



# Species-specific responses of macrophyte production to the increasing CO<sub>2</sub> environment with potential ecosystem implications involved in the Baltic Sea

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## Abstract

Macrophytes vary in their ability to utilize carbon in the form of HCO<sub>3</sub><sup>-</sup> and/or CO<sub>2</sub> for photosynthesis. Some functional groups that solely use CO<sub>2</sub> for photosynthesis could receive competitive advantages from the predicted increase in CO<sub>2</sub> compared to groups with efficient carbon acquisition strategies of HCO<sub>3</sub><sup>-</sup>. The aim of this study was to identify carbon use strategies in the common macrophytes (macroalgae, charophytes, seagrass, and other angiosperms) that represent a broad range of functional traits to CO<sub>2</sub> concentrations in the northeastern Baltic Sea. Mechanistic assessment of the carbon physiology of macrophytes was used to predict productivity and competitive interactions between different functional groups under future climate. Carbon use strategies in macrophytes were determined by analysing the carbon isotopes ( $\delta^{13}\text{C}$ ), pH drift experiments, and photosynthesis versus dissolved inorganic carbon. In addition, habitat mapping data was used to interpret the potential implications of the elevated CO<sub>2</sub> to this coastal ecosystem. The results suggested that the primary productivity of macrophytes is often limited by carbon availability, and the increasing CO<sub>2</sub> concentrations in the brackish Baltic Sea are expected to enhance photosynthetic production. While all species tested showed evidence of carbon concentrating mechanisms (CCMs), differential levels of CCM activity indicate varying levels of competitive fitness in a future high-CO<sub>2</sub> environment. Overall, macrophytes which inhabit the shallowest and deepest parts of the vegetated zone are expected to experience physiological benefits under future CO<sub>2</sub> conditions, while intermediate communities dominated by the perennial brown alga *Fucus vesiculosus* may experience loss of fitness. These fitness differences have implications for competitive interaction and species range under future climate.

**Keywords** Baltic Sea · Brackish water · Carbon dioxide · Carbon physiology · Macrophytes · Ocean acidification

## Introduction

Changing seawater carbon chemistry driven by increasing atmospheric carbon dioxide (CO<sub>2</sub>) is likely to have broad implications for marine ecosystems and the services that they provide (IPCC 2022). As suggested by the term “Ocean Acidification”, research to date on elevated ocean carbon has predicted predominantly negative consequences for calcifying organisms (e.g. Kuffner et al. 2008; Kroeker et al. 2013; Wittmann and Pörtner 2013; Cornwall et al. 2014; Bednaršek et al. 2019). For non-calcifying macroalgae and seagrasses, an increase in CO<sub>2</sub> concentration has often been shown to enhance photosynthesis and boost primary productivity (Koch et al. 2013; Kram et al. 2016). However, the possible impacts of the predicted ~200% increase in CO<sub>2</sub> concentrations over the next 100 years on the photosynthesis

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of foundation primary producers have received less attention (IPCC 2022). In addition to elevated carbon concentrations in seawater, organisms will also be affected by a shift in the relative speciation of available inorganic carbon (Koch et al. 2013; Wittmann and Pörtner 2013; van der Loos et al. 2019). Carbon dioxide is the primary substrate for carbon fixation by RUBISCO (Beer et al. 2014) and an increase in this energetically inexpensive form has the potential to enhance primary productivity broadly (Hepburn et al. 2011; Koch et al. 2013).

The majority of submerged macrophytes have  $\text{CO}_2$  concentrating mechanisms (CCMs) and the ability to utilise the more abundant  $\text{HCO}_3^-$  (~90% under current pH) as the carbon source for photosynthesis (Giordano et al. 2005). Carbon concentrating mechanisms act mainly via the direct uptake of  $\text{HCO}_3^-$  or its conversion into  $\text{CO}_2$  through the action of internal and/or external carbonic anhydrase (Giordano et al. 2005). There are different types of CCMs present in macrophytes with varying energetic performances (Giordano et al. 2005; Cornwall et al. 2017); this can drive differential organismal responses to elevated carbon. Functional groups include CCM species with a low affinity for DIC (carbon-limited CCM species), CCM species that can downregulate  $\text{HCO}_3^-$  use for photosynthesis at high  $\text{CO}_2$  concentrations, and CCM species with high affinity for  $\text{CO}_2$  (CCM does not downregulate at high  $\text{CO}_2$ ) (Giordano et al. 2005). Macrophytes that possess CCMs and are capable of utilizing additional  $\text{CO}_2$  will likely benefit from ocean acidification, while species that cannot utilize additional  $\text{CO}_2$  will not gain a photosynthetic advantage from OA. Understanding the carbon use strategies of key macrophyte species is essential in predicting how marine ecosystems will function under increased  $\text{CO}_2$  concentrations (e.g. Hepburn et al. 2011). Appropriate management and protection of key habitat-forming species could reduce the impacts of a changing marine environment.

The photosynthesis of primary producers in coastal waters is most often limited by light (Desmond et al. 2015) and nitrogen availability (Elser et al. 2007). The dissolved inorganic carbon (DIC) concentration in the ocean is around 2.4 mM (Cole et al. 2021) which is generally not considered limiting for photosynthesis. Some earlier studies have shown that macroalgal productivity is not saturated at in situ DIC concentrations (Holbrook et al. 1988; Surif and Raven 1989). In fact, high photosynthetic rates, slow diffusion, and limited mixing often result in situations where DIC is depleted at the cell surface, limiting productivity (Wheeler 1980). This is particularly likely during periods with high light and sufficient nutrients combined with restricted water flow. Dense macrophyte beds can create a hydrodynamic environment of slowed flow and reduced mixing (Hurd 2000), leading to nutrient drawdown (e.g. Stephens and Hepburn 2014) and

localized carbon limitation within the macrophyte community (France and Holmquist 1997). Additional  $\text{CO}_2$  delivery from anthropogenic emissions into carbon-limited systems could broadly influence primary productivity and alter established competitive interactions.

In the Baltic Sea dissolved inorganic carbon is spatially and temporally variable and strongly correlated with salinity and alkalinity (Müller et al. 2016). Moreover, the carbonate system in the Baltic Sea region is also affected by the atmosphere–seawater gas exchange, river runoff, sediments, eutrophication, hydrological processes (upwelling) and biological productivity (Kulinski and Pempkowiak 2012). Broader differences in the characteristics of different water masses can also occur (Müller et al. 2016). The Baltic Sea is characterized by a range of productive benthic coastal ecosystems that typically receive high levels of light and are subjected to extended periods of low water motion. This highly productive system can be viewed as the ideal environment to study the carbon limitation of photosynthesis, particularly during periods of high light and low wind typical in the spring and summer.

