

#### The atmospheric carbon sequestration potential of man-made tidal lagoons

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1	The atmospheric carbon sequestration potential of man-made tidal lagoons
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15	Abstract

16 Understanding sequestration of carbon by coastal ecosystems is central to addressing 17 the role they play in climate change mitigation. To quantify this process, accurate 18 measurements of CO<sub>2</sub> fluctuation, coupled with variations in residence time of coastal 19 water-bodies are required. Nearshore ecosystems, including coastal lagoons, may 20 provide an effective sink for atmospheric carbon dioxide, particularly those containing 21 productive biota such as seagrass. However, the rate and pattern of carbon 22 sequestration in seagrass meadows across a range of environmental settings is still 23 poorly constrained. In this study, we utilize a robust physical tidal model, along with 24 biogeochemical dissolved inorganic carbon (DIC) assessment, to estimate water 25 residence time and net sequestration of atmospheric CO<sub>2</sub> in an intertidal lagoon 26 containing a seagrass (Zostera noltii) meadow. Total alkalinity and pH measurements 27 taken from advected water mass exchanged with the open ocean at inlet boundaries 28 are used to calculate DIC and  $pCO_2$ . A predictive model of hydrodynamics provides 29 good approximation of mean water residence time to within 6 hr (± 3 s.d). Results 30 indicate that during the daytime study period the lagoon is a sink for carbon, having a mean net ecosystem productivity (NEP) of  $3.0 \pm 0.4$  mmol C m<sup>-2</sup> hr<sup>-1</sup>. An equivalent diel 31 NEP range of between 15.23 and -9.24 mmol C m<sup>-2</sup> d<sup>-1</sup> is calculated based on reported 32 33 shallow water pelagic respiration rates. Moreover, approximately 4% of DIC availability 34 occurs from atmospheric CO<sub>2</sub> transfer to lagoon water. However, a negative diel rate of  $-82 \pm 81$  mmol C m<sup>-2</sup> d<sup>-1</sup> is found, assuming overnight respiration ascertained from 35 36 converted Zostera noltii O<sub>2</sub> utilization. We hypothesize that analogous regional

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- 37 nearshore ecosystems provide baseline study sites suitable to elucidate the carbon
- 38 capture potential of planned, nearby tidal range energy schemes.

### 39 Keywords

40 Coastal lagoons; Atmosphere-ocean carbon exchange; Tidal energy; Carbon sinks;
41 Dissolved Inorganic Carbon; Irish Sea coastal modelling

# 42 **1. Introduction**

43 Coastal lagoons, saline ponds and barrier systems occupy around 13% of 44 coastal areas worldwide and accommodate important productive habitats such as 45 seagrass meadows (Barnes, 1989). Despite their sparse ocean coverage (<0.2%), 46 seagrass meadows play an important role in carbon sequestration and burial, 47 estimated to be between 20 and 112 Tg C yr<sup>-1</sup> (Duarte et al., 2010; Kennedy et al., 48 2010; Fourgurean et al., 2012). However, not all seagrass meadows are net 49 autotrophic (Duarte et al., 2010); many nearshore coastal ecosystems are thought to 50 contribute to atmospheric  $CO_2$  levels by acting as a net source, with heterotrophic 51 processes that produce CO<sub>2</sub> outweighing autotrophic processes that consume it (Mork 52 et al., 2016). Coastal lagoons can be productive environments due to high nutrient 53 levels in both sediments and water, and are frequently colonized by benthic plants due 54 to suitable sunlight penetration in the shallow water column. They represent a valuable 55 resource for both fisheries and blue carbon initiatives, supported by research finding 56 that shallow water autotrophic biota provide a functional sink for atmospheric CO<sub>2</sub> 57 (Tokoro et al., 2014).

