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CO_2 budget of cultured mussels metabolism in the highly productive Northwest Iberian upwelling system

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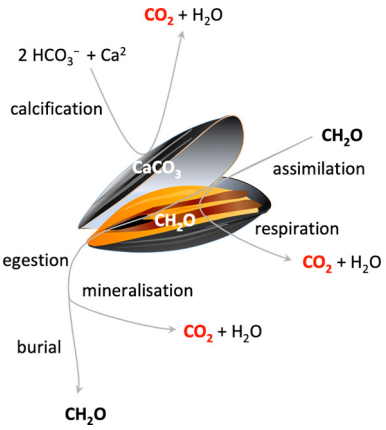
HIGHLIGHTS

- Carbon footprint (CF) due to mussel physiology during culture time is calculated.
- Water carbonate chemistry and hydrography alter the CF of mussels.
- Seeding time and harvesting size modulate the CF of mussel culture.
- The CF associated to mussel flesh varies from 92 to 578 kg CO_2/ton of mussel flesh.
- Return to sea/incineration produces the most positive/negative impacts on the CF

GRAPHICAL ABSTRACT



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ABSTRACT

Assessing the carbon footprint of marine bivalve aquaculture demands an accurate estimation of the CO_2 release associated to capital goods and aquaculture operations but also to the metabolic CO_2 budget of the cultured species. Nowadays, there are discrepancies on the processes to include in that budget, how to estimate them, and which scale should be applied, from individual to ecosystem. Site-specific environmental conditions and culture methods also affect significantly the estimates. Here, we have gathered environmental, biochemical and metabolic data from published scientific articles, reports and existing databases to present the metabolic CO_2 budget for mussel aquaculture in the coastal inlets of the Northwest Iberian upwelling. We analyse the contribution of mussel flesh and shell production jointly and separately. At the individual scale, the shell CO_2 budget is estimated from CO_2 removal by shell matrix protein synthesis and CO_2 release during calcification and respiration to support shell maintenance. Organic carbon in mussel flesh and CO_2 released by respiration to support flesh maintenance contribute to the flesh CO_2 budget. Only calcification and respiration processes are considered when estimating the metabolic carbon footprint of individual mussels because organic carbon in mussel flesh and shell returns to the atmosphere as CO_2 in a relatively short period. While the metabolic carbon footprint associated to mussel shell remains constant at 365 kg CO_2 per ton of shell, it varies from 92 to 578 kg CO_2 per ton of mussel flesh. This large variability depends on mussel seeding time and harvesting size, due to the differential seasonal growth patterns of flesh and shell. Inclusion of the CO_2 potentially immobilised in mussel faeces buried in the sediments would lead to a reduction of the metabolic carbon footprint estimates by up to 6 % compared with the individual estimates.

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1. Introduction

Marine bivalve aquaculture activities remove (or release) organic and inorganic carbon forms from (to) the water column, altering the carbon chemistry of the water parcel where these bivalves are cultured (Filgueira et al., 2015, 2019; Morris and Humphreys, 2019). An accurate assessment of the contribution of bivalve aquaculture to coastal ocean acidification, and the evaluation of the carbon footprint resulting from bivalve metabolism, requires estimating several processes occurring at the community scale, where the CO_2 released or removed by the cultured bivalves must be considered an important contributor.

In this regard, calcium carbonate ($CaCO_3$) is by far the main carbon species produced by marine bivalves as shell represents from 60 % to 95 % of the total fresh weight of bivalves and from 90 % to 99 % of bivalve shells is $CaCO_3$ (Alonso et al., 2021). Shell $CaCO_3$ is produced from bicarbonate (HCO_3^-), leading to a net release of CO_2 to the water column (Ware et al., 1992; Humphreys et al., 2018; Morris and Humphreys, 2019). Although considering the $CaCO_3$ in bivalve shells as a CO_2 sink has been a common practice in bivalve aquaculture studies (e.g. Munari et al., 2013; Filgueira et al., 2015, 2019; Jansen and van den Bogaart, 2020) it has changed recently to align with ocean biogeochemistry studies (Morris and Humphreys, 2019), which rightly does not include it in the CO_2 budget. Note that calcification removes inorganic carbon but not CO_2 from the water column and shell $CaCO_3$ does not reduce the carbon footprint because it does not contribute to reduce atmospheric CO_2 (Ware et al., 1992). Furthermore, when bivalve shells end together with organic wastes in municipal incinerators, they release from 395 to 440 kg of CO_2 per ton of shell according to the equation $CaCO_3 \rightarrow CO_2 + CaO$ (Alonso et al., 2021), increasing considerably the overall carbon footprint of bivalve aquaculture. A specific section of this manuscript is devoted to this controverted issue. Bivalve respiration also releases CO_2 to the water column, contributing to acidification and increasing the metabolic component of the carbon footprint of the culture. On the contrary, organic carbon in mussel flesh and shell remove CO_2 from the water column (Filgueira et al., 2019; Morris and Humphreys, 2019). Other metabolic processes such as ammonium excretion, that increase the total alkalinity of the water column, and burial in the sediments of the organic carbon in mussel faeces, that eventually remove CO_2, can also affect the CO_2 budget of bivalve aquaculture (Gattuso et al., 1998; Carlsson et al., 2010; Filgueira et al., 2019). Nowadays, there is still a lack of consensus on the biological processes to consider or how to include them in the CO_2 budget of bivalve aquaculture, on the variety of approaches to estimate those processes, and on the relevant scale to apply, from the individual to the ecosystem level (Filgueira et al., 2015, 2019). In this regard, temperature, salinity, pH, total alkalinity, food quality and availability, differential seasonal growth of flesh and shell and cultivation technology can all affect the metabolic CO_2 budget of bivalve aquaculture (Fuentes-Santos et al., 2019; Filgueira et al., 2015, 2019).

The large coastal inlets of the Northwest (NW) Iberian coast, collectively known as Galician Rías (Fig. 1), supported a sustained production of 230,000 metric tons $year^{-1}$ of Mediterranean mussels (*Mytilus galloprovincialis*) over the period 2007–2019, which represents 47 % of the European and 15 % of the World production (Labarta and Fernández-Reiriz, 2019). Fertilisation by coastal upwelling in spring and summer ensures elevated primary production (Arístegui et al., 2009) at low seston concentrations (Figueiras et al., 2002) because of the reduced renewal time of these coastal inlets (Álvarez-Salgado et al., 2000; Villegas-Ríos et al., 2011). As a result, during feeding of *M. galloprovincialis* in hanging ropes elevated substrate absorption efficiencies (up to 90 %; Irisarri et al., 2013) occur at moderate clearance rates (3.2 to 6.4 L $indv^{-1}$ h^{-1} for 50 to 75 mm mussels; Filgueira et al., 2008) that result in high flesh yields (Blanton et al., 1987; Álvarez-Salgado et al., 2017) and no pseudo-faeces generation (Duarte et al., 2008). Elevated dissolved oxygen levels in the upwelled waters and reduced renewal times guarantee that these coastal inlets remain well oxygenated and carbonate ion oversaturated (Álvarez et al., 1999; Pérez et al., 2000; Gago et al., 2003). These reduced renewal rates also produce a rapid dilution of the effect of the mussel rafts on the carbon chemistry of the water column, which are not easily detected through direct measurements but through indirect carbon budget estimations with box models (Rosón et al., 1999; Gago et al., 2003). These conditions contrast with the oxygen deficiency and carbonate ion unsaturation of the Namibian, Peruvian and Californian coastal upwelling systems (Mohrholz et al., 2008; Feely et al., 2008; Vargas et al., 2016; Hernández-Ayón et al., 2019).

The orography and oceanography of the Galician Rías, together with the joint know-how of local farmers and scientists, explain the high efficiency, fast growth and elevated production of this mussel culture system (Labarta and Fernández-Reiriz, 2019). These high absorption efficiency and fast growth rates should guarantee a low metabolic carbon footprint of mussel aquaculture in Galicia. However, this has not been evaluated yet. In contrast, the carbon footprint associated to capital goods (400 kg CO_2 per ton of fresh mussels) and culture operations (30 kg CO_2 per ton of fresh mussels), were estimated by Iribarren et al. (2011) more than a decade ago. Therefore, the main aim of this work is to estimate the CO_2 budget of the metabolic processes involved in the growth of *M. galloprovincialis* cultured in Galicia. For this purpose, we have gathered local hydrographic and CO_2 system data, as well as the biochemical composition and metabolic rates of mussels cultured in the Galician coast, from published scientific articles, reports and existing databases.