The Baltic Sea hosts many macrophyte species that provide food and shelter for numerous plant and animal species and are an important spawning substrate for fish (Kautsky et al. 2017). Moreover, submerged macrophytes have shown a potential to mitigate and adapt to climate change through the uptake and storage of carbon (Kennedy et al. 2010; McLeod et al. 2011; Krause-Jensen and Duarte 2016). So far, macrophyte research in the Baltic Sea has primarily focused on how spatial and temporal patterns of salinity, light, temperature, and nutrient load define the patterns of biomass and productivity of these important primary producers (e.g. Martin et al. 2006; Paalme et al. 2011; Jonsson et al. 2018; Barboza et al. 2019).

Charophytes (*Chara* spp.) are algae with well-developed complex thalli, anchored to sediment by rhizoids, and forming dense beds in shallow sheltered soft-bottom habitats (Schubert and Blindow 2003). Benthic macroalgae dominate in rocky shores habitats in the Baltic Sea (Kautsky et al. 2017). The most important habitat-forming species in shallow-water hard-bottom algal communities in the NE Baltic is bladderwrack *Fucus vesiculosus* (Torn et al. 2006; Jonsson et al. 2018). Fast-growing filamentous macroalgae (e.g. *Cladophora glomerata*, *Ulva intestinalis*, and *Pylaiella littoralis*) are very common in the whole shallow coastal zone (Eriksson and Bergström 2005). Red macroalgae grow as a rule in deeper water, where attached *Furcellaria lumbricalis* is the main habitat-forming species (Bučas et al. 2009). In addition to the attached form, the unique unattached loose-lying red algal community formed primarily by *F. lumbricalis*, in association with *Coccolytus truncatus* inhabits the soft bottom of Kassari Bay (Kersen 2013). *Zostera marina*

is the only seagrass in the NE Baltic, but as one of the most common macrophytes it is regarded as a keystone species on sandy bottoms (Boström et al. 2014). Submerged angiosperms *Myriophyllum spicatum* and *Stuckenia pectinata* are widespread in soft-bottom substrates and often form mixed communities with *Z. marina* (Gustafsson 2013).

In previous work we found that macroalgae in the north-eastern part of the Baltic Sea are expected to respond differentially to elevated carbon (Albert et al. 2020; Pajusalu et al. 2020). The aim of this study was to identify carbon use strategies in the most common macrophytes (macroalgae, charophytes, seagrass, and other angiosperms), representing a broad range of functional traits to CO<sub>2</sub> concentrations in the northeastern Baltic Sea. Mechanistic assessment of the carbon physiology of macrophytes was used to predict productivity and competitive interactions between different functional groups under future climate. Carbon use strategies in macrophytes are determined by the natural abundances of carbon isotopes ( $\delta^{13}\text{C}$ ) (Raven et al. 2002), pH drift experiments (Maberly 1990), and measurements of photosynthesis versus (vs.) dissolved inorganic carbon (P vs. DIC) (Beardall and Roberts 1999). In addition, extensive habitat mapping data was used to advise potential implications of the increased CO<sub>2</sub> concentrations to benthic communities in the northeastern part of the Baltic Sea.

In the current study we predict that DIC limitation would be most severe within sheltered, dense, shallow water charophyte beds (*Chara* spp.) and that species in these habitats would exhibit strong affinities for HCO<sub>3</sub><sup>-</sup>. On the other hand, DIC limitation in shallow-water hard-bottom algal communities dominated by the slow metabolism brown algal

species *Fucus vesiculosus* is likely to be less severe. Fast-growing filamentous macroalgae would respond positively to elevated CO<sub>2</sub>, as this would enhance their photosynthesis in dense macroalgal communities with high-CO<sub>2</sub> demand during the daytime. We predict that red macroalgae inhabiting deeper water would respond positively to elevated CO<sub>2</sub> due to energetic constraints of active carbon uptake in a low-light environment. The responses of angiosperms would be likewise defined by their thallus height and density as well as the exposure of their habitat. The only seagrass in the northeastern Baltic Sea, *Z. marina*, has shorter leaves, and its habitat is less dense compared to its oceanic conspecifics. As its habitat is primarily found in moderately exposed soft bottom areas, responses of *Z. marina* to elevated CO<sub>2</sub> would be similar to hard bottom macroalgal communities.