58 Current global carbon budgets show a deficit that is unattributed of 0.6 Gt C yr<sup>-1</sup> 59 (Le Quere et al., 2018). The oceanic sink of anthropogenic  $CO_2$  for the period 2002 to 60 2011 is estimated at 2.5  $\pm$  0.5 Pg C yr<sup>-1</sup> (Le Quere et al., 2013), with oceanographers 61 researching understudied parts of the ocean, such as marginal seas and nearshore 62 ecosystems as potential missing sinks. Bauer et al. (2013) and Borges et al. (2005) 63 suggest (with some uncertainty) that temperate marginal seas may reduce atmospheric 64 CO<sub>2</sub> by some 0.45 Pg C yr<sup>-1</sup>, with nearshore wetland and estuarine ecosystems almost 65 nullifying this sink by emitting around 0.35 to 0.40 Pg C yr<sup>-1</sup>. It is suggested that future 66 research should focus on increasing high resolution carbonate system parameter data 67 (Mork et al., 2016) in highly productive nearshore systems, such as those containing 68 seagrass (Borges et al., 2005; Dai et al., 2009; Jiang et al., 2011). Tidal range power 69 schemes, such as the proposed Swansea Bay tidal lagoon<sup>A</sup> may provide an 70 opportunity to fabricate carbon-sequestering nearshore ecosystems that increase the 71 potential to offset atmospheric carbon deficits.

A http://www.tidallagoonpower.com/projects/swansea-bay/

72 Roche et al. (2016) suggest that accurate resource assessments relating to 73 marine renewable energy (MRE) schemes are required to elucidate physical, 74 ecological and social uncertainties when spatially refining developments to help 75 achieve carbon reduction targets. Tidal lagoons provide an important potential 76 resource for the MRE development mix, being both a predictable and controllable 77 renewable energy source. The feasibility and scope of planned UK tidal lagoon energy 78 schemes has undergone extensive examination by the 'Hendry Review'. However, 79 uncertainty exists as to their future, given the high initial capital costs involved and 80 possible inability to produce electricity at a competitive price. Additional benefits, such 81 as regeneration, recreational activities and flood protection are suggested (Neill et al., 82 2018; NIC, 2018), however, the opportunity to incorporate carbon offsetting might also 83 provide a second potential revenue source, increasing financial feasibility.

84 A naturally restricted lagoon is defined as having two or more frictional inlets. 85 with definite tidal regimes, whereas choked lagoons characteristically have one or 86 more long narrow inlets with greater water residence time (Kjerfve, 1986). Residence 87 time is a quantitative measure allowing spatial and temporal estimation of the rate at 88 which water mass ingresses and egresses a control domain. It is effectively the time 89 taken for a particle entering the domain to leave again for the first time (Delhez et al., 90 2014). Ecosystem issues such as depletion in fish production have been related to 91 limited seawater circulation and renewal (Tsihrintzis et al., 2007), because flushing has 92 a limiting impact on nutrient input (Newton and Mudge, 2005). Salt concentration, along 93 with nutrient and alkalinity balance may be reduced by inputs of freshwater from 94 surface run-off, contributories, heavy and prolonged precipitation or by evaporation. It 95 should be noted that larger lagoon systems are characteristically more stable and likely 96 to encourage species diversity (Barnes, 1989). Ultimately, water balance, composition 97 and quality depends on exchange at boundaries and the resultant residence time 98 (Orfila et al., 2005; Rynne et al., 2016).

99 Coastal lagoons are important areas for autotrophic processes resulting in net 100 carbon accumulation in sediments but are susceptible to anthropogenic impacts. 101 Industrial activities such as fossil fuel combustion and cement manufacturing have 102 increased atmospheric CO<sub>2</sub> concentration, influencing water pH. Terrestrial 103 deforestation and habitat clearing have created aquatic imbalances known as cultural 104 eutrophication and siltation, often manifested by increased turbidity, algal production, 105 decreased light availability and dissolved oxygen levels (Kennedy and Bjork, 2009; 106 Zouiten et al., 2013). Ultimately, this may cause loss of benthic plants and oxidation of 107 sediments leading to net heterotrophic activity, causing the lagoon to act as a carbon 108 source rather than a sink. It is, therefore, important to be able to robustly model carbon 109 dynamics in order to assess whether ecosystems are CO<sub>2</sub> sources or sinks.

