *A. improvisus* (Y, U and Cd), *M. trussulus* (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

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).

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 ($2,010 \pm 310$ µg g^{-1} – $3,220 \pm 210$ µg g^{-1}) and Sr ($1,170 \pm 100$ µg g^{-1} – $2,250 \pm 190$ µg 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 ($3,940 \pm 320$ µg g^{-1} – 80 ± 30 µg 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 at 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

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 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 μm) 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 (Pruysers 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.

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 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 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 μm fraction and decrease with increasing both fraction size and depth of the sediment. This may by 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 the sediment properties belong to factors controlling concentration of trace elements in the shells.

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 ± 15.0 μg g^{-1}, Ba: 17.0 ± 6.70 μg g^{-1}) than in barnacles (Mn: 625 ± 160 μg g^{-1}, Ba: 73.0 ± 20.1 μg 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 μg g^{-1}, while that in *A. improvisus* ranged from 187 to 307 μg 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

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 biomineralization 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 bimineralic *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.

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

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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
1060 collection.

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

[a] Based on Uścinowicz (2011)

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

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

[a] Based on Żmudziński (1990)

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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).

Barnacle *Amphibalanus improvisus*: CALCITE

Element (El)	Sample size, n	Mean conc. [$\mu g\,g^{-1}$]	SD	Weight ratio El/Ca [arbitrary]	Molar ratio El/Ca [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
Element (El)	Sample size, n	Mean conc. [$\mu g\,g^{-1}$]	SD	Weight ratio El/Ca [arbitrary]	Molar ratio El/Ca [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
Element (El)	Sample size, n	Mean conc. [$\mu g\,g^{-1}$]	SD	Weight ratio El/Ca [arbitrary]	Molar ratio El/Ca [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

Element (El)	Sample size, n	Mean conc. [µg g⁻¹]	SD	Weight ratio El/Ca [arbitrary]	Molar ratio El/Ca [mmol/mol]
U	40	0.03	0.024	0.0001	0.02
Cd	37	0.01	0.008	0.00002	0.01

Element (El)	Sample size, n	Mean conc. [µg g⁻¹]	SD	Weight ratio El/Ca [arbitrary]	Molar ratio El/Ca [mmol/mol]
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 (El)	Sample size, n	Mean conc. [µg g⁻¹]	SD	Weight ratio El/Ca [arbitrary]	Molar ratio El/Ca [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
	[µg g⁻¹]				[µg g⁻¹]					
Amphibalanus improvisus [a]	316000	2850	2250	3940	625	73	3.90	1.34	0.11	0.06
Balanus sp. [o]		1600 – 5000			80 – 3800					
Balanus sp. [z]					39 – 313			<18.2	0 – 1.48	
Balanus balanoides [d]					77					

Species										
Amphibalanus reticulatus [h]				1000 – 2000						
Cerastoderma glaucum [a]	348000	3220	1700	80	11.9	15.0	4.08	0.140	0.011	0.096
Cerastoderma glaucum [g]	400000			280	26		0.16	17	0.015	
Cerastoderma edule [r]								1.11 – 4.42		0.03 – 4.94
Limecola balthica [a]	345000	3100	1770	80	7.9	13.0	3.0	0.14	0.007	0.034
Macoma (=Limecola) balthica [s]								0.68		
Mya arenaria [a]	363000	3080	2160	150	1.40	2.60	0.031	0.015	0.002	0.006
Mya arenaria [i]							9.5		0.05	
Mytilus trossulus [a]	344000	2010	1170	1060	54	17	14	1	0.091	0.053
Mytilus trossulus [j]			1185							
Mytilus trossulus [g]	310000			1400	120		0.16	24	0.029	
Mytilus trossulus [g]	420000			1700	90		<0.02	5.2	0.009	
Mytilus edulis [e]			970	970	24.2	3.31	<dl	0.321		0.007
Mytilus edulis [x]			862	856	0.13	0.26	<dl	0.385		0.0009
Mytilus edulis [n]	398000									
Mytilus galloprovincialis [v]							9.54	1.19		
Mytilus galloprovincialis [i]							10	7.3		
Mytilus galloprovincialis [b]	360000	2500 – 4000	500 – 800	900 – 1400	<160	0 – 3.8	0 – 5.5	0 – 5.0	0 – 3.0	