## Materials & methods

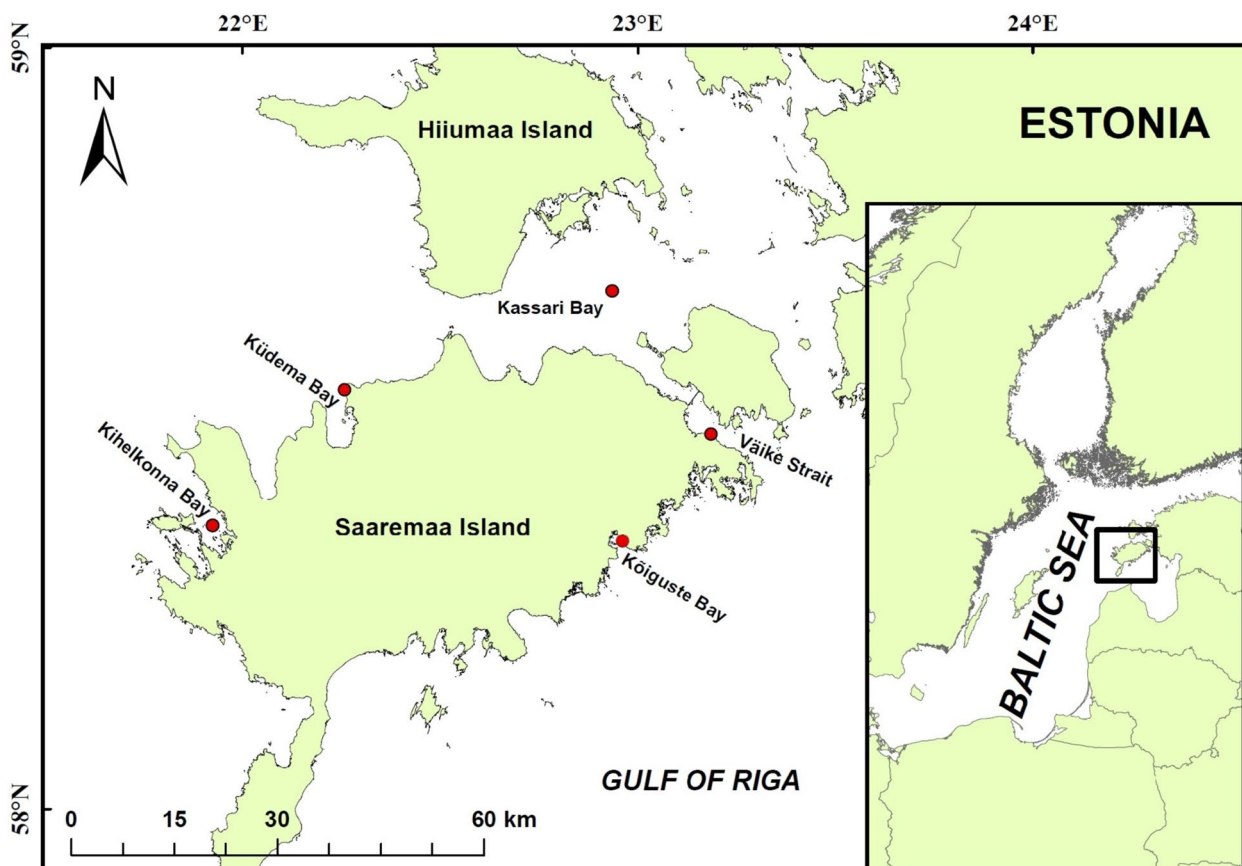
### Studied macrophyte species and collection sites

The study focuses on the most dominant macrophyte species in different benthic communities in the northeastern part of the Baltic Sea (Phytobenthos databases of the Estonian Marine Institute, University of Tartu). For this study, we selected six groups of macrophytes that grow in different habitats throughout the Estonian coastal waters (Table 1).

For laboratory experiments, macrophyte species were collected around Saaremaa Island in the West Estonian Archipelago Sea (northern Baltic Sea) in five different bays in July

**Table 1** Studied macrophyte species and collection sites

Group	Species	Site Name	Coordinates	Collection depth
<i>Chara</i>	<i>Chara aspera</i> Willd	Väike Strait	58.3069°N, 23.1221°E	1.5 m
	<i>Chara connivens</i> Salzm. ex Braun			
	<i>Chara tomentosa</i> L.			
	<i>Chara canescens</i> Loisel			
<i>Fucus</i>	<i>Fucus vesiculosus</i> L.	Küdema Bay	58.56190°N, 22.28082°E	1 m
Filamentous macroalgae	<i>Cladophora glomerata</i> (L.) Kützing	Küdema Bay	58.56219°N, 22.28287°E	0.5 m
	<i>Ulva intestinalis</i> L.			
	<i>Pylaiella littoralis</i> (L.) Kjellm			
Red macroalgae (attached forms)	<i>Furcellaria lumbricalis</i> (Hudson) J.V. Lamouroux	Kõiguste Bay	58.35667°N, 22.98880°E	5 m
	<i>Ceramium tenuicorne</i> (Kützing) Waern			
(unattached forms)	<i>Furcellaria lumbricalis</i> (Hudson) J.V. Lamouroux	Kassari Bay	58.69934°N, 22.94536°E	7 m
	<i>Coccolytus truncatus</i> (Pallas) M.J. Wynne & J.N. Heine			
<i>Zostera</i>	<i>Zostera marina</i> L.	Kihelkonna Bay	58.37997°N, 21.9601°E	3 m
Other angiosperms	<i>Myriophyllum spicatum</i> L.	Kõiguste Bay	58.3710°N, 22.9799°E	1 m
	<i>Stuckenia pectinata</i> (L.) Börner			



**Fig. 1** Location of collection sites in the West Estonian Archipelago, NE Baltic Sea

2018 (Fig. 1; Table 1). All specimens were placed in coolers containing water collected at the site and transported to the lab immediately and cleaned of visible epiphytes prior to the start of the laboratory experiments.

### Photosynthesis vs. DIC curves

The photosynthesis of each macrophyte species was quantified at different dissolved inorganic carbon levels to analyse the carbon acquisition of macrophytes across a range of DIC concentrations. For this experiment five macrophyte species were selected, representing the greatest biomass contributors to their benthic community. After harvesting, the individuals were acclimated in seawater chambers with gentle aeration for 24–72 h before experiments. Before experimental use, all seawater was sterilized using an AquaCristal 18W ultraviolet sterilizer and passed through a 1.2  $\mu\text{m}$  pore size glass microfiber filter (GF/F,  $\varnothing$  47 mm). To maintain the pH throughout each experimental trial and prevent subsequent changes in carbon speciation, seawater was buffered with 15 mM Tris. Since Tris buffer has been known to inhibit the productivity of some macroalgal species, the effect of Tris buffer on each experimental species was tested by measuring

the  $\text{O}_2$  evolution of individuals (Axelsson et al. 2000), and no significant effect at  $p < 0.05$  was found. These tests also indicated that pH within buffered chambers remained stable for the experimental duration.

Inorganic carbon was removed from the Tris-buffered seawater by sparging with nitrogen gas (following the method in Beardall and Roberts 1999). The seawater pH was lowered to 3 with 1 M HCl solution. Acidified seawater was bubbled with nitrogen gas for 2 h and then 1 M NaOH was used to raise pH to the *in-situ* level of 8.2. Species were sealed in 245 mL cylindrical airtight chambers under a photosynthetically saturating irradiance of  $400 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ . The water temperature in chambers was maintained at  $10^\circ\text{C}$  with a flowing water bath. Oxygen levels within each chamber were monitored using Ocean Optics NeoFox-TP oxygen probes connected to Ocean Optics NeoFox Viewer software. A two-point calibration, achieved by bubbling seawater with nitrogen and ambient air, was used to configure the oxygen probes before experimental use. Stir bars within each chamber provided mixing and prevented the formation of that could inhibit photosynthesis.