2. Material and methods

2.1. Quantifying the components of the metabolic CO_2 budget at the individual level

The biological processes that can directly or indirectly consume or produce CO_2, or modify the total alkalinity (*TA*) of the water column, during individual mussel growth are: 1) flesh net growth; 2) shell net growth, including calcification and matrix protein synthesis; 3) respiration, to cover costs of flesh and shell synthesis and maintenance; 4) faeces egestion and subsequent microbial degradation; and 5) ammonium excretion. On the one hand, CO_2 is consumed during flesh net growth, shell matrix protein synthesis and faeces egestion and burial, while CO_2 is produced during calcification, respiration and microbial degradation of faeces (Fig. 2a). On the other hand, *TA* increases during flesh net growth, shell matrix protein synthesis, faeces egestion and ammonium excretion and decreases during calcification and microbial mineralization of faeces (Fig. 2b). Respiration does not affect *TA* because the degradation of carbohydrates and lipids to CO_2 and H_2O does not alter the ion balance of the water column (Fraga and Álvarez-Salgado, 2005). Quantification of the CO_2 and *TA* fluxes associated to each biological process will be detailed in the subsections below.

To quantify these processes for the Mediterranean mussels cultured in the Galician Rías at the individual level we have collected size-dependent biomass, biochemical composition and physiological data from published research articles, reports and datasets on in situ and laboratory measurements with mussels cultivated in suspended culture on commercial rafts of two Galician Rías (Ría de Arousa and Ría de Ares-Betanzos; Fig. 1), as well as from biological model outputs (Fuentes-Santos et al., 2019). Table 1 and Appendix A compile all the relevant compositional and physiological data from the Mediterranean mussels of Galicia that we use in our calculations. The sources of all this data are also indicated in Table 1 and the methods used to obtain them are summarised in Appendix B. Only faeces egestion (Appendix A) and sinking rates (Appendix C) correspond to unpublished experiments that are presented for the first time in this manuscript.

We have used this information to estimate the CO_2 release or removal and the *TA* increase or decrease per individual during the culture period, from seeding to harvesting. When local data are not available for some specific processes (e.g., the energy needed to cover the metabolic costs of shell synthesis and maintenance), we relied on the literature. Furthermore, it should be highlighted that some metabolic rates used in this manuscript (e.g., net flesh and shell growth, calcification) can be easily estimated from biomass determination at seeding and harvesting time. However, other rates (e.g., ammonium excretion, respiration, egestion) require

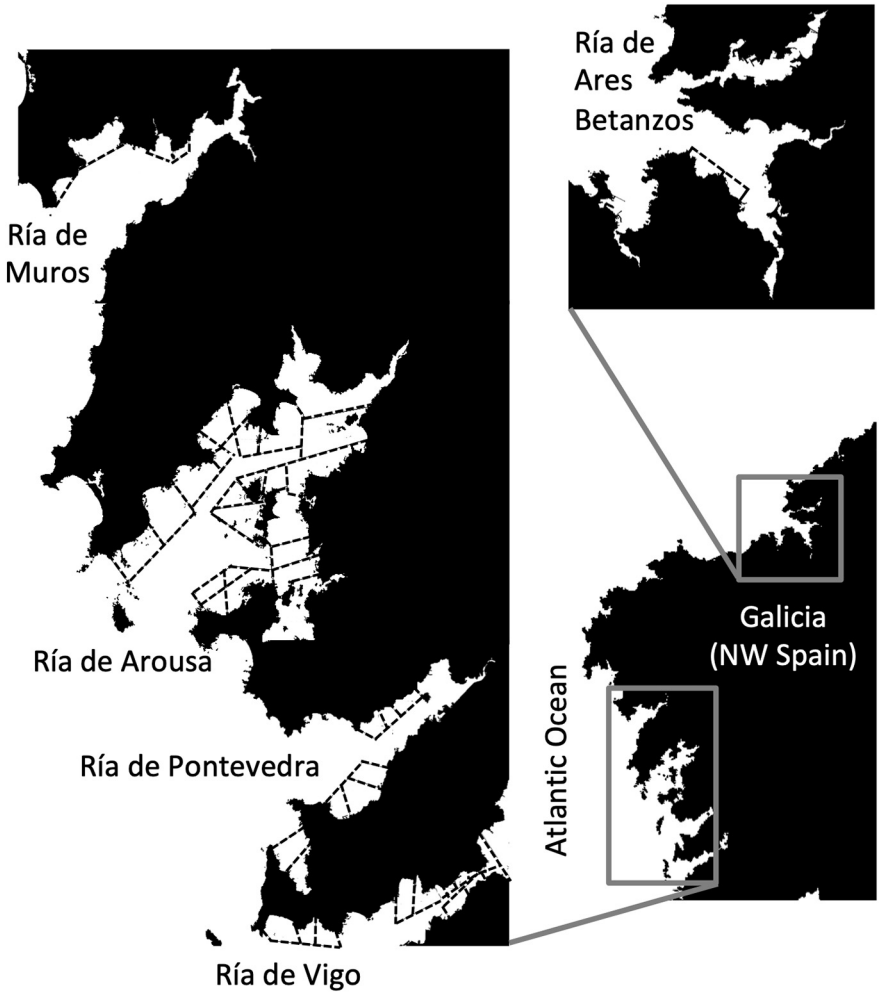

Fig. 1. Map of the Galician Rías with the location of the mussel polygons (dotted lines).

performing size-dependent physiological experiments. The rates derived from these physiological experiments were time-scaled to the culture period to normalise all rates to a common time frame (ca. annual). The good performance of the Mediterranean mussel growth model of Fuentes-Santos et al. (2019) for the Galician Rías, parameterised with these physiological experiments, supports the time up-scaling applied in this manuscript. Finally, it should also be noted that different mussels were used to produce each dataset, except for the case of the respiration and ammonium excretion rates.

2.1.1. Net growth

Mussel seeds of 10–20 mm are cultured until 50 mm (legal minimum market size) and 75 mm (medium commercial size) in the Galician Rías (Labarta and Fernández-Reiriz, 2019). At the end of the culture cycle, the flesh yield varies between 18 % for mussels harvested in March, just after the spawning season, and 30 % for mussels harvested in October, after the upwelling season (Álvarez-Salgado et al., 2017). These flesh yields, presented in Álvarez-Salgado et al. (2017), were obtained from farmers, who cook the mussels before weighting them. Therefore, we have used an experimental conversion factor of 1.478 to transform cooked into fresh flesh weight (database 1, Table 1).

We propose to calculate the net growth of individuals seeded at 15 mm and harvested at both 50 and 75 mm. Table 2 summarises their characteristics at the time of seeding and harvesting. For the purposes of these calculations, a fixed median cooked flesh yield of 22.7 % is used (Álvarez-Salgado et al., 2017), which is equivalent to a fresh flesh yield of 33.5 % using the conversion factor in database 1 of Table 1. The median shell and flesh fresh weights of a 15 mm mussel are 0.148 and 0.074 g $indv^{-1}$, respectively. At the time of harvesting of a 75 mm mussel they are 11.0 and 5.6 g $indv^{-1}$, respectively (database 2, Tables 1, 2).

To estimate the CO_2 stored in mussel shells during growth, we have to consider that the organic matrix represents 4.5 % of the shell weight of the Mediterranean mussels of Galicia and $CaCO_3$ is the remaining 95.5 % (database 3, Table 1). Given that >95 % of the shell organic matrix are proteins (Gnaiger and Bitterlich, 1984; Keith et al., 1993), particularly conchin ($C_{30}H_{48}O_{11}N_9$; Martínez-García et al., 2017) and that 51 % of conchin is carbon, mussels store 0.25 g $indv^{-1}$ of organic carbon in the matrix protein while growing from 15 to 75 mm. Therefore, 0.92 g CO_2 $indv^{-1}$ are removed from the water column to produce these shell proteins. Concerning the CO_2 stored in mussel flesh, taking into account that organic carbon represents about 45.5 % of the dry flesh weight (database 4, Table 1) and using 0.211 as conversion factor between fresh and dry flesh weight (database 2, Table 1), the organic carbon stored in mussel flesh is 0.53 g $indv^{-1}$ (equivalent to a removal of 1.93 g CO_2 $indv^{-1}$). All these growth parameters for a mussel growing from 15 to 50 mm are also summarised in Table 2.