110 In this study, we provide a method to quantify simply and robustly mean lagoon 111 NEP rates based on observed boundary flux estimates of DIC and modelled water 112 exchange through the tidal channels. The study site has restricted water exchange with 113 the open ocean through man-made inlets and is located in the vicinity of proposed sites 114 for tidal lagoon power schemes that will follow similar water exchange regimes. As 115 such similar regional ecosystems may provide analogous baseline study sites for 116 proposed MRE schemes. A physical-chemical box model approach provides volumetric 117 water exchange estimates at lateral boundaries from simulations provided by a one-118 dimensional (1-D) MATLAB model. Modelled hydrodynamics are well validated; thus, 119 errors are constrained. Biogeochemical field measurements along with meteorological 120 data allow air-sea CO<sub>2</sub> transfer rates to be estimated over a complete tidal cycle. This 121 short-term study demonstrates the utility of this approach and identifies the potential for 122 annual carbon budgeting in semi-enclosed productive coastal lagoons using high-123 resolution temporal data.

124

### 125 **2. Methods**

# 126 2.1 Study site

127 Sampling occurred in the Inland Sea (53°16.475'N, 4°35.000'W), a small (radius 128 and surface area at low tide ~890 m and 2.5 km<sup>2</sup>, respectively), shallow (~2 m at low 129 tide), temperate, micro-tidal (<2 m range) coastal lagoon. The nearshore ecosystem is 130 sandwiched between road and rail embankments in a channel that separates Holy 131 Island from the island of Anglesey in Wales, UK (Figure 1). The lagoon was formed in the early 19<sup>th</sup> century when Stanley Embankment (water inlet ~17 m wide and 100 m 132 133 long) was constructed to provide a transport route through to Holyhead. At the opposite 134 end of the lagoon, Four Mile Bridge provides a much narrower road bridge and 135 passage for water to enter (~6 m wide by 10 m long). The area is both a designated 136 Landscape Character Area (LCA) and Area of Outstanding Natural Beauty (AONB) and 137 provides an important well-balanced nursery and ecosystem for many different fish and 138 marine plant species. Further detail on the area is provided by Hill (1994).

139 Seawater exchange with the Irish Sea occurs through the two narrow man-140 made inlets in the embankments. The hydrodynamic regime of the lagoon is dominated 141 by semi-diurnal advective mixing of seawater at lateral boundaries. Periodic tidal 142 forcing outside the basin is choked by the restricted inlets so that the tide in the Inland 143 Sea has a lower amplitude than that of the open ocean (Hill, 1994). The lagoon 144 supports a meadow of Zostera noltii, a small seagrass species of the intertidal zone of 145 Europe and Africa (Auby and Labourg, 1996). This species exhibits strong seasonality in its above-ground biomass, ranging from 0.4 g DW m<sup>-2</sup> in spring to 70 g DW m<sup>-2</sup> in 146 147 summer (Papadimitriou et al., 2006). There are a number of proposed MRE

- 148 developments for this region, including a tidal range lagoon scheme to the east at
- 149 Colwyn Bay (Roche et al., 2016).
- 150



Figure 1. Location of the Inland Sea showing the restricted channels to the north at Stanley Embankment (B) and to the south at Four Mile Bridge (C). Modelled boundary conditions are based on data supplied by Holyhead harbour primary tide gauge station (A) and meteorological data is taken from stations at Valley (D) and Rhoscolyn (E).