Before the first addition of the DIC solution, the oxygen level in each chamber was monitored for  $\sim 15$  min to

ensure that the internal carbon stores of the species were depleted and that there was no significant carbon remaining in the chamber. Aliquots of 0.3 M  $\text{NaHCO}_3^-$  solution were injected into the  $\text{O}_2$  evolution chamber at 8–10 min intervals to increase the DIC concentration (working concentrations: 0.2, 0.6, 1.2, 2, 3, 4.5, 7, 10 mM). Following the conclusion of the trial, samples were dried at 60 °C until a constant weight was achieved. Photosynthetic rates of each species at each DIC concentration were normalized to dry weight ( $\mu\text{mol O}_2 \text{ h}^{-1} \text{ gDW}^{-1}$ ) for further analysis.

### pH drift experiment

The pH drift experiment aimed to determine the relative  $\text{HCO}_3^-$  affinity of macrophyte species (e.g. Maberly 1990; Murru and Sandgren 2004; Cornwall et al. 2012). Since carbon speciation is coupled with acidity, macrophytes that exclusively fix  $\text{CO}_2$  (obligate  $\text{CO}_2$  users) cannot raise the pH of water beyond a certain threshold. At pH levels of 9 in seawater ( $\approx 35$  psu and  $2300 \mu\text{mol L}^{-1}$  carbonate alkalinity) and above, inorganic carbon in seawater is primarily available as  $\text{HCO}_3^-$  and any trace amounts of  $\text{CO}_2$  still present are too low to support normal photosynthetic activity for obligate  $\text{CO}_2$  users. Due to differences in salinity and DIC availability between the seawater and the brackish water used in this study, a revised pH compensation point was calculated from data from the sites using the R package *seacarb* (Gattuso et al. 2022). In this study, the pH compensation point was taken to be 9.2 for brackish water. The pH drift method is a simple and effective way of interrogating macrophyte carbon physiology.

Approximately  $\sim 0.5$ – $0.6$  g wet weight section was cut from each field species and acclimatised for 24 h in tanks of sterile filtered seawater at ambient temperature. Each replicate ( $n = 3$  per species) was sealed into an air-tight 60 mL clear plastic chamber filled with seawater at pH 8.15 and placed onto a shaker table set to 70 rpm. The location of each container on the shaker table was randomized and specimens were maintained under a continuous irradiance of  $65 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$  at 15 °C for the duration of the experiment.

Measurements of  $\text{pH}_{\text{NBS}}$  (National Bureau of Standards scale) in the chambers were recorded at 24, 32, and 48 h. After the final timepoint, species were removed, and containers were left open for 48 h to allow re-equilibration with the atmosphere. At this time, pH was measured again to test for the effect of macrophyte exudates on seawater pH. All pH readings were taken with a Mettler Toledo InLab Expert Pro-ISM-IP67 pH-electrode (accuracy:  $\pm 0.001$  and resolution:  $\pm 0.002$ ) connected to a Mettler Toledo model Seven2Go pro S8 pH/Ion meter and was calibrated with NBS buffers.

### Carbon isotope ( $\delta^{13}\text{C}$ ) analysis

Carbon isotope ( $\delta^{13}\text{C}$ ) tissue analysis was conducted on macrophyte species ( $n = 3$  per species) to determine each species' dependency on diffusive  $\text{CO}_2$  supply vs. carbon concentrating mechanism (CCM) for carbon acquisition. In general,  $\delta^{13}\text{C}$  values below  $-30\text{‰}$  indicate a reliance on diffusive  $\text{CO}_2$  supply and the absence of a functional CCM. Values of  $\delta^{13}\text{C}$  above  $-10\text{‰}$  indicate the presence of an active CCM. Macrophytes with  $\delta^{13}\text{C}$  tissue values that fall between  $-30$  and  $-10\text{‰}$  are likely to have a combination of carbon uptake methods at their disposal (Raven et al. 2002).

Macrophyte species were cleaned of visible epiphytes and then dried at 60 °C until a constant weight was achieved. A mortar and pestle were used to grind dried species to a fine powder which was stored in microcentrifuge tubes until analysis. To prevent cross-contamination, mortar and pestle were cleaned with acetone between species. For analysis, 1 mg of sample was weighed into capsules and processed using an elemental analyzer (FlashEA 1112 HT, Thermo Scientific) interfaced through a ConFlo IV dilutor device (Thermo Scientific) with an isotope ratio mass spectrometer (Delta V Plus, Thermo Scientific). The C isotope composition is reported as per mill respective to Vienna Pee Dee Belemnite (V-PDB) and calibrated using international IAEA standards IAEA-CH-3 and IAEA-CH-6. Long-term reproducibility precision and accuracy were  $\pm 0.1\text{‰}$ .

### Statistical methods

For the P vs. DIC experiment statistical analysis was conducted using the R statistical software platform (R Core Team, 2017). The Michaelis–Menten curve (Johnson and Goody 2011) was fitted to plots of photosynthetic rate vs. DIC concentration. The Michaelis–Menten equation is  $P = P_{\text{max}} / \text{DIC} + K_{0.5}$ , where  $P_{\text{max}}$  is the point at which the maximum photosynthetic rate of the organism is reached, and  $K_{0.5}$  is the concentration of DIC at which the photosynthetic rate of the organism is half of  $P_{\text{max}}$  (Johnson and Goody 2011). A maximum likelihood, non-linear mixed effects modelling approach, using the lme4 package in R (Bates et al. 2015) was used. This approach allowed a single model to be used, whilst accounting for species-level (fixed factor) and individual-level (random factor, replicate incubation id) variability in  $P_{\text{max}}$  and  $K_{0.5}$ . Within-species comparisons of  $P_{\text{max}}$  and  $K_{0.5}$  were made using simultaneous t-tests, using the R package multcomp (Hothorn et al. 2008). For the pH drift experiment, Kruskal–Wallis H test was used to analyse differences in pH compensation points (48-h values) among macrophyte species using the Statistica (TIBCO Software Inc.) version 13. Spearman's Rank-Order correlation was conducted to find the relationship between

pH compensation points and  $\delta^{13}\text{C}$  values of studied species. For all statistical analyses, a probability of 0.05 was used to determine statistical significance.

Published maps of macrophyte species obtained from an open-source data PlanWise4Blue portal (<https://gis.sea.ee/adrienne>) allowed us to assess the potential implications of the elevated  $\text{CO}_2$  environment to the coastal ecosystem of the Baltic Sea.