Finally, mussel flesh synthesis increases the *TA* of the water column. The *TA* change associated to organic mussel flesh synthesis has been estimated taking into account that mussel flesh is mainly composed of carbohydrates, lipids, proteins and phosphorus compounds (as shown in database 4, Table 1). Carbohydrates and lipids, which only contain C, O and H, do not contribute to *TA*. Conversely, proteins (average formula weight, $C_{138}H_{217}O_{45}N_{39}S$) and P-compounds (average formula weight, $C_{45}H_{76}O_{31}N_{12}P_5$) do contribute to *TA*. These average formulae

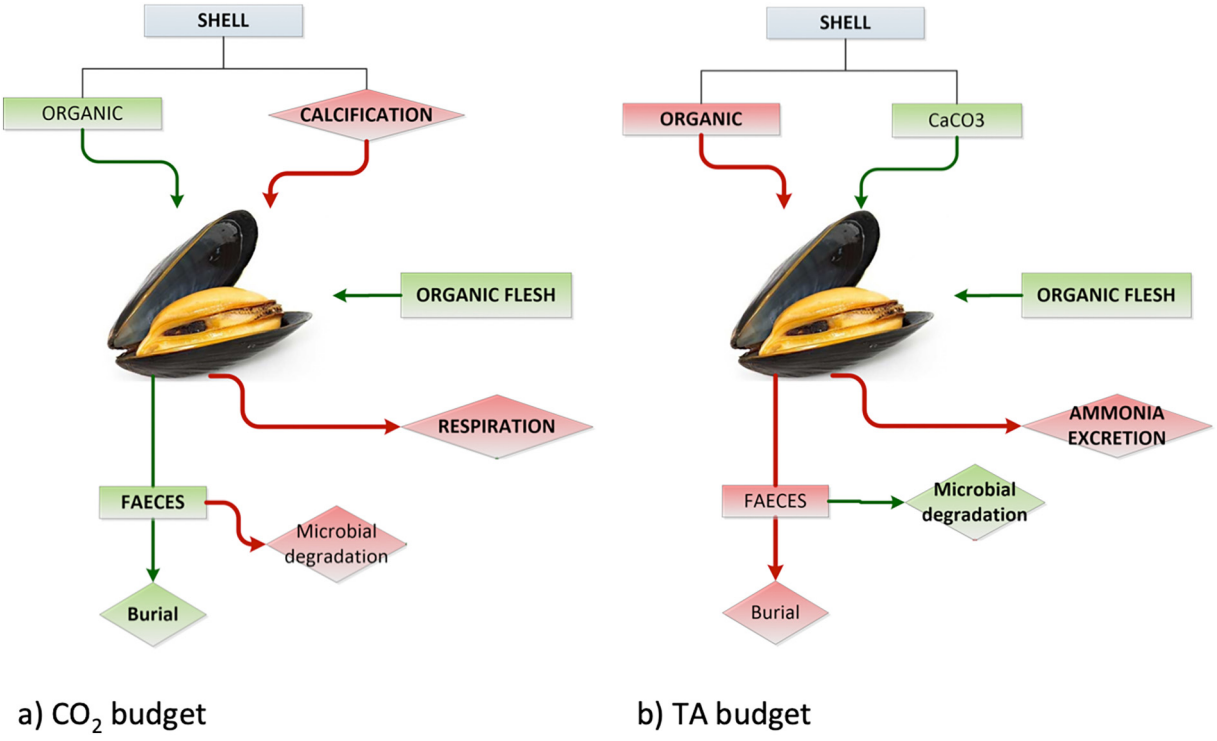

Fig. 2. Impact of the processes involved in cultured mussel growth on the inorganic carbon (a) and total alkalinity (b) of the water column where mussels are cultured. Red (green) arrows indicate processes that release (remove) inorganic carbon and TA.

are characteristic of marine phytoplankton (Fraga and Álvarez-Salgado, 2005) and here we assume that are also valid for mussels feeding on phytoplankton. The N and P content of proteins and P-compounds are the reason behind the *TA* changes that they produce because this N and P is ultimately produced from the dissolved inorganic nitrogen and phosphorus in the water column mediated by phytoplankton. We also assumed that inorganic nitrogen is in the form of nitrate (a well-founded guess in a coastal upwelling system) and inorganic phosphorus is in the form of phosphate. With these considerations in mind, Fraga and Álvarez-Salgado (2005) estimated that protein and P-compounds synthesis increase *TA* by 0.306 and 0.312 mol per mol of C, respectively (see Appendix D for a detailed explanation of these calculations). Here we use an average rate of 0.310 mol per mol of C for both compound classes. Therefore, for a mussel of 75 mm, the change of *TA* due to shell proteins synthesis is $+0.66{\cdot}10^{-2}$ mol $indv^{-1}$ and for flesh proteins and nucleic acids synthesis, which represent 59.5 % and 8.6 % of the dry flesh weight (database 4, Table 1), is $+0.89{\cdot}10^{-2}$ mol $indv^{-1}$. It should be noted that while the proportions of carbohydrates, lipids and proteins reported in Table 1 were obtained from Mediterranean mussel collected in the Rías (see Appendix B), the contribution of P-compounds was calculate from the %P in blue mussel flesh found in the literature (Buer et al., 2020).

2.1.2. Calcification

The synthesis of $CaCO_3$, occurs following the reactions:

$$2\,HCO_3^{-} + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O \quad (1)$$

$$CO_2 + CO_3^{2-} + H_2O \longleftrightarrow 2\,HCO_3^{-} \quad (2)$$

According to Eq. (1), during calcification, mussels take inorganic carbon (C_T), in the form of HCO_3^-, to produce $CaCO_3$ and release CO_2 in a 1:1 ratio, but part of this CO_2 is removed by the equilibrium reaction in Eq. (2) (Ware et al., 1992). Therefore, although 3.05 and 10.4 g $indv^{-1}$ of $CaCO_3$ are produced by a Mediterranean mussel of Galicia during growth from 15 to 50 and 75 mm respectively (Table 2), CO_2 is not removed but released to the water column by calcification. Furthermore, calcification is accompanied by a *TA* reduction in a C_T:*TA* molar ratio of 1:2 (Frankignoulle and Canon, 1994). For a mussel of 75 mm, the change of *TA* due to $CaCO_3$ synthesis is $-20.8{\cdot}10^{-2}$ mol $indv^{-1}$. Therefore, the impact of mussel $CaCO_3$ synthesis on *TA* is opposite and >10-fold the impact of organic carbon synthesis.

The fraction of CO_2 released to the water column during calcification, termed as Φ by Frankignoulle and Canon (1994), can be estimated from salinity, temperature, *TA* and *pH* with the CO_2 system equations using the R seacarb package (Gattuso et al., 2021; R Core Team, 2022) and the carbonate constants of Lueker et al. (2000), fluoride constant of Perez and Fraga (1987) and hydrogen sulphate constant of Dickson (1990).

Annual average water temperature in the surface layer (<15 m) of the mussel cultivation areas of the Galician rías varies from 14.42 to 15.05 °C and salinity from 34.2 to 35.3 (Doval et al., 2016). *TA* varies between 2296 and 2370 μmol kg^{-1} (Pérez et al., 2000; Gago et al., 2003) and pH (total hydrogen ion scale) from 7.90 to 8.16 (Padín et al., 2020). Using average values of 35.0 and 2350 μmol kg^{-1} for salinity and *TA*, Φ ranges from 0.60 to 0.79 when considering summer maximum (22 °C) and winter minimum (12 °C) temperatures (Nogueira et al., 1997; Doval et al., 2016) and pH ranging from 7.90 to 8.16. For a mean Φ of 0.70, which agrees with a recent estimate by Morris and Humphreys (2019) for the same area, the CO_2 production due to calcification for mussel growing from 15 mm to 50 mm or 75 mm are 0.94 and 3.20 g CO_2 $indv^{-1}$, respectively (Table 2).