# 152 2.2 Biogeochemical model

A simple theoretical 1-D biogeochemical model, adapted from Jiang et al. (2011) (Figure 2) is used to examine the extent to which lagoon DIC concentration is influenced by CO<sub>2</sub> gas exchange caused by a combination of:

- 156 (i) air-sea exchange (surface boundary)
- 157 (ii) physical mixing (lateral boundary)
  - (iii) biological influences (seabed and water column)
- 158 159

160 DIC determination is outlined in section 2.4. We apply the fundamental principles of a

tracer (in this case DIC) entering and exiting a semi-enclosed system and assume (a)

162 lagoon volume is conserved and (b) a fully mixed water column. Therefore, tracer

- 163 concentration (*c*, in mmol C kg<sup>-1</sup>) in a varying water depth over time is given by eq (1)
- 164 (Williams and Fellows, 2011):

$$\frac{d}{dt}\rho c \frac{V}{A_S} = \sum F_{out} - F_{in} = F_{MIX} - F_{GAS} - F_{BIO}$$
(1)

167 In the above equation,  $\rho$  is water density (kg m<sup>-3</sup>), V system volume (m<sup>3</sup>), A<sub>S</sub> surface 168 area (m<sup>2</sup>), and F is the tracer flux (mmol C m<sup>-2</sup> hr<sup>-1</sup>) entering (F<sub>in</sub>) and exiting (F<sub>out</sub>) the 169 system at the boundaries. DIC fluxes in and out of the lagoon can further be expressed 170 as the sum of the partial fluxes generated by a number of biogeochemical processes 171 within the lagoon:

- 172 (i) Physical mixing during transport by advection over ebb and flood tidal cycles,
  173 riverine input, and upwelling (F<sub>MIX</sub>).
- 174 (ii) Ecosystem respiration, adding respired organic carbon as CO<sub>2</sub> to the water,
  175 and ecosystem production removing DIC species (aqueous CO<sub>2</sub>, bicarbonate
  176 ions) from the water into biomass and calcium carbonate (CaCO<sub>3</sub>) precipitation
  177 and dissolution, combined as F<sub>BIO</sub>.
- 178(iii)Air-sea exchange of  $CO_2$  ( $F_{GAS}$ ). If  $F_{in} > F_{out}$ , there will be a net increase in DIC179concentration in the lagoon water, and vice versa.
- 180



Figure 2. Biogeochemical 1-D model of carbonate system exchange dynamics when accounting for associated air-sea gas exchange, biological activity and physical processes in a nearshore shallow water ecosystem.

181

#### 182 2.2.1 Biological processes

We simplify the approach to carbon dynamics in the lagoon by considering a semi-enclosed system (Figure 3). At first approximation, we assume that the contribution from CaCO<sub>3</sub> precipitation and dissolution is negligible (Barron et al., 2006). Based on eq (1), at steady state  $F_{BIO}$  is equivalent to NEP, the balance between gross primary production and community respiration,  $F_{BIO} = NEP = GPP + CR$ . By 188 convention, the transfer of carbon from atmosphere to seawater and lagoon to ocean

189 due to respiration have negative values.

190



Figure 3. Schematic box model of the Inland Sea and its perceived inorganic carbon exchange. Lateral tidal mixing (Mix), biological (Bio) and gas (Gas) exchanges will drive net DIC concentration levels within the lagoon.

191

# 192 2.2.2 Air-sea exchange

193 In this study, we determine  $F_{GAS}$  with the bulk formula method as  $F_{GAS}$  = 194  $\alpha k \Delta p CO_2$ . Where  $\alpha$  is the solubility coefficient of  $CO_2$  (mmol m<sup>-3</sup> µatm<sup>-1</sup>), *k* is gas 195 transfer velocity (m hr<sup>-1</sup>; a function of wind speed) and  $\Delta p CO_2 = p CO_{2W} - p CO_{2A}$  (µatm), 196 the air-sea difference in the partial pressure of  $CO_2$ . Subscripts *W* and *A* refer to water 197 and atmosphere respectively.