## Results

### Carbon physiology

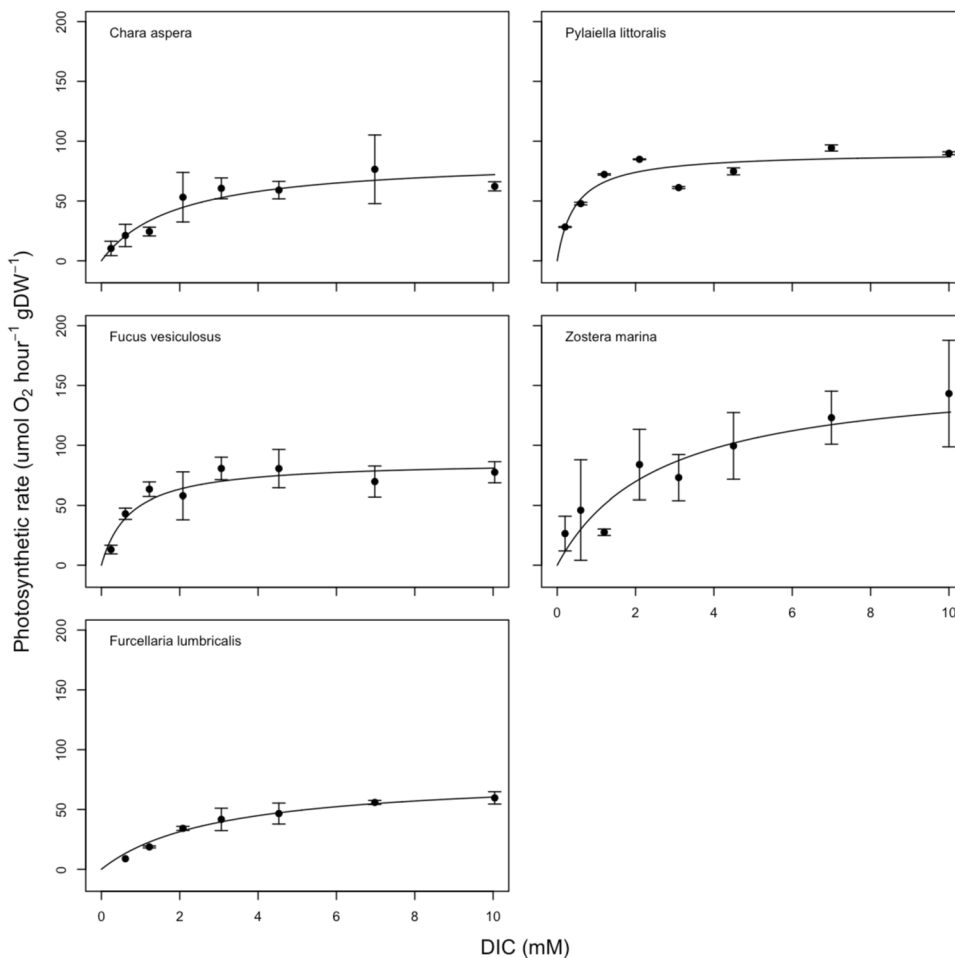
*Zostera marina* had significantly higher  $P_{\text{max}}$  than *C. aspera* (*post-hoc* test;  $p=0.040$ ), *F. vesiculosus* ( $p=0.020$ ), and *P. littoralis* ( $p=0.031$ ), but not *F. lumbricalis* (unattached) ( $p=0.057$ ) (Fig. 2; Table 2). *Zostera marina* had higher  $K_{0.5}$  compared to *F. vesiculosus* ( $p=0.047$ ) and *P. littoralis* ( $p=0.006$ ). No other statistically significant differences in  $P_{\text{max}}$  or  $K_{0.5}$  were observed.

**Table 2** The half-saturation constant ( $K_{0.5}$  [DIC]) and maximum photosynthetic rates ( $P_{\text{max}}$ ) of *C. aspera*, *F. vesiculosus*, *F. lumbricalis* (unattached), *P. littoralis*, and *Z. marina*  $\pm$  SE ( $n=3$  per species)

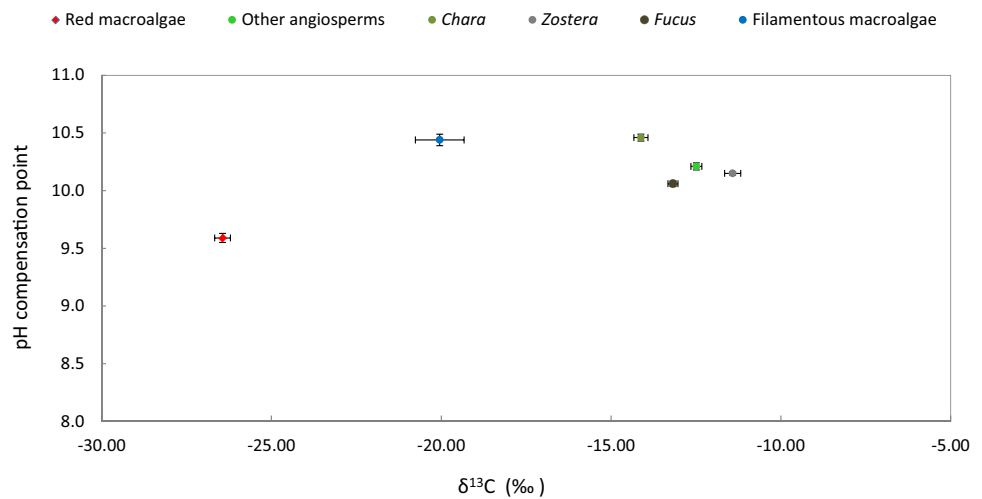
	$K_{0.5}$ [mM DIC]	$P_{\text{max}}$ ( $\mu\text{mol O}_2 \text{ h}^{-1} \text{ gDW}^{-1}$ )
<i>Chara aspera</i>	$1.92 \pm 0.87$	$85.78 \pm 18.3$
<i>Fucus vesiculosus</i>	$0.74 \pm 0.32$	$86.88 \pm 15.0$
<i>Furcellaria lumbricalis</i>	$3.00 \pm 1.90$	$78.44 \pm 23.5$
<i>Pylaiella littoralis</i>	$0.46 \pm 0.26$	$90.81 \pm 14.6$
<i>Zostera marina</i>	$2.62 \pm 0.59$	$161.15 \pm 19.1$