2.1.3. Respiration

Respiration covers the energy costs of the synthesis and maintenance of mussel flesh and shell. Here, we estimate the CO_2 release into seawater due to this process using the allometric relationship between empirical mussel respiration rates (in mL O_2 h^{-1}) and shell length (in mm) obtained by Arranz et al. (2016) with mussels collected in the Ria de Ares-Betanzos (database 5, Table 1). Integration of the allometric equation between the seeding (15 mm) and the two harvesting sizes (50 and 75 mm)

Table 1
Summary of compositional and physiological data from Mediterranean mussels in the Galician Rías. Empirical methods to obtain the data/equations presented in this table are summarised in Appendix B of the supplementary materials. 1), 5), 7) and 8) P2.5 and P97.5 represent the 95 % confidence intervals ([P2.5, P97.5] = [value − 1.96·SE, value + 1.96·SE], were SE is the standard error and 1.96 is the critical value for the symmetric confidence interval with confidence level 0.95 in the standard normal distribution. Given the high determination coefficient (R^2), *p*-values of the estimated coefficients are $p < 10^{16}$ in all cases. 2) and 3) P2.5 and P97.5 are the 2.5 and 97.5 percentiles of the observed data.

Dataset						Description
1) Conversion factors between, fresh, cooked and dry flesh yield						
	N	Factor	P2.5	P97.5	R^2	
CWt vs *FWt*	118	1.478	1.437	1.520	0.8349	Tissue weight fresh (*FWt*), cooked (*CWt*) and dry (*DWt*). Field data form mussel culture monitoring in the Ria de Ares-Betanzos (PROINSA mussel database)
DWt vs *FWt*		0.211	0.205	0.217	0.9824	

Dataset					Description
2) Mussel shell dry weight (g) in relation to their size (shell length, mm)					
	N	Median	Mean	P2.5	P97.5	
Shell length, 15 mm		0.148	0.207	0.086	0.590	
Shell length, 50 mm	533	3.341	3.224	2.295	3.786	Field data from mussel culture monitoring in the Ria de Ares-Betanzos (PROINSA mussel database)
Shell length, 75 mm		11.043	10.719	9.538	11.379	

Dataset					Description
3) Organic matter content of mussel shell (%)					
	N	Median	Mean	P2.5	P97.5	
Shell length		34.0	35.8	15.5	67.0	
% organic	436	4.53 %	4.75 %	3.54 %	6.86 %	Data from laboratory experiments (Arranz et al., 2016; Fuentes-Santos et al., 2017) and field data from culture monitoring in the Ria de Ares-Betanzos (Fernández-Reiriz and Labarta, mussel lab database)
% inorganic		95.5 %	95.3 %	93.1 %	96.5 %	

Dataset						Description
4) Biochemical composition of mussel flesh (%)						
	N	Median	Mean	Min.	Max.	
% inorganic		26.4 %	26.5 %	20.6 %	40.4 %	
% organic		73.6 %	73.5 %	59.6 %	79.4 %	
%proteins	60	59.5 %	58.7 %	50.5 %	67.9 %	Field data collected in the Ria de Ares-Betanzos (Fernández-Reiriz and Labarta, mussel lab database), except for the
% carbohydrates		7.4 %	8.0 %	4.1 %	16.1 %	fraction of phosphorus compounds that was taken from Buer et al. (2020)
% Lipids		9.0 %	9.2 %	6.2 %	13.2 %	
% P compounds		8.6 %				

Dataset						Description
.5) Mussel respiration rates (*R*, mL O_2 h^{-1})						
	N	A	P2.5, P97.5	B	P2.5, P97.5	
$R = a \cdot (\text{shell length})^b$	48	$6.8 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$, $1.1 \cdot 10^{-4}$	2.048	1.906, 2.447	Laboratory experiments with mussels collected in the Ria de Ares-Betanzos (Arranz et al., 2016)

Dataset						Description
6) Biochemical composition of mussel faeces (%)						
	N	Median	Mean	Min.	Max.	
% inorganic	68	73.6 %	71.9 %	49.1 %	84.1 %	
% organic		26.4 %	28.1 %	15.9 %	50.9 %	
%proteins	30	35.0 %	36.3 %	26.5 %	50.0 %	Field data collected in the Ria de Arousa (Freites et al., 2003) and the Ria de Ares-Betanzos (Zúñiga et al., 2014,
% carbohydrates		20.0 %	19.6 %	13.3 %	25.3 %	Fernández-Reiriz et al., 2017), except for the fraction of phosphorus compounds that was taken from Buer et al. (2020).
% Lipids		9.8 %	10.1 %	6.7 %	17.7 %	
% P compounds		8.6 %				

Dataset						Description
7) Mussel ammonium excretion rates (*Exc*, μg N h^{-1})						
	N	A	P2.5, P97.5	B	P2.5, P97.5	
$Exc = a \cdot (\text{shell length})^b$	48	$3.9 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$, $9.9 \cdot 10^{-3}$	2.074	1.943, 2.269	Laboratory experiments with mussels collected in the Ria de Ares-Betanzos (Arranz et al., 2016)

Dataset						Description
8) Clearance rate (*CR*, L h^{-1})						
	n	A	P2.5, P97.5	B	P2.5, P97.5	
$CR = a \cdot (\text{shell length})^b$	142	$3.98 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$, 6.13 10^{-3}	1.71	1.607, 1.808	Laboratory experiments with mussels collected in the Ria de Ares-Betanzos (Filgueira et al., 2008)

yields average respiration rates of 0.094 mL O_2 $indv^{-1}$ h^{-1} ($4.2 \cdot 10^{-6}$ mol O_2 $indv^{-1}$ h^{-1}) and 0.195 mL O_2 $indv^{-1}$ h^{-1} ($8.7 \cdot 10^{-6}$ mol O_2 $indv^{-1}$ h^{-1}) during growth to 50 mm and 75 mm, respectively. Oxygen consumption is then converted into carbon units using a respiratory quotient (*RQ*) of 0.85 mol C mol O_2^{-1} (Gnaiger, 1983; Filgueira et al., 2019), resulting in CO_2 releases of $157 \cdot 10^{-6}$ and $325 \cdot 10^{-6}$ g CO_2 $indv^{-1}$ h^{-1} for mussels harvested at 50 and 75 mm, respectively (Table 2). Since the respiration-size relationship used in this work was estimated for mussels

Table 2
Morphometric, compositional and physiological characteristics of juvenile (15 mm) and adult (50 and 75 mm) mussels cultured in the Galician Rías. Numbers produced from the data/equations collected in Table 1. Calculation procedures are described through the manuscript.

	15 mm	50 mm	75 mm	50–15 mm	75–15 mm
Total wet weight (g $indv^{-1}$)	0.222	5.02	16.60	4.80	16.38
Flesh yield (%)	33.5 %	33.5 %	33.5 %		
Flesh wet weight (g $indv^{-1}$)	0.074	1.7	5.6	1.6	5.5
Organic C content of mussel flesh (%)	9.6 %	9.6 %	9.6 %		
Organic C content of mussel flesh (g $indv^{-1}$)	0.007	0.16	0.53	0.15	0.53
CO_2 eq in mussel flesh (g $indv^{-1}$)	0.026	0.59	1.96	0.57	1.93
Shell wet weight (g $indv^{-1}$)	0.148	3.34	11.04	3.2	10.9
Organic matter content of mussel shell (%)	4.5 %	4.5 %	4.5 %		
Organic C content of mussel shell (g $indv^{-1}$)	0.003	0.08	0.26	0.08	0.26
CO_2 eq in organic mussel shell (g $indv^{-1}$)	0.013	0.29	0.95	0.28	0.94
$CaCO_3$ content in mussel shell (%)	95.5 %	95.5 %	95.5 %		
$CaCO_3$ content in mussel shell (g $indv^{-1}$)	0.141	3.19	10.54	3.05	10.40
CO_2 released by bio-calcification (g $indv^{-1}$)				0.94	3.20
CO_2 released by respiration (10^{-6} g $indv^{-1}$ h^{-1})				157	325
N-NH_4^+ released by excretion (10^{-6} g $indv^{-1}$ h^{-1})				5.97	12.26
Faeces production (10^{-3} g $indv^{-1}$ h^{-1})				0.60	0.79
Organic matter content in faeces (%)				26.4 %	26.4 %
Organic C content in the organic fraction of faeces (%)				38.0 %	38.0 %
Organic C production by faeces (10^{-6} g $indv^{-1}$ h^{-1})				61	79
CO_2 removed (released) by faeces egestion (degradation) (10^{-6} g $indv^{-1}$ h^{-1})				222	291

with shell length between 15 and 50 mm, predictions for 75 mm individuals should be taken with caution. Oxidation of carbohydrates and lipids during respiration processes does not affect the *TA* of the water column (Fraga and Álvarez-Salgado, 2005).