Shell weight ratio element/Ca	Na/Ca	Sr/Ca	Mg/Ca	Mn/Ca	Ba/Ca	Cu/Ca	Pb/Ca	Cd/Ca	U/Ca
	[arbitrary]			[mg/g]					
Amphibalanus improvisus [a]	0.012	0.009	0.007	1.978	0.231	0.012	0.0042	0.0003	0.0002
Amphibalanus amphitrite [t]		0.01							
Balanus balanoides [u]	0.009	0.009	0.01	0.0005					
Balanus balanoides [u]	0.010	0.007	0.01	0.001					
Balanus balanoides [u]	0.017	0.008	0.01	0.0003					

Shell molar ratio element/Ca	Na/Ca	Sr/Ca	Mg/Ca	Mn/Ca	Ba/Ca	Cu/Ca	Pb/Ca	Cd/Ca	U/Ca
	[mmol/mol]			[µmol/mol]					
Amphibalanus improvisus [a]	15.7	3.3	20.5	1438	67.3	7.71	0.82	0.070	0.057
Amphibalanus improvisus [p]		4.20	20.55	0.71					
Balanus balanus [c]	20.49	3.85	14.83	0.077	0.055				
Mya arenaria [a]	14.8	2.72	0.68	2.80	2.09	0.053	0.008	0.002	0.003
Mya arenaria [m]		2.1 – 2.45	1.0 – 1.9	0.06 – 0.14	1.7 – 3.7		0.002 – 0.005		
Mytilus trossulus [a]	10.16	1.55	5.07	114.16	14.40	25.44	0.56	0.094	0.026
Mytilus edulis [w]				40 – 190					
Mytilus edulis [l]		1.1 – 1.6	2.5 – 6.0						
Mytilus edulis [f]		1.92	8.67						

Mytilus edulis [k]		1.34 – 1.5	5.1 – 7.86	13 – 35					
Mytilus edulis [n]		0.7 – 1.5	2.5 – 12.0	100 – 450	20 – 70		0.2 –1.3		
***Cerastoderma glaucum* [a]**	16.1	2.23	0.378	24.9	12.6	7.3	0.078	0.011	0.046
Cerastoderma edule [y]		1.6	1.5	20 – 60	15		0.01		

1070 <dl – below the detection limit

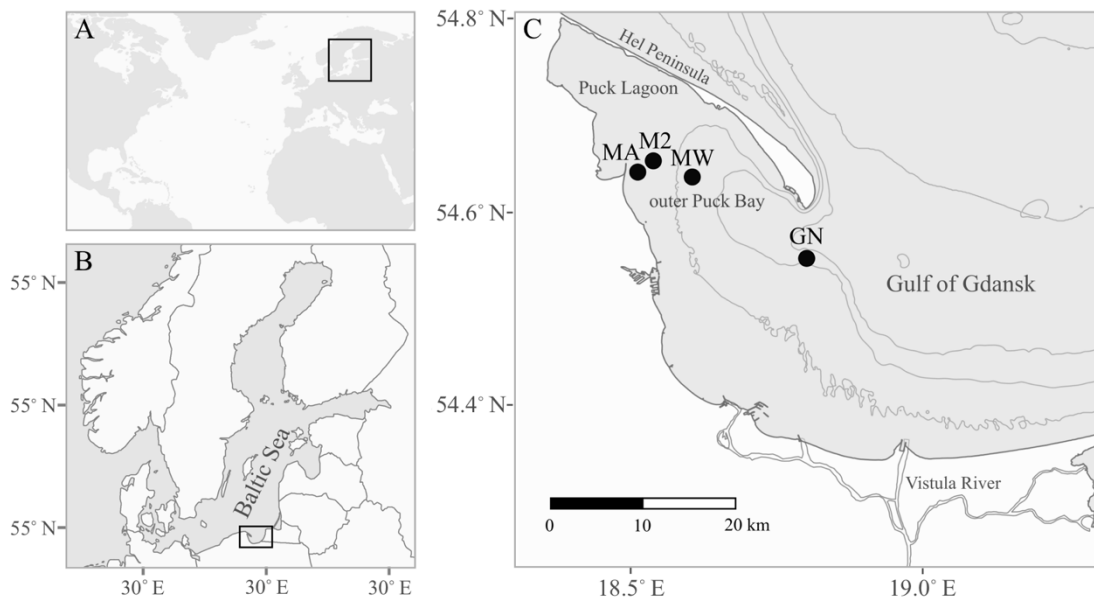
[a] Baltic Sea, Gulf of Gdańsk (this study), [b] Adriatic Sea, Croatia (Rončević et al., 2010), [c] Arctic (Iglikowska et al., 2018), [d] Atlantic, USA (Blanchard and Chasteen, 1976), [e] North Sea, Germany (Ponnurangam et al., 2018), [f] Baltic Sea, Germany (Heinemann et al., 2008), [g] Baltic Sea, 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 1075 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)

1080

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.