The results from the pH drift experiments showed that all studied species ( $n=3$  per species) within 6 groups raised pH above 9.2 (Fig. 3), suggesting that they can all use  $\text{HCO}_3^-$  for photosynthesis. pH compensation points ranged between 9.31 and 10.51 for the studied species. Red macroalgae did exhibit a significantly lower pH compensation point than filamentous algae (Kruskal Wallis H test,  $p<0.001$ ) and *Chara* ( $p<0.001$ ); however, there was no significant difference compared to other studied macrophyte groups ( $p>0.05$ ) (Fig. 3). *Chara* and filamentous algae had

**Fig. 2** The photosynthetic rate of *C. aspera*, *F. vesiculosus*, *F. lumbricalis* (unattached), *P. littoralis*, and *Z. marina* ( $n=3$  per species) at different concentrations of dissolved inorganic carbon (mM)



**Fig. 3** Comparison of pH compensation points versus carbon stable isotope ( $\delta^{13}\text{C}$ ) values of the studied macrophyte groups (macroalgae, charophytes, seagrass, and other angiosperms)



higher pH compensation points compared to other studied species. In addition, *Zostera* and other angiosperms had higher pH compensation points compared to *Fucus* and red macroalgae. There was a correlation between pH compensation points and  $\delta^{13}\text{C}$  values of the studied macrophyte species (Spearman  $R=0.34$ ,  $p < 0.05$ ).

The carbon isotope ( $\delta^{13}\text{C}$ ) values of studied species ( $n=3$  per species) fall between  $-30$  and  $-10\text{‰}$ . The only exception was the red macroalgal species *Coccolytus truncatus* with  $\delta^{13}\text{C}$  value estimated at  $-36.20 \pm 0.11\text{‰}$  (mean  $\pm$  SE). The highest mean  $\delta^{13}\text{C}$  value was measured for seagrass *Zostera* followed by other angiosperms, *Fucus* and *Chara* (Fig. 3). Compared to other studied species, filamentous macroalgae had more negative mean  $\delta^{13}\text{C}$  value, and red macroalgae had substantially more negative value with high differences among species (Fig. 3).

## Discussion

This study demonstrates that the common submerged macrophytes (macroalgae, charophytes, seagrass, and other angiosperms) in the Baltic Sea likely have carbon concentrating mechanisms (CCMs). All studied species, except for the red macroalga *C. truncatus*, have the mechanism to take up both carbon forms  $\text{CO}_2$  and  $\text{HCO}_3^-$  for photosynthesis. Our results showed a high level of variability in carbon isotope discrimination in studied species within 6 groups, indicating the use of a different type of CCMs.

**Chara** The pH drift experiment showed that the *Chara* group has the best capability to raise pH (above 10) compared to other macrophytes, although a significant difference was only detected in comparison with red macroalgae. This indicates an effective CCM operation since at pH 9.2 in brackish water the concentration of  $\text{CO}_2$  is too low to

support photosynthetic activity for obligate  $\text{CO}_2$  users. The high  $\delta^{13}\text{C}$  values of the *Chara* group also show the use of  $\text{HCO}_3^-$  for photosynthesis. It could be suggested that in sheltered dense charophyte beds, energetically inexpensive  $\text{CO}_2$  is used up quickly, and therefore they have developed an effective CCM. However, the results of the DIC experiment indicated that *C. aspera*, which is the dominant species of the studied community, might be carbon limited by natural DIC levels. Pajusalu et al. (2015) found that *C. aspera* in the Estonian coastal waters showed a slightly positive response to elevated  $p\text{CO}_2$  on a short-term basis. In addition, *Chara tomentosa* L. from the same study area exhibited a significant increase in net primary production rates when the  $\text{CO}_2$  concentration was elevated up to  $2000 \mu\text{atm}$ . Therefore, *Chara* could gain the photosynthetic advantage of elevated  $\text{CO}_2$  by downregulating the CCM operation e.g., switch from an  $\text{HCO}_3^-$  to  $\text{CO}_2$ -based metabolism. This could mean that increased  $\text{CO}_2$  concentration will have an overall positive impact on sheltered parts of the northeastern Baltic Sea where *Chara* spp. grow.

**Fucus** The perennial brown alga *F. vesiculosus* had a high  $\delta^{13}\text{C}$  value (close to  $-10\text{‰}$ ) and a final pH value above 10, indicating an efficient use of  $\text{HCO}_3^-$ . The results of the DIC experiment showed that the photosynthetic rate of *Fucus* only slightly increased with increasing DIC concentrations in water (Albert et al. 2020). The low  $K_{0.5}$  value of *Fucus* suggests a high affinity for DIC, and the carbon saturation is achieved at the same concentrations as naturally occurring in the shallow coastal Baltic Sea. This is consistent with our earlier research, which showed that *Fucus*, with a slow metabolism, had no response to increased  $\text{CO}_2$  levels, at least on a short-term basis in the northern Baltic Sea (Pajusalu et al. 2013). Similarly, Graiff et al. (2015) found a weak positive effect of increased  $p\text{CO}_2$  levels on the growth of *F. vesiculosus* in the western Baltic Sea.

**Filamentous macroalgae** This study focused on the three most dominant fast-growing filamentous macroalgae – *U. intestinalis*, *C. glomerata* (greens), and *P. littoralis* (brown) in the northern Baltic Sea. These filamentous algae had lower  $\delta^{13}\text{C}$  values than other tested groups, with the exception of the red macroalgae. The pH compensation point of filamentous algae was well over pH 10, indicating the use of  $\text{HCO}_3^-$ . Larsson et al. (1997) investigated two different carbon acquisition systems for *U. intestinalis* and showed that species growing in different habitats use different  $\text{HCO}_3^-$  acquisition mechanisms for photosynthesis. Pajusalu et al. (2013) showed that increased  $\text{CO}_2$  levels in seawater favoured the photosynthetic activity of *U. intestinalis*. Cornwall et al. (2012) found that the proportion of  $\text{CO}_2$  compared to  $\text{HCO}_3^-$  used in photosynthesis increased under short-term  $\text{CO}_2$  enrichment in the fleshy *Ulva* spp. It could be suggested that *U. intestinalis* has efficient use of  $\text{HCO}_3^-$  under high pH and low  $\text{CO}_2$  conditions, and species can also downregulate energetically expensive  $\text{HCO}_3^-$  use when there is enough  $\text{CO}_2$  available. Green macroalgae differ from brown algae in having an inducible mechanism allowing photosynthesis at high pH, probably via  $\text{HCO}_3^-$  (Carlberg et al. 1990). The low  $K_{0.5}$  value of *P. littoralis* suggests that this species is carbon saturated or close to saturation at current DIC concentrations in seawater. Moreover, the results of the DIC experiment showed no difference between the photosynthetic rates of filamentous *P. littoralis* and perennial alga *F. vesiculosus* at different DIC concentrations (Albert et al. 2020). Similarly, our research has shown that the nutrient uptake mechanisms of *P. littoralis* were similar to *F. vesiculosus* but were significantly different compared to *U. intestinalis* (authors' unpublished data). There are likely different types of CCMs present in the studied filamentous macroalgae. Brown filamentous algae had a CCM with a high affinity for DIC, while green algae might downregulate the  $\text{HCO}_3^-$  use when there is enough  $\text{CO}_2$  available (lower CCM activity at high  $\text{CO}_2$  concentrations).