198

# 199 2.2.3 Physical mixing

200 By observing any two of the four measurable carbonate system parameters, 201 pH, DIC, total alkalinity (TA) and  $pCO_2$ , along with water temperature and salinity, it is 202 possible to determine the remaining parameters. In this study, DIC in lagoon water is 203 determined from field observations of pH and TA at lateral boundaries. The physical 204 processes of tidal advection, upwelling, and river discharge contribute to DIC mixing at 205 ecosystem boundaries. Advection of nutrients from ocean tides dominate the Inland 206 Sea, no other significant contributories exist. The tidal exchange of water through the 207 man-made inlets provides fluxes calculated from the product of volumetric flow 208 throughput, U (m<sup>3</sup> hr<sup>-1</sup>) and water density. The mixing of lagoon and ocean water 209 includes tracer concentration, such that  $F_{MIX} = c_L \rho U_{out} - c_O \rho U_{in}$  whereby subscripts in 210 and out describe exchange on flood and ebb tides and subscripts L and O indicate 211 lagoon and ocean concentrations, respectively.

212

#### 213 2.3 Hydrodynamic model

The hydrodynamic model provides a means to estimate volumetric channel throughput, *U*. Following Hill (1994), the tide in the Inland Sea is modelled by 216 considering the balance between the pressure gradient force caused by the slope of 217 the water surface and bottom friction:

218

$$g\frac{\eta_O - \eta_L}{L} = k_D \frac{u^2}{H + \eta_m}$$
(2)

219

Where *g* is the gravitational acceleration constant (9.81 m s<sup>-2</sup>),  $\eta_o$  is surface elevation relative to mean sea level in the open sea (m), and  $\eta_L$  is surface elevation relative to mean sea level in the lagoon (m). The depth-averaged along-channel current velocity *u* (m s<sup>-1</sup>, positive when flow is into the lagoon), and  $k_D$  the dimensionless drag coefficient in a channel of length *L* and depth *H* below mean sea level (m). Mean surface elevation in the channel is denoted by  $\eta_m = (\eta_0 + \eta_L) / 2$ . The continuity equation is:

$$A_{S}\frac{d\eta_{L}}{dt} = ub(H + \eta_{m})$$
(3)

227

and we consider ideal channels of width *b* (m), whose cross section does not alter. Crucially, however, in addition we allow the surface area of the lagoon to change with the tide, assuming the lagoon has sloping sides and a conical shape. If the sides slope at an angle  $\theta$  (°) to the horizontal, the surface area of the lagoon varies with elevation according to:

233

 $A_{S} = \pi \left( r_{0} + \frac{\eta_{L}}{\tan \theta} \right)^{2}$ (4)

234

The subtidal lagoon radius,  $r_0$  (m) is that at lowest-tide, assumed constant with depth beyond this.

237 Tidal forcing in the open sea can be represented by a sum of harmonics:238

$$\eta_{\rm O} = \sum_{n=1}^{\rm N} a_n \cos(\omega_n t - \kappa_n)$$
(5)

239

Where  $a_n$  and  $\kappa_n$  are the amplitude (m) and phase (°) of *n* (1-N) tidal constituents with an angular frequency  $\omega_n = \frac{2\pi}{T_n}$  with  $T_n$  being the period (s) of the constituent. For this study, twelve of the main harmonic constituents are used to represent surface elevation change due to astronomical forcing. Tidal boundary forcing at the Inland Sea is assumed to occur at the same phase and amplitude as that at Holyhead harbour (A in Figure 1). The flow in the channels is derived by solving eq (2) for *u* and then using eq (3) to update the elevation in the Inland Sea. The equations are solved using a thirty-second-time step with meteorological influences neglected. *U* is derived from the product of channel flow velocity and cross-sectional area, which varies with depth over time.

250

# 251 2.4 Water residence time and NEP

252 Water exchange and mixing through the channels will not occur instantly and 253 concentrations due to mixing will alter slowly and be affected by a proportion of water 254 returning into the domain soon after leaving. Therefore, the average residence time of 255 the water must be factored into calculations. In order to account for this mixing 256 process, we approach the problem using the tracer pulse method that associates the 257 residence time (T) of a system (in this case the lagoon basin) with *n* measured tracer 258 flux concentration observations ( $F_{tr}$ ) at any given point on the periphery during an 259 elapsed time (t) by means of the transport equation: 260

$$T = \frac{\sum_{n=0}^{\infty} F_{tr} t}{\sum_{n=0}^{\infty} F_{tr}}$$
(6)