Furthermore, we have estimated the metabolic costs of shell synthesis and maintenance to split the energy obtained from respiration between shell and flesh metabolism. Since there are no data to do these estimates for the Galician mussels, we reviewed the literature to search for energy cost values applicable to our case study. We obtained that the total costs of mussel shell synthesis and maintenance would be 0.22 and 0.74 g CO_2 for mussels harvested at 50 and 75 mm, respectively (see Appendix E for a detailed description of the calculations). These numbers should be considered with caution given that they are estimates not from local data but from the literature.

2.1.4. Faeces egestion and subsequent microbial degradation

Egestion data were obtained from sequential physiological experiments in the Ría de Arousa (Fig. 1) during two culture cycles, in 1995–96 (Freites et al., 2003) and 1998 (Fernández-Reiriz et al., 2017), covering from seeding (20 mm) to thinning-out (50–60 mm). From these data, faeces production during growth has been estimated as a function of shell length using a generalized additive model (GAM) with Gaussian family (Wood, 2017) (see Appendix A), resulting in $0.603{\cdot}10^{-3}$ g $indv^{-1}$ h^{-1} for mussels growing from 15 to 50 mm and $0.791{\cdot}10^{-3}$ g $indv^{-1}$ h^{-1} for mussels growing from 15 to 75 mm (Table 2). Note that the GAM fit smooths the estimated faeces production to a constant value out of the observation domain (20 to 60 mm). These egestion estimates agree with the expected reduction of the physiological and metabolic performance in large mussels (Pérez-Camacho et al., 2000; McKindsey et al., 2011), but further experimental work is required to check this hypothesis.

Faeces are composed of a major mineral fraction (73.6 %) and a minor organic fraction (26.4 %) prone to microbial degradation (database 6, Table 1) (Zúñiga et al., 2014; Fernández-Reiriz et al., 2017). This organic fraction contains about 38 % of carbon (database 6, Table 1). Therefore, from the viewpoint of the CO_2 budget, organic carbon represents about 10 % of the total weight of faeces (= 26.4 %·38 %), which translates into a potential removal of $222{\cdot}10^{-6}$ and $291{\cdot}10^{-6}$ g CO_2 $indv^{-1}$ h^{-1} for 50 mm and 75 mm mussels, respectively (Table 2).

The fate of mussel faeces, preservation vs. microbial degradation, dictates the net contribution of faeces egestion to the removal of CO_2 from the water column in the form of organic carbon. The fate of mussel faeces is also affected by their sinking rate from the rafts. Unpublished experiments (see Appendix C) have shown that, independently of the size of mussel faeces, sinking rates were quite constant, 1.6 (95 % CI = [1.3, 2.1]) cm s^{-1}, indicating that faeces density was not size dependent, at least in this case.

Finally, given the faeces egestion rates, the biochemical composition of the organic fraction of faeces, and the inorganic N and P sources to produce these faeces (nitrate and phosphate), we estimate that egestion increases the *TA* of the water column by $0.88{\cdot}10^{-6}$ and $1.16{\cdot}10^{-6}$ mol $indv^{-1}$ h^{-1} for mussels harvested at 50 and 75 mm, respectively (Table 2). As for the case of the calculation of the contribution of mussel flesh production to *TA*, we assume that the biochemical composition of proteins and P-compounds is about the same than in the phytoplankton that the mussels feed, which contain 52.5 % and 37.6 % of carbon, respectively (Fraga and Álvarez-Salgado, 2005). Therefore, we use the above calculated average *TA* change of 0.310 mol per mol of C for both compound classes, which collectively represent 43.6 % of the organic fraction of faeces (database 6, Table 1). Note that subsequent microbial degradation of faeces would lead to a proportional decrease of *TA*.

2.1.5. Ammonium excretion

Ammonium excretion during growth has been estimated through the allometric relationships obtained by Arranz et al. (2016) with mussels collected in the Ria de Ares-Betanzos (database 7, Table 1). As for the respiration rates, integration of this allometric equation from seeding (15 mm) to harvesting sizes (50 and 75 mm) yields mean ammonium excretion rates of $0.426{\cdot}10^{-3}$ and $0.876{\cdot}10^{-3}$ mmol N $indv^{-1}$ h^{-1} for individuals of 50 and 75 mm, respectively (Table 2).

Ammonium excretion increases the *TA* of the water parcel where mussels are cultured by 1 mol per mol of NH_4^+ released to the water column (Fraga and Álvarez-Salgado, 2005). Therefore, the impact of ammonium release on *TA* varies from $0.426{\cdot}10^{-6}$ to $0.876{\cdot}10^{-6}$ mol $indv^{-1}$ h^{-1} in 50 mm and 75 mm mussels, respectively (Table 2).

2.2. Mediterranean mussel culture in the Galician Rías

In Galicia, mussels are cultured on hanging ropes tied to floating rectangular structures made of eucalyptus wood, known as mussel rafts. The standard size of rafts is 20 m × 25 m, and they are separated about 100 m from each other. On average, each mussel raft sustains 500 ropes, 12 m long (Labarta and Fernández-Reiriz, 2019). For a seeding density of about 1100 indv m^{-1} of rope, each raft would store $4.4{\cdot}10^6$ mussels, given that 2/3 of the ropes are in production simultaneously (Labarta, 2004), yielding

an average production of about 75 metric tons y^{-1}. These mussel rafts are organised around demarcated cultivation areas, named "polygons" (Fig. 1). The 2-layer subtidal circulation in these coastal inlets experiences a deceleration when crossing a cultivation polygon due to the body drag exerted by mussel rafts. A deceleration up to 40–60 % has been observed in the polygon of Lorbé, in the Ria de Ares Betanzos (Duarte et al., 2008, 2014; Cranford et al., 2014), where the measured subtidal currents within mussel rafts commonly range from 2 to 3 cm s^{-1} (Pérez-Camacho et al., 1995, 2014; Piedracoba et al., 2014; Aguiar et al., 2017). This well-studied polygon contains 100 rafts distributed in 5 rows with 20 rafts per row. Given that the rafts are separated 100 m from each other, the total surface area of this polygon is 0.76 km^2, the volume of water that crosses the polygon per day at an average speed of 2.5 cm s^{-1} would be $2980 \cdot 10^7$ L and the time that this volume of water takes to go across the polygon would be 7.3 h.

How does this water renewal rate compare with the clearance rate of Mediterranean mussels of Galicia? Filgueira et al. (2008) obtained an allometric relationship between empirical clearance rates (in L h^{-1}) and shell length (in mm) (database 8, Table 1), which yields average clearance rates of 1.62 and 2.91 L h^{-1} for individuals growing from 15 to 50 mm and 15 to 75 mm, respectively. Therefore, the average amount of water cleared by the $4.4 \cdot 10^8$ mussels ($= 4.4 \cdot 10^6$ mussels/raft × 100 rafts) growing in the polygon is $1.700 \cdot 10^7$ L d^{-1} for mussels growing from 15 to 50 mm and $3.073 \cdot 10^7$ L d^{-1} for mussels growing from 15 to 75 mm. This yields clearance efficiencies, i.e. mussel clearance rates divided by water renewal rates, of 57 % for mussels harvested at 50 mm and 103 % form mussels harvested at 75 mm. As these mean clearance efficiencies are below or close to 100 %, re-filtration would not be relevant and it would be acceptable to calculate the impact of these mussels on the chemistry of the water body that flows through the polygon simply as an accumulation of the effect of individual mussels assuming that the 4.4×10^8 showed the same behaviour (i.e., the same calcification, respiration, excretion, etc. rates). However, Cranford et al. (2014) noticed that re-filtration is possible under slow circulation conditions (<2 cm s^{-1}) at the end of the culture cycles, when large mussels have a higher filtration capacity.