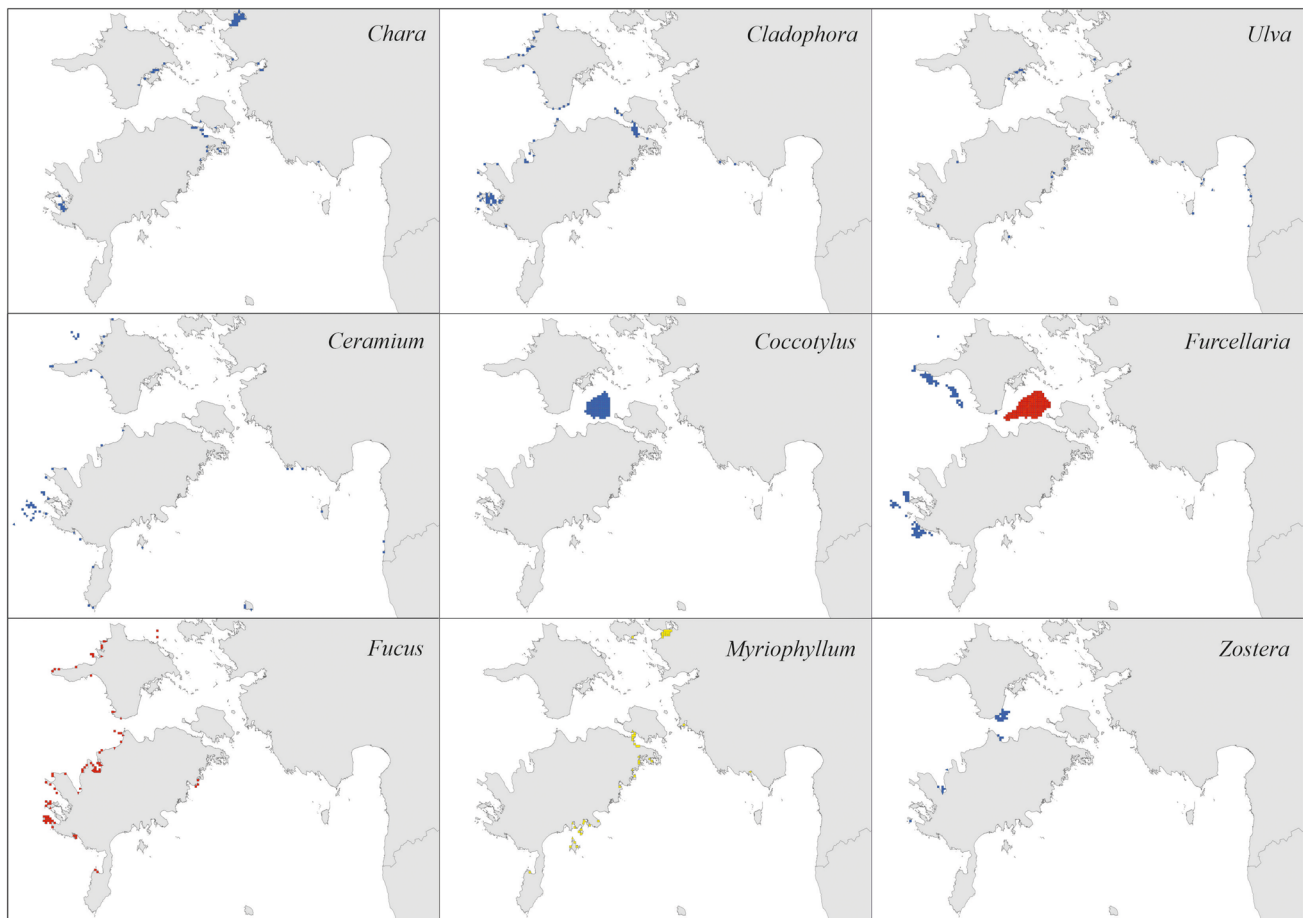
**Red macroalgae** Red macroalgae typically found in deeper waters exhibited the lowest average  $\delta^{13}\text{C}$  value compared to other studied groups, indicating less effective CCM. This was especially true for *C. truncatus* whose  $\delta^{13}\text{C}$  value was outside of the considered range of any bicarbonate use ( $< -30\%$ ). Similarly, the lowest average pH compensation point was measured for red macroalgae; however, there was a significant difference only with *Chara* and filamentous algae. However, all studied red macroalgae were able to raise the pH above 9.2, suggesting that they use  $\text{HCO}_3^-$  for photosynthesis. Earlier studies have found that many red algal species lack CCMs and use only  $\text{CO}_2$  for photosynthesis, probably due to energetic constraints of active carbon uptake in a low-light environment (Raven et al. 2005; Hepburn et al. 2011; Kübler and Dudgeon 2015). Based on the DIC experiment *F. lumbricalis* (unattached) might be

carbon limited, due to low affinity for DIC (carbon-limited species), however, the photosynthetic gain from OA is likely lower compared to *C. truncatus* (Pajusalu et al. 2020) and *C. tenuicorne* (Albert et al. 2020). Our results suggested that red macroalgae preferentially use  $\text{CO}_2$  over  $\text{HCO}_3^-$ , i.e., they might downregulate  $\text{HCO}_3^-$  when there is enough  $\text{CO}_2$  available and are likely benefit the most out of all groups studied under future elevated  $\text{CO}_2$  conditions.