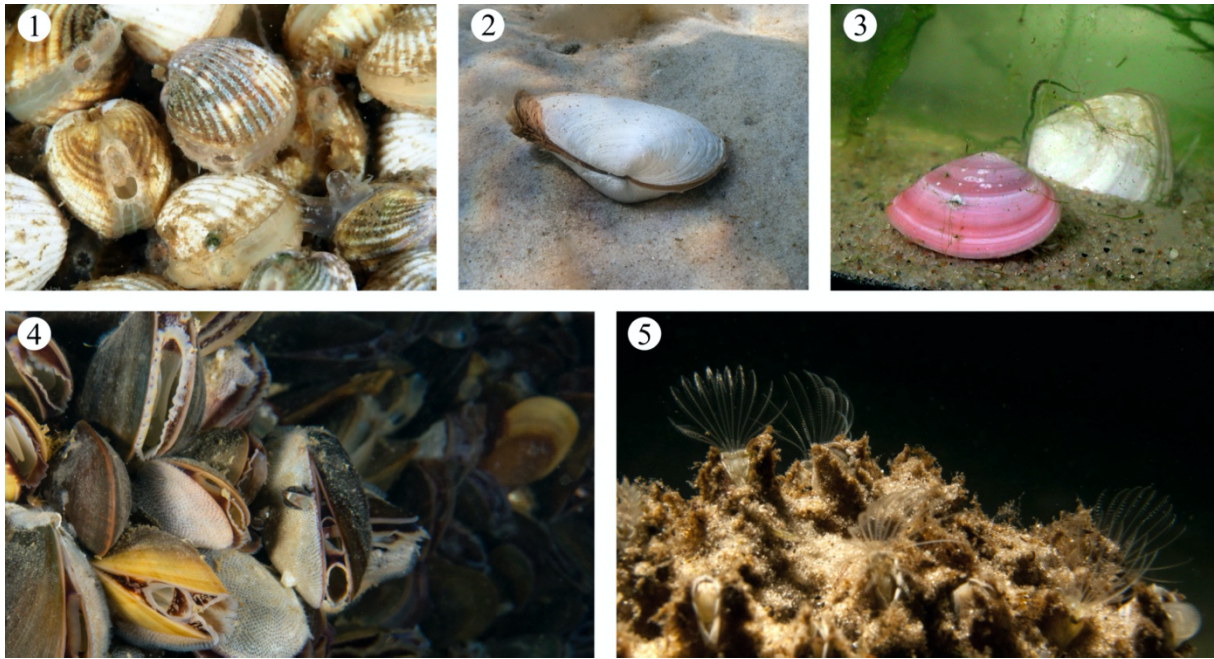



Figure 2. The investigated species photographed *in situ*, clams: (1) *Cerastoderma glaucum*, (2) *Mya arenaria*, and (3) *Limecola balthica*, mussels (4) *Mytilus trossulus* and barnacle (5) *Amphibalanus improvisus*.