3. Results and discussion

In this section we will differentiate between the biological processes that 1) can be estimated directly from individual mussel rates (i.e., calcification, respiration, flesh growth and shell matrix protein synthesis); and 2) do not only depend on mussels themselves but on organic matter preservation mechanisms, or the role of other organisms present in the ecosystem (e.g., organic matter processors). The latter includes faeces egestion and subsequent microbial degradation and ammonium excretion. Therefore, we will present and discuss firstly the individual and secondly the environmental CO_2 budgets from the CO_2 removal or release rates and *TA* increase or decrease estimated in the previous section. Finally, we will dedicate a third subsection to discuss about the fate of shell $CaCO_3$ after the farm gate and its implications for carbon footprint estimates.

It should be noted that the individual rates estimated in the previous section for the physiological processes involved in the mussel culture of the Galician Rías are integrated averages over the whole culture period, from seeding to harvesting. This means that we have assumed average flesh yields as well as respiration, ammonium excretion and faeces egestion rates over the culture period, which is equivalent to assume that the amount and quality of the food supplied to mussels is also constant through the culture period.

3.1. Individual CO_2 budget: the importance of the culture period

The individual CO_2 budget (B) for the Mediterranean mussels of Galicia is calculated as:

$$B = CaCO_3 + R - (Corg_{flesh} + Corg_{shell}) \quad (3)$$

where $CaCO_3$ and R are the CO_2 released by calcification and respiration, and $Corg_{flesh}$ and $Corg_{shell}$ the CO_2 removed by flesh and shell matrix protein synthesis (summarised in Table 2).

While shell matrix protein and $CaCO_3$ synthesis, as well as the associated CO_2 release, depend primarily on mussel seeding and harvesting sizes, flesh synthesis and respiration also vary with the time to reach the harvesting size. Table 3, taken from Fuentes-Santos et al. (2019), shows that the Mediterranean mussels of Galicia seeded in autumn (September) may take more than twice the time to reach the target size than those seeded in spring (April). This is associated to the slower growth rates during the winter months, the spawning in early spring, and the differential seasonal growth of mussel flesh and shell (Fuentes-Santos et al., 2017, 2019). To take into account the impact of the variable length of the culture cycle on the CO_2 budgets, we have considered the four extreme scenarios arising from the combination of two seeding months (April and September) and the two harvesting sizes (50 and 75 mm). A 15 mm individual takes from 3.5 to 8.5 months to achieve 50 mm and from 5 to 11 months to achieve 75 mm (Table 3). Given that these numbers were obtained with an individual-based model that does not account for density effects, it is more realistic to increase these periods by 20 %, i.e. from 4 to 10 months for 50 mm individuals and from 6 to 13 months for 75 mm individuals, which are closer to the culture periods observed by Galician mussel farmers (Labarta, 2004; Perez-Camacho et al., 2013).

CO_2 released during calcification is calculated by multiplying $CaCO_3$ production (Table 2) times the mean value of Φ for each scenario, estimated by averaging the temperature and pH dependent values of Φ from the seeding to the harvesting time. It results that Φ ranges from 0.69 for the mussels seeded in April and harvested at 50 mm to 0.72 for the mussels seeded in September and harvested at 75 mm. Consequently, the CO_2 release associated to calcification ranges from 0.92 to 3.31 g CO_2 $indv^{-1}$ (Fig. 3). Comparatively, the CO_2 released by respiration, as estimated multiplying the CO_2 release rates (Table 2) by the culture times, varies from 0.45 to 3.04 g CO_2 $indv^{-1}$. These rates represent from 43 % to 118 % of the CO_2 released by calcification depending on the seeding period and harvesting size (Fig. 3). Particularly, respiration exceeds calcification for mussels seeded in September, which present much longer cultivation times. Respiration values from 52 % to 76 % of the CO_2 released by calcification were obtained for *Mytilus edulis* in Brittany (Hily et al., 2013) and 262 % for *Mytilus galloprovincialis* in the Po Delta river (Munari et al., 2013).

Concerning the CO_2 removal associated to the production of flesh organic carbon, it does not depend only on the harvesting size but also on its timing as follows from the seasonal variability of mussels flesh yield reported by Álvarez-Salgado et al. (2017). Particularly, for the scenarios considered in this work, harvesting times vary from late June to early September, when the fresh flesh yields are 33 % and 40 %, respectively, once cooked was transformed into fresh flesh weight (database 1 in Table 1). Consequently, CO_2 removed by mussel flesh ranges from 0.56 g CO_2

Table 3
Time (in days) that 15 mm juvenile mussels need to reach 50 and 75 mm as a function of seeding time. Values were calculated with the model of Fuentes-Santos et al. (2019). (*) months (May to August) when mussel seeds are not available.

	50 mm			75 mm		
	Median	95 %	CI	Median	95 %	CI
January	173	164	184	217	204	237
February	147	138	159	189	175	210
March	128	119	137	169	152	189
April	106	96	116	146	128	169
May*	87	77	103	129	107	160
June*	73	58	92	125	90	320
July*	71	51	93	317	109	363
August*	108	80	264	341	318	372
September	252	210	284	329	309	366
October	247	226	268	305	288	341
November	233	221	250	284	265	318

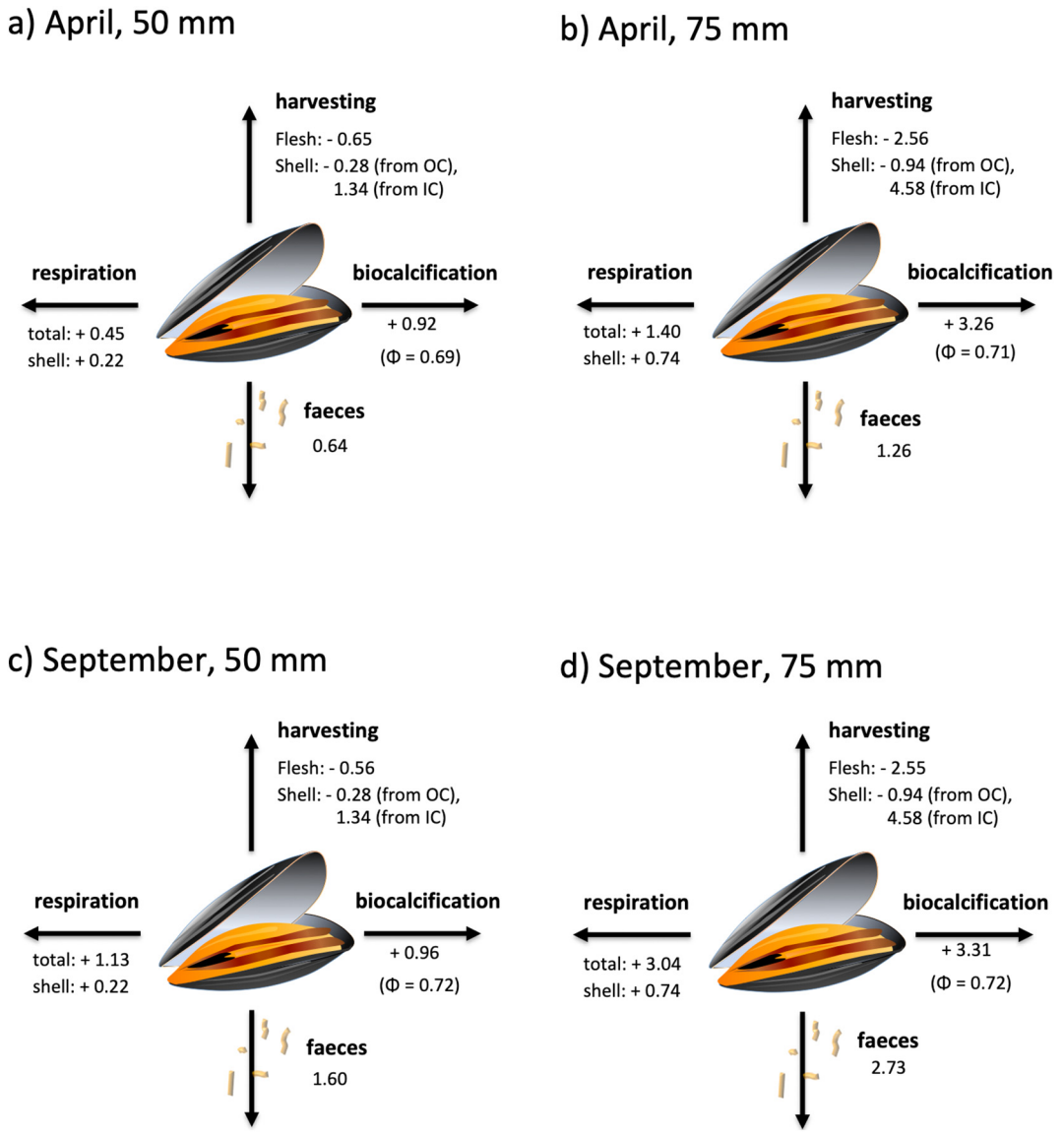

Fig. 3. CO_2 fluxes (in g CO_2 $indv^{-1}$) associated to the biological processes involved in mussel growth for the four scenarios tested: a) 50 mm mussel/seeding in April (120 days to harvesting); b) 50 mm mussel/seeding time September (300 days to harvesting); c) 75 mm mussel/seeding time April (180 days to harvesting); and d) 75 mm mussel/seeding time in September (390 days to harvesting). OC: organic carbon; OI: inorganic carbon.