**Other angiosperms** As expected, based on the  $\delta^{13}\text{C}$  and final pH values, other angiosperms are similar to the seagrass *Z. marina*. The efficiency of  $\text{HCO}_3^-$  uptake mechanisms in submerged angiosperms varies largely between families and species (Hussner et al. 2016). Similarly, earlier research has shown that both species, *S. pectinata* and *M. spicatum* can use  $\text{HCO}_3^-$  and  $\text{CO}_2$  for photosynthesis (Madsen and Sand-Jensen 1991; Maberly and Madsen 2002; Hussner et al. 2016). Furthermore, *M. spicatum* seems to be the most efficient  $\text{HCO}_3^-$  user compared to *M. heterophyllum* and *M. aquaticum* within this genus. Thus, *M. spicatum* seems to be the better competitor in dense macrophyte beds with self-induced  $\text{CO}_2$  depletion during the day in the field, but also *M. heterophyllum* can withstand and grow under  $\text{CO}_2$  depletion even at pH > 10 (Hussner et al. 2015).

**Zostera** The eelgrass *Z. marina*  $\delta^{13}\text{C}$  value was close to  $-10\%$ , consistent with the common range of values previously presented in the literature (Raven et al. 2002). The pH drift experiment showed that *Z. marina* could raise pH above 10, indicating the use of  $\text{HCO}_3^-$ . Numerous studies have suggested that many species of seagrass, including *Z. marina*, utilize  $\text{HCO}_3^-$  for photosynthesis (e.g. Invers et al. 1999; Raven et al. 2002). For example, Beer and Rehnberg (1997) found that *Z. marina* uses  $\text{HCO}_3^-$  as a major source of inorganic carbon, and bulk  $\text{CO}_2$  contributed only marginally (less than 20%) for photosynthesis at pH 8.2. Furthermore, Young et al. (2018) found that  $\delta^{13}\text{C}$  signatures of *Z. marina* decreased significantly when exposed to higher  $\text{CO}_2$ , and isotopic mixing models suggested a switch from primary  $\text{HCO}_3^-$  use to  $\text{CO}_2$  use and potential downregulation of CCM. Our pH drift experiment and  $\delta^{13}\text{C}$  value showed an effective CCM operation. However, our DIC experiment showed that the photosynthetic half-saturation point of *Z. marina* was achieved at  $\sim 2.6$  mM of DIC concentration. Nevertheless, the DIC concentration was  $\sim 1.4$  mM measured in the current study in *Zostera* natural community. This suggests that even though *Z. marina* possesses an effective CCM the current availability of DIC in the coastal Baltic Sea does not always meet the demand for the species when growing in dense stands. Our results from the DIC experiment showed that the photosynthetic rates of *Z. marina* were significantly higher than other studied species, allowing greater use of DIC. Also, studies in the Atlantic Ocean have shown that the photosynthesis of *Z.*





**Fig. 4** Hotspot areas of the key macrophyte species (obtained from <https://gis.sea.ee/adrienne>) and their expected trends under elevated CO<sub>2</sub> concentrations in the study area (based on the results of the

experiments in this article): blue indicates an increase in depth range, yellow a stable range and red a decrease in depth range

*marina* might be limited by the current DIC availability (Beer and Rehnberg 1997; Zimmerman et al. 1997), despite the fact that the concentration of DIC is higher in the Atlantic Ocean (~2.2 mM) (Ohlson 1991) than in the Baltic Sea. Our findings indicate a positive impact of the increase of CO<sub>2</sub> concentration on *Z. marina*, especially in the case of possible downregulation of CCM as referred by Young et al. (2018).

### Potential implications for future development of macrophyte communities

The northeastern part of the Baltic Sea has extensive shallows with dense populations of various macrophyte species of marine, brackish and freshwater origin (Kautsky et al. 2017). The current study suggested that the primary productivity of macrophytes is often limited by carbon availability during their active growth period, and additional CO<sub>2</sub> delivery into this coastal ecosystem could enhance primary productivity. However, the experiments in this

study indicated that macrophytes have different types of carbon-concentrating mechanisms, and as a result various responses to elevated CO<sub>2</sub>.

Elevated carbon will have a positive impact on sheltered parts of the shallow coastal northern Baltic Sea where charophytes (*Chara* spp.) grow. By contrast, the habitat-forming brown algae *F. vesiculosus* will not experience significant photosynthetic benefits under future CO<sub>2</sub> conditions. Lower competitive fitness of this species under future carbon conditions could lead to shifts in the distribution of *F. vesiculosus* habitat, with implications for species richness. *Fucus vesiculosus* habitat is the most species-rich macroalgal habitat in the Baltic Sea, and a reduction in the area of such habitat will inevitably lead to a reduction in species richness (Schagerström et al. 2014). In the shallowest part of the vegetated zone dominated by green filamentous algae, an expansion of the algal range is expected.

Red macroalgal species that typically grow in deeper waters likely will benefit the most under future elevated CO<sub>2</sub> concentrations. However, we predict the likely loss of the drifting form of

*F. lumbricalis* community due to competitive interaction with *C. truncatus* under elevated CO<sub>2</sub> conditions. Thus, the elevated carbon has the potential to influence the efficiency of the wild harvest of this loose-lying red algal community and the quality of the product provided. Other angiosperms that are widespread in sheltered soft-bottom and often form mixed communities with *Z. marina* are expected to experience a stable range under future conditions. The photosynthesis of *Zostera* is expected to enhance under elevated CO<sub>2</sub> conditions in the northern Baltic Sea where the species grows in its lowest observed salinity levels. Overall, macrophytes which inhabit the shallowest and deepest parts of the vegetated zone are expected to experience physiological benefits under future CO<sub>2</sub> conditions, while intermediate communities dominated by the perennial brown alga *F. vesiculosus* may experience loss of fitness. These fitness differences have implications for competitive interaction and species range under future climate (Fig. 4).

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**Author contributions** LP, CH, JK, TP, DP, GM conceptualized the study; all authors participated in the field study; LP, GA, EF, AK, DP, AP, KT performed the laboratory experiments; LP, GA, JK, TP, DP, AP performed the data analyses; LP wrote the first draft of the manuscript; all authors reviewed and edited the manuscript.

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**Data availability** Data and material will be made available upon reasonable request.

## Declarations

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

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