261

We solve the steady state condition of eq (6) by integrating over time the multiple tracer DIC flux observations to reveal the solution to tracer transport for a time step equal to a tidal cycle:

265

$$NEP = \frac{1}{T_{TC}} \int_{0}^{TC} F_{MIX} - F_{GAS} dt$$
 (7)

266

Water residence time during a tidal cycle ( $T_{TC}$ ) is the ratio of the mean volume of the lagoon  $V_L$ , (m<sup>3</sup>) to the tidal prism volume,  $V_{TP}$ , (m<sup>3</sup> hr<sup>-1</sup>) which is the difference between high and low tide volumes or throughput in the channel(s) over an ebb tide (Sheldon and Alber, 2006). For an implicit timescale of a tidal cycle,  $V_{TP}$  represents the volume change or throughput over the tidal period,  $T_{TC}$ .

$$T_{TC} = \frac{V_L}{V_{TP}} = \frac{\overline{V}}{\Delta V / T_{TC}}$$
(8)

In the above equation, the overbar represents the integrated mean values of the
polynomial curve fit. We assume negligible difference in concentration values at each
lagoon entrance at all times.

277

### 278 **3. Applied theory**

### 279 **3.1 Measurements and Analysis**

280 Sampling was conducted in surface waters in daylight hours during an ebb tide 281 pilot study on 1 August 2013 (JD 213) and over a complete tidal cycle during spring 282 tide on 20 August 2013 (JD 232) within a 20 m radius of the culvert entrances at Four 283 Mile Bridge and Stanley Embankment (Figure 1). No precipitation occurred during this 284 time. Single-point current velocity measurements were taken in triplicate at 10- or 15-285 minute intervals at channel inlets during ebb tides throughout July and August using a 286 Braystoke BFM002 miniature current flow meter. Combined half hour moving averages 287 of these measurements were used to validate model estimates (section 3.2). Solar 288 irradiance was determined from hourly moving averages of data supplied by the 289 observatory at Hilbre Island (53°22.980'N, 3°13.680'W) and is used to support 290 evidence of thermal changes in the lagoon.

291 The seawater DIC concentration, partial pressure of  $CO_2$  in seawater ( $pCO_{2W}$ ) 292 and hence the air-sea CO<sub>2</sub> transfer rate (F<sub>GAS</sub>), were all computed from temperature, 293 practical salinity, TA, and pH measurements using CO2Calc version 1.2.0 (Robbins et 294 al., 2010). Parameters were determined by setting the seawater pH scale using the 295 Dickson and Millero (1987) re-fit of the Mehrbach et al. (1973) stoichiometric 296 dissociation constants of dissolved CO<sub>2</sub>, the stoichiometric dissociation constant of 297 HSO<sub>4</sub><sup>-</sup> (K<sub>HSO4</sub>) in Dickson (1990), the total boron concentration in Lee et al. (2010) and 298 air-sea transfer rate parameters of Wanninkhof (1992). Combined hourly moving 299 averages of wind velocity data provided from meteorological stations at Valley 300 (53°16.980'N, 4°33.780'W, 9 m elevation) and Rhoscolyn (53°14.760'N, 4°34.980'W, 301 13 m elevation) on Anglesey were included to calculate gas transfer velocity (k), in 302 order to estimate the air-sea  $CO_2$  flux also (section 2.2.2). The global average for 303 atmospheric CO<sub>2</sub> concentration (396.7 ppm, NOAA, 2013) was utilized in all 304 calculations of the air-sea pCO<sub>2</sub> gradient necessary for the computation of the air-sea 305 CO<sub>2</sub> transfer rate, as local values are not available nor were in-situ values recorded.