$indv^{-1}$ for individuals seeded in September and harvested in June at 50 mm to 2.56 g CO_2 $indv^{-1}$ for individuals seeded in April and harvested in September at 75 mm (Table 2, Fig. 3). Finally, organic carbon in the shell matrix protein ranges from 0.27 g CO_2 $indv^{-1}$ for mussels harvested at 50 mm to 0.92 g CO_2 $indv^{-1}$ for mussels harvested at 75 mm, i.e. less than half of the CO_2 stored in mussel flesh (Table 2, Fig. 3).

Therefore, the individual CO_2 budget (Eq. (3)) for the mussels cultured in the Galician Rías ranges from a net release of 0.46 g CO_2 $indv^{-1}$ for mussels seeded in April and collected with 50 mm to 2.88 g CO_2 $indv^{-1}$ for mussels seeded in September and collected with 75 mm (Fig. 3, row 1 of Table 4). When dividing these rates by the mussel fresh weight, the CO_2 budgets would range from 65.8 to 265 kg CO_2 per ton of fresh mussels. The most and less favourable situations correspond to mussels seeded in April and collected with 75 mm and mussels seeded in September and collected with 50 mm, respectively. These individual CO_2 budgets could be used as a proxy to the contribution of mussel aquaculture to coastal acidification and indicates that the choice of seeding time and harvesting size can have a major effect on the contribution of Mediterranean mussels culture on the acidification of the Galician Rías.

Although a considerable amount of CO_2 is removed from the seawater where mussels are cultured in the form of mussel flesh, $Corg_{flesh}$ is consumed in days to months as fresh or processed/canned food and returned to atmospheric CO_2. Therefore, this removable carbon should not be considered in metabolic carbon footprint or long-term coastal acidification estimates. For the case of $Corg_{shell}$, depending on the final use of mussel shells, this organic carbon could be partly immobilised (Morris et al., 2019; Alonso et al., 2021). However, for the purposes of this work we will consider that $Corg_{shell}$ returns back to the atmosphere in the form of CO_2 in a short period of time. Therefore, a proper individual carbon footprint estimate of mussel metabolism must consider only $CaCO_3$ and R in Eq. (3). In that case, the metabolic carbon footprint estimate ranges from a net release of 1.38 to 6.35 g CO_2 $indv^{-1}$ or from 257 to 438 kg CO_2 per ton of fresh mussels (row 2 in Table 4).

Filgueira et al. (2015, 2019) argued the convenience of separating flesh and shell metabolisms to include in the shell CO_2 budget only the fraction of respiration used to cover the metabolic cost of matrix protein synthesis and calcification. The proposal sounds reasonable since mussels are primarily cultured as a food source because of their flesh, whereas mussel shell

Table 4
Individual estimates (in g CO_2 $indv^{-1}$ and kg CO_2/ton) for the four situations tested: 50 mm mussel CO_2 budget/seeding in April (120 days to harvesting), 50 mm mussel/seeding time September (300 days to harvesting), 75 mm mussel/seeding time April (180 days to harvesting) and 75 mm mussel/seeding time in September (390 days to harvesting).

	April				September			
	50 mm		75 mm		50 mm		75 mm	
	120 d		180 d		300 d		390 d	
	g CO_2/indv	kg CO_2/ton	g CO_2/indv	kg CO_2/ton	g CO_2/indv	kg CO_2/ton	g CO_2/indv	kg CO_2/ton
1 $CaCO_3$ + R − ($OrgC_{flesh}$ + $OrgC_{shell}$)	0.46	91	1.19	66	1.27	265	2.88	159
2 $CaCO_3$ + R	1.38	273	4.67	257	2.09	438	6.35	350
3 (R − R_{shell}) − $OrgC_{flesh}$	−0.42	−225	−1.89	−260	0.36	226	−0.25	−34
4 R − R_{shell}	0.24	127	0.67	92	0.91	578	2.30	318
5 $CaCO_3$ + R_{shell} − $OrgC_{Shell}$	0.87	273	3.08	283	0.91	284	3.13	287
6 $CaCO_3$ + R_{shell}	1.14	357	4.00	367	1.18	369	4.04	371
7 $CaCO_3$ + R − Burial	1.30	257	4.34	239	1.91	401	5.91	325

potentially has a wide variety of environmental, agricultural and industrial uses (Morris et al., 2019; Alonso et al., 2021). Therefore, it is interesting to discriminate between the metabolic carbon footprint of mussels associated to the food industry, B_{flesh} (i.e., to mussel flesh), from that linked to other uses, B_{shell} (i.e., to mussel shell):

$$B_{flesh} = (R - R_{shell}) - Corg_{flesh} \quad (4)$$

$$B_{shell} = CaCO_3 + R_{shell} - Corg_{shell} \quad (5)$$

where R_{shell} is the CO_2 produced by the fraction of respiration used to cover the metabolic costs of shell matrix protein synthesis and calcification (see subsection about respiration). Our values of R_{shell}, 0.22 and 0.74 g CO_2 $indv^{-1}$ for mussels harvested at 50 and 75 mm (Fig. 3), represent from 20 % to 50 % of the total CO_2 released by respiration depending on the seeding time and target size. These numbers are somewhat compatible with the 20 % suggested by Hawkins and Bayne (1992) and 20–28 % by Duarte et al. (2010) from indirect calculations based on the ratio of energy contained in bivalve shell to flesh, and with the energy allocated to shell formation in the two-structures net-production Dynamic Energy Budget (DEB) model by Fuentes-Santos et al. (2019). These authors simulated the growth of *M. galloprovincialis* in the Galician Rías and obtained that the portion of energy devoted to shell synthesis and maintenance is 29 %–38 % for mussels growing from 15 to 50 mm and 24 %–35 % for mussels growing from 15 to 75 mm.

The CO_2 budget of mussels flesh (Eq. (4)) ranges from a net CO_2 removal of 1.89 g CO_2 $indv^{-1}$ for mussels of 75 mm seeded in April, which would produce pH increase, to a net release of 0.36 g CO_2 $indv^{-1}$ for mussels of 50 mm seeded in September, which would contribute to coastal acidification (row 3 in Table 4). When only R and R_{shell} are considered in Eq. (4), the metabolic carbon footprint estimates results in a net CO_2 release from only 92 kg CO_2 per ton of fresh mussel flesh for mussels of 75 mm seeded in April to as much as 578 kg CO_2 per ton of fresh mussel flesh for mussels of 50 mm seeded in September (row 4 in Table 4). Concerning the CO_2 budget of mussel shells (Eq. (5)), CO_2 release ranges from 0.87 to 3.13 g CO_2 $indv^{-1}$ for mussels harvested at 50 and 75 mm, respectively (row 5 in Table 4). When only $CaCO_3$ and R_{shell} are considered in Eq. (5), the metabolic carbon footprint estimate range from 1.14 to 4.04 g CO_2 $indv^{-1}$ or a quite constant value of 365 kg CO_2 per ton of fresh mussel shell (row 6 in Table 4). Therefore, while the metabolic carbon footprint normalised to mussel fresh weight is highly dependent on the seeding time and harvesting size for mussel flesh, it is quite stable and independent of these culture management issues for mussel shell.