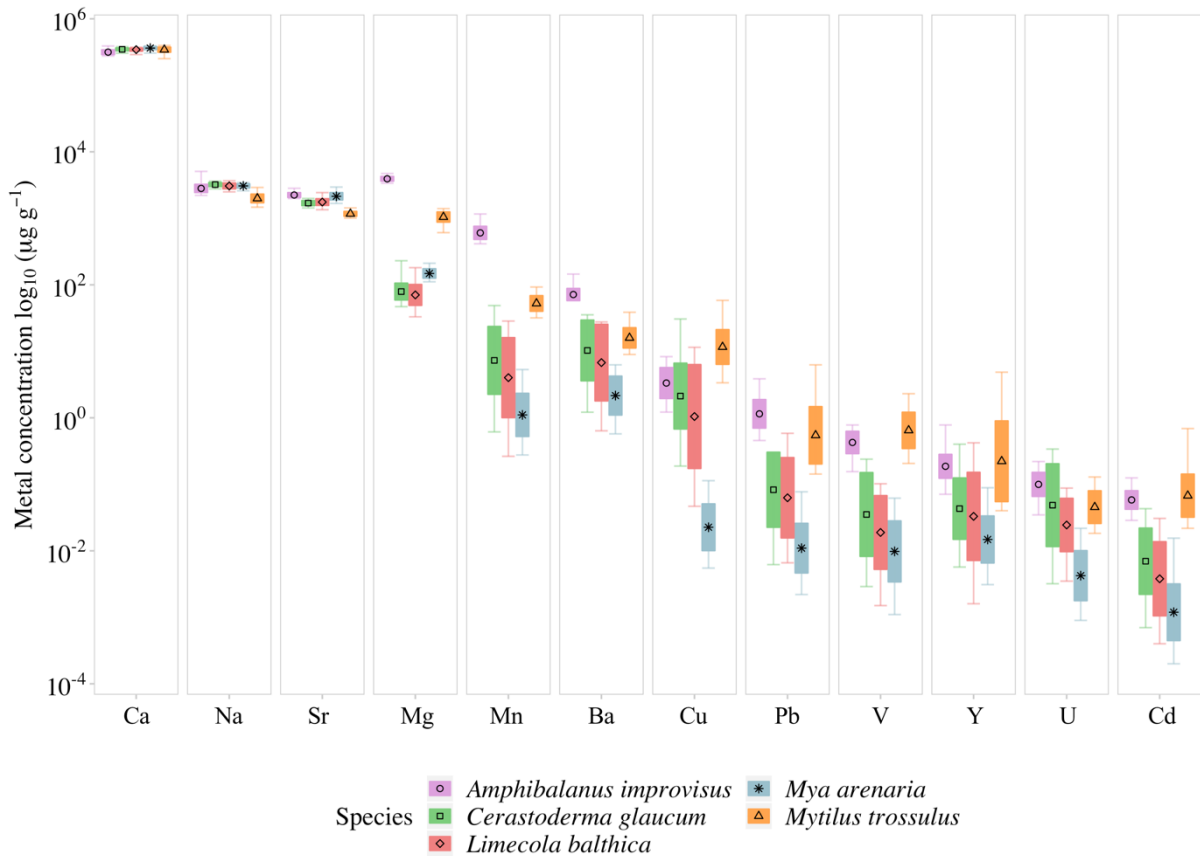



Figure 3. The distribution of logarithmically transformed mean elemental concentrations in shells of studied species (grouped by colour). The boxplots represent standard deviations (±1SD) around means, and whiskers indicate the minimum and maximum concentrations for each studied species.