306 Salinity was measured in sub-samples in the laboratory at ambient temperature 307 (18 - 22°C) using a portable conductivity meter (WTW Cond 3110) with a WTW 308 Tetracon 325 probe. TA was determined within four days of collection from 309 refrigerated, unfiltered, un-poisoned seawater samples stored in 500 mL borosilicate 310 bottles with ground-glass stoppers sealed with vacuum grease (Apiezon M). The TA

311 analysis was conducted by potentiometric titration with HCl of sample aliguots of 312 known weight at constant temperature in a jacketed vessel using a Metrohm Titrando 313 888 unit. The automatic burette, pH meter, Pt temperature probe, Ag/AgCI/KCI 314 reference electrode, and glass electrode were calibrated with buffers traceable to SRM 315 from NIST and PTB (Merck, pH 2.00, 4.01, 7.00, 9.00 and 10.00 at 25°C). Daily 316 duplicate potentiometric titrations of CRMs yielded 2227.70  $\pm$  0.68 µmol kg<sup>-1</sup> for Batch 317 #102 (n = 19, certified TA = 2227.46  $\pm$  0.67 µmol kg<sup>-1</sup>) and 2221.22  $\pm$  1.44 µmol kg<sup>-1</sup> 318 for Batch #112 (n = 6, certified TA = 2223.26  $\pm$  0.89 µmol kg<sup>-1</sup>). The coefficient of 319 variation as relative standard deviation for TA was better than 0.2%.

320 A combined glass electrode and temperature probe (Inlab, 0.1°C resolution) 321 coupled to a portable Mettler Toledo SG2 (MT+2) pH meter were used for seawater 322 temperature and pH measurements. The Inlab combination electrode was calibrated 323 using the buffers described above in a jacketed vessel at constant temperature every 324 2°C from 5 to 20°C and at 25°C. Linear regression of electrode-buffer potential E (in 325 mV) versus NIST buffer pH yielded the electrode-specific apparent standard potential 326  $(E_{o})$  and potentiometric slope as a function of temperature (Figure 4a). The 327 potentiometric slope deviated by 1.2% from ideal electrochemical behavior as 328 expressed by the Nernst slope in the temperature range of 10 to 25°C.

329 The E<sub>o</sub> and potentiometric slope temperature functions were used to compute 330 seawater pH on the NIST scale from the in-situ electrode-seawater E and temperature 331 measured at 15-minute intervals by immersing the electrode in the main water mass for 332 a period of no less than 120 s. The MT+2 pH meter offered 1 mV resolution, equivalent 333 to 0.02 pH unit measurement uncertainty. The seawater pH on the seawater scale 334  $(pH_{SWS})$  was determined from  $pH_{NIST}$  as  $pH_{SWS} = pH_{NIST} + \log(f_{H+})$ , with  $f_{H+}$  equal to the 335 apparent proton activity coefficient determined at the in-situ salinity as a function of 336 temperature by potentiometric titration (outlined above) as described in Gleitz et al. 337 (1995). For this purpose, the Inlab electrode was coupled to the Metrohm titration 338 system, and Inland Sea water was titrated for TA in triplicate every 5°C from 10°C to 339 25°C. The  $f_{H+}$  exhibited a linear temperature dependency at S = 34.9 of the seawater 340 sample (Figure 4b).

341



Figure 4. (a) Measured and ideal (Nernst) potentiometric slope (*RTIn10/F*) and apparent standard potential ( $E_o$ ) as a function of temperature of the Mettler Toledo Inlab combination pH-temperature probe using NIST buffer solutions. (b) Apparent proton activity coefficient ( $f_{H^+}$ ) as a function of temperature at S = 34.9 in seawater. The straight lines through the data represent linear regression fits.

# 343 3.2 Hydrodynamic model validation

Thirty-minute moving averages of single point flow measurements during ebb tide through both channels of the Inland Sea compare well against model outputs (Figure 5). Mean ( $\pm$  1 s.d) channel velocities of 1.65  $\pm$  0.10 m s<sup>-1</sup> (n = 14), 1.74  $\pm$  0.18 m s<sup>-1</sup> (n = 11), and 1.02  $\pm$  0.04 m s<sup>-1</sup> (n = 10) were recorded using the flow meter on 17 July 2013 (JD 198), 19 July 2013 (JD 200), and 1 August 2013 (JD 213), respectively. Simulated model outputs for the same periods provided 1.37  $\pm$  0.12 m s<sup>-1</sup> (n = 64), 1.66  $\pm$  0.06 m s<sup>-1</sup> (n = 45), and 1.05  $\pm$  0.05 m s<sup>-1</sup> (n = 44).