3.2. Environmental CO_2 budget: some ecosystem level considerations

The CO_2 removed by egested mussel faeces is driven by their burial in the sediments (*Burial*) and its estimation requires some previous considerations. Considering a faeces sinking velocity of 1.6 cm s^{-1} (see Section 2.1.4) and a subtidal current velocity of 2.5 cm s^{-1} within the mussel rafts (see Section 2.2) and that mussel faeces are produced uniformly throughout the 12 m of the 500 hanging ropes of a standard mussel raft of 20 m × 25 m (Labarta and Fernández-Reiriz, 2019), it would result that about 60 % of the sinking faeces should be collected by a sediment trap deployed 1 m below the ropes. Conversely, currents would disperse the remaining about 40 % of the faeces to the surroundings of the raft. However, Zúñiga et al. (2014) collected only from 10 to 45 % (mean, 27 %) of the potentially settling particles, suggesting that a substantial part of the faeces, even 50 %, could be trapped between the matrix of hanging ropes and be mineralised in situ (Cranford et al., 2007; Jansen et al., 2012; McKindsey et al., 2011 and references therein). The rest of mussel faeces would be preserved or mineralised in the sediments given that most of the mussel rafts are anchored at maximum bottom depths of 35 m and, therefore, faeces will deposit in the sediments in <30 min. At a sinking velocity of 1.6 cm s^{-1} and a current velocity of 2.5 cm s^{-1}, most of the faeces sinking to the bottom should not be deposited below the rafts but dispersed by the currents in the surrounding areas between rafts. McKindsey et al. (2009, 2011) stated that the dispersion/decay rate of biodeposits is modulated by the energy in the studied environment, controlling in the last term the biodeposit density below the culture areas, as verified by Mendez Martínez et al. (2011) and Villacieros-Robineau (2017) in the Galician Rías. Note also that the mineralization rate of the organic fraction of mussel biodeposits varies widely from <1 % to 10 % d^{-1} depending on water temperature, organic faeces composition and the culture method (Smaal and Prins, 1993; Cranford et al., 2007; Jansen et al., 2012; van Broekhoven et al., 2015). This means that mineralization of 99 % of the daily production of faeces would last from 45 to >450 days.

With these considerations in mind, only about 50 % of egested mussel faeces would deposit on the sediments, being susceptible to be buried. According to Arístegui et al. (2009), 84 % of the particulate organic matter deposited on the sediments of the Galician Rías, containing a natural mixture of biogenic organic matter that includes mussel faeces, is mineralised while 16 % is buried. Using these proportions, it results that 0.05 to 0.22 g CO_2 $indv^{-1}$ will be removed in the form of buried faeces. Inclusion of this process in the metabolic carbon footprint estimate would yield a net release from 1.33 to 6.13 g CO_2 $indv^{-1}$, or 252 to 411 kg CO_2 per ton of fresh mussels (row 7, Table 4). Therefore, when *Burial* is considered in the metabolic carbon footprint estimates, the CO_2 released by the culture of the Mediterranean mussels of Galicia would reduce up to 6.1 % for the case of 50 mm mussels seeded in September.

3.3. Fate of shell $CaCO_3$ after the farm gate

Although CO_2 is not removed during the production of the 3.05 to 10.4 g $indv^{-1}$ of biogenic $CaCO_3$ (Table 2), mussel shells store large amounts of CO_2, from 1.34 to 4.58 g CO_2 $indv^{-1}$, or 420 kg CO_2 per ton of mussel shell. Mussel shells from fresh sales to individual consumers normally end together with organic wastes in municipal landfills and/or

incinerators. In this process CO_2 in $CaCO_3$ is immediately mobilized to the atmosphere, increasing dramatically the carbon footprint of mussel aquaculture value chain since these 420 kg CO_2 per ton of mussel shell have to be added to the estimates in Table 4. Therefore, this CO_2 release should be reduced through the implementation of a more sustainable management of municipal waste (Alonso et al., 2021). On the other hand, the shells of mussels derived to industrial processing can be easily made available in sufficient amounts for environmental, agricultural and industrial applications that guarantee a long-term inertisation of shell $CaCO_3$, preferentially in the same region where they are processed to further reduce the overall environmental impact and carbon footprint related to its logistics. According to Labarta and Fernández-Reiriz (2019), 60 % of mussel production in Galicia goes for fresh sales and 40 % to the transformation industry. Assuming this ratio, 57,700 tons of shell $CaCO_3$ would be available from mussels processed in Galicia every year.

The most effective application to reduce the carbon footprint associated to the metabolism of cultured mussels would be returning shells back to the carbonate oversaturated marine waters of the Galician coast (Álvarez et al., 1999; Pérez et al., 2000; Gago et al., 2003), which would ensure a long-term CO_2 sequestration until carbonate ion undersataturation occurs and $CaCO_3$ dissolves. Note that $CaCO_3$ dissolution would imply returning to water the carbonate ion removed to produce the shells, cancelling out the carbon footprint associated to mussel shell production (Renforth and Henderson, 2017; Bach et al., 2019; Alonso et al., 2021). Implementation of this application would require a monitoring program of their negligible environmental impact before obtaining administrative permits to conduct the activity.

Other possible applications to avoid the immediate liberation of CO_2 from shell $CaCO_3$ would be correction of pH in acidic Galician soils (Colmeiro et al., 1994; Paz-Ferreiro et al., 2012). Since about 50 % of the CO_2 trapped in agricultural limestone contribute to CO_2 sequestration (West and McBride, 2005), preparing finely grinded $CaCO_3$ from mussel shells to correct soil acidity would constitute a straightforward and low carbon footprint alternative, valid for partial immobilisation of the CO_2 in shell $CaCO_3$. An industrial application with tradition in Galicia is the paper industry, where $CaCO_3$ is used as filler in alkaline wood free papermaking processes. The paint industry could be considered too, where $CaCO_3$ is used as a primary extender. In these applications, $CaCO_3$ maintains its structure and, therefore, can ensure a long-term preservation of the CO_2 stored in shell $CaCO_3$. Other industrial applications compatible with the requirement of long-term CO_2 storage are being developed in Galicia, including the use of shell $CaCO_3$ as aggregate for concrete (Martínez-García et al., 2017, 2019) or as a building insulation material (Martinez-García et al., 2020).

4. Conclusions

The metabolic carbon footprint of Mediterranean mussels cultured in the coastal upwelling system of the NW Iberian Peninsula is of the same order of the carbon footprint associated to capital goods + operations and, therefore, should not be neglected. The metabolic carbon footprint is strongly affected by culture management strategies, particularly the seeding time and harvesting size, which regulate the growth rate and timing of the culture cycle. Thus, the metabolic carbon footprint associated to calcification and respiration processes ranges from 257 to 438 kg CO_2 per ton of fresh mussels depending on these managerial issues. It would slightly reduce to values from 252 to 411 kg CO_2 per ton of fresh mussels when burial in the sediments of organic carbon in mussel faeces considered. Furthermore, the most effective way to cancel out the metabolic carbon footprint associated to mussel shell synthesis would be returning the shells to sea, where eventual dissolution of $CaCO_3$ would take place in carbonate undersaturated waters. In that case, only mussel respiration would contribute to the metabolic carbon footprint, which would range from 72 to 210 kg CO_2 per ton of fresh mussels. All these estimates are preliminary, because quantifications at the ecosystem level are not straightforward and would require a coupled hydrodynamic-biogeochemical-mussel cultivation modelling approach for the Galician Rías. We are taking the first steps towards this end by incorporating C, N and P removal and release rates into our mussel DEB model, the first able to simulates mussel shell and flesh independently (Fuentes-Santos et al., 2019), which is crucial to model the differential effect of mussel shell and flesh in the carbonate chemistry of the water parcel where the mussels are cultured.

In the NW Iberian upwelling, coastal bottom waters are still oversaturated but it is predicted that they will become undersaturated at the end of this century because of ocean acidification. $CaCO_3$ can also be dissolved in the acid interstitial waters of the sediments where shells can be buried. If mussel shells are not returned to sea, they should be used in local applications that ensure a relatively long-term stability of the $CaCO_3$ because liberation to the atmosphere of the CO_2 trapped in shell $CaCO_3$ would imply an additional carbon footprint of the culture of 420 kg CO_2 per ton of mussel shell.

Data availability statement

The raw data supporting the conclusions of this article will be made available upon request to the authors, with the exception of dataset 1 to 2 in Table 1 because they are industry data owned by the company PROINSA.

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Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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