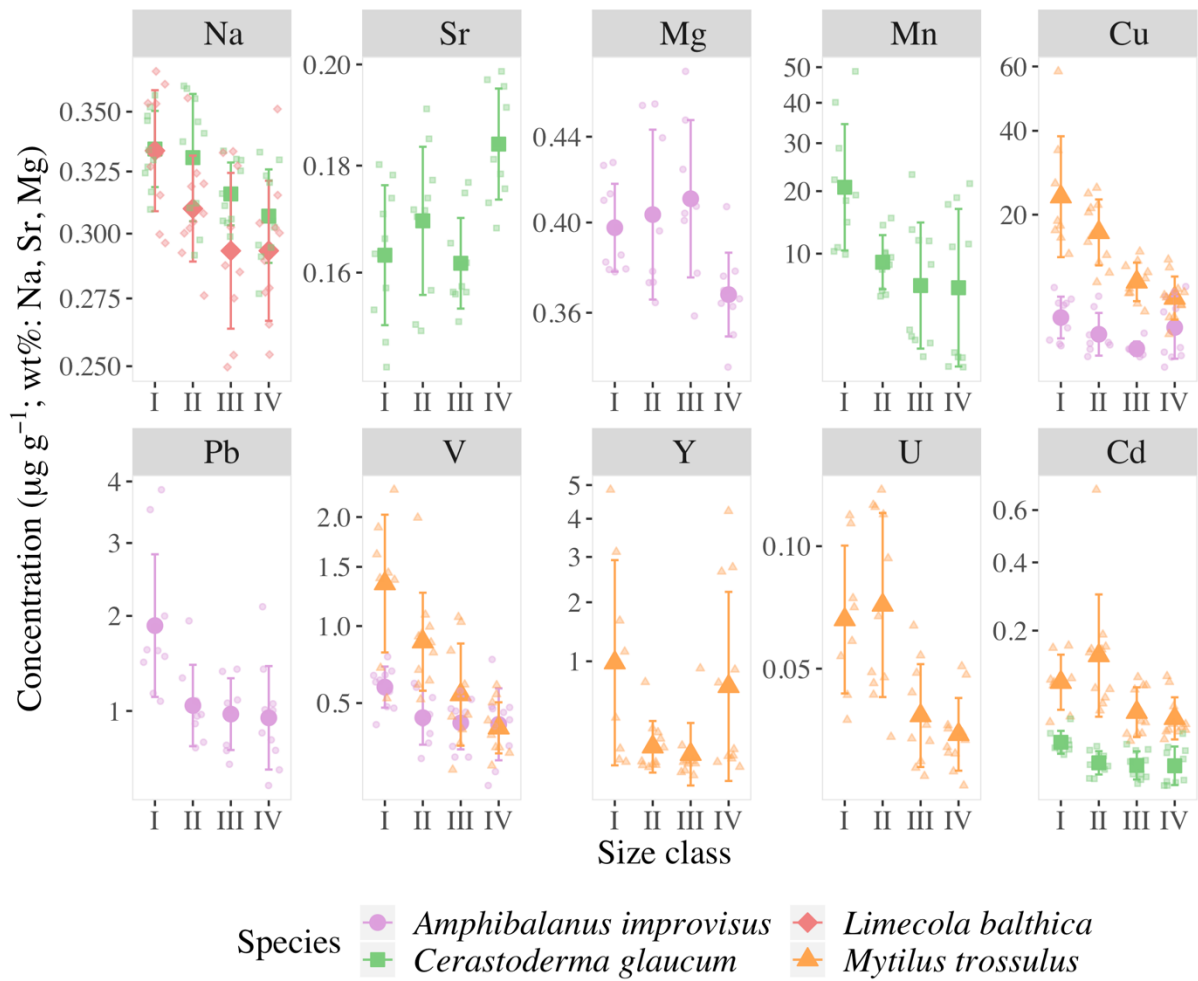



Figure 4. The mean concentrations of elements with statistically significant differences between the four size classes (for size class details see Table 2) in the shells of studies species, error bars indicate standard deviations (±1SD). Concentrations of Mn, Cu, Pb, Cd, V and Y are presented in square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

1095

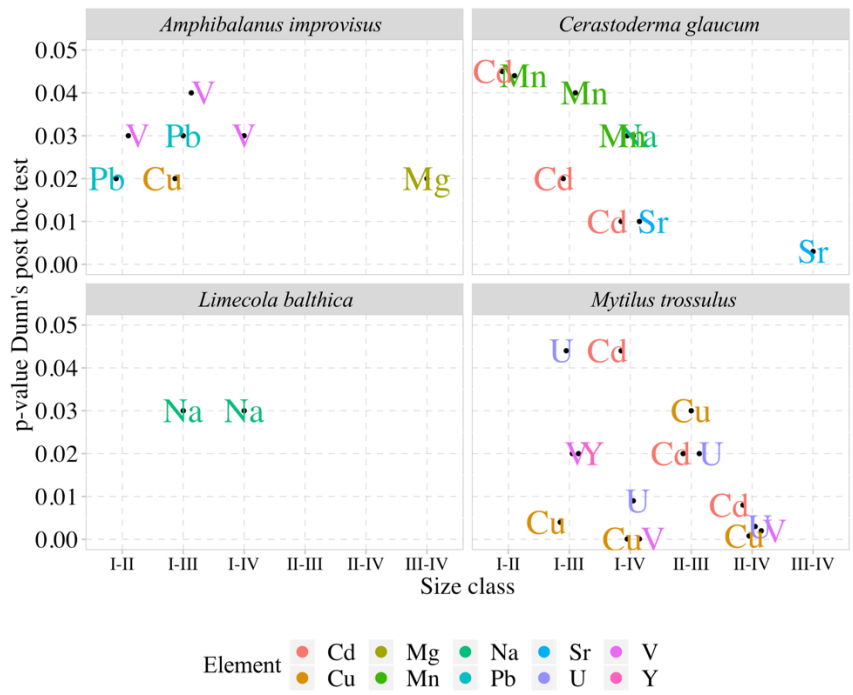



Figure 5. Pairwise comparisons of elements in the shells of studied species with statistically significant differences ($p < 0.05$) between size classes (for size class details see Table 2).