Figure 5. Modelled and observed channel currents. Negative values denote water ebbing away from the lagoon as it empties. Observations were made at culvert entrances to the lagoon at (a) Four Mile Bridge and (b) Stanley Embankment.

353 Modelled boundary tidal forcing, expressed as ocean elevation and phase 354 change at Holyhead (degrees converted to decimal days to provide comparison continuity) for 1 July 2013 (JD 182) to 31 August 2013 (JD 243) inclusive are compared 355 356 to values published by EasyTide, having decimeter resolution (Figure 6). Mean (± 1 357 s.d) variation in modelled ocean surface elevation above chart datum (ACD) against 358 published values is 9.5  $\pm$  0.4 cm and the mean variation in phase 1.74°  $\pm$  0.07° 359 equivalent to  $0.06 \pm 2.4 \times 10^{-3}$  hr (n = 239). Field observations of high and low water 360 times within the Inland Sea are used to validate modelled lagoon phase dynamics 361 (Table 1). These compare well to model predictions; the mean deviation of the 362 modelled lagoon phase is  $3.06^{\circ} \pm 2.50^{\circ}$  or  $0.11 \pm 0.09$  hr (n = 9). Tidal range within the 363 lagoon was also recorded on various days during the study, these observations 364 deviated from modelled lagoon elevation by 2.0  $\pm$  0.7 cm (n = 4). Modelled lagoon 365 surface area minimum and maximum values of 2.43 km<sup>2</sup> and 6.50 km<sup>2</sup> were estimated 366 for the period.

367



Figure 6. Modelled boundary forcing (red line) based on tidal harmonics at Holyhead compared to published EasyTide data (blue crosses). Simulated lagoon elevation change (blue line) is also plotted.

368

Table 1 Observations of lagoon high and low water times used to validate modelled lagoon tidalphase and range.

Lagoon tidal phase (hh:mm GMT)										
observed	model	error								
JD192 09:37	09:45	+00:08								
JD198 14:20	14:12	-00:08								
JD200 08:47	08:49	+00:02								
JD200 16:15	16:26	+00:11								
JD213 07:56	07:59	+00:03								
JD213 15:19	15:20	+00:01								

JD232 06:57	07:02	+00:05
JD232 11:25	11:23	-00:02
JD232 18:52	19:09	+00:17

Lagoon tidal	n)	
JD200 0.45	0.46	+0.01
JD213 0.42	0.43	+0.01
JD232 0.49	0.47	-0.02
JD232 0.46	0.50	+0.04

# 373 **4. Results**

374 Mass balance of DIC is controlled by a combination of physical and biological 375 These include temperature change, water mixing, photosynthetic processes. 376 production of organic material, respiration of marine biota, calcium carbonate 377 precipitation and dissolution, and air-sea transfer of CO<sub>2</sub> across the surface boundary layer. Photosynthesis, CaCO<sub>3</sub> precipitation and CO<sub>2</sub> evasion all consume DIC, while 378 379 respiration, CaCO<sub>3</sub> dissolution and CO<sub>2</sub> transfer from atmosphere recycle carbon back 380 into the DIC pool from the organic, mineral and gaseous phases, respectively 381 (Papadimitriou et al., 2012). An imbalance, therefore, in the sinks and sources of DIC 382 will result in a net change in the DIC concentration in an aquatic system.

383 During these processes, the marine CO<sub>2</sub> system will re-equilibrate, with 384 consequent changes in parameters such as pH and the pCO<sub>2w</sub> of the system. The 385 change in DIC concentrations derived from the empirical observations in this study are 386 considered to be the result of influence from some, or all, of the processes of gas 387 exchange, advection and net ecosystem productivity, leading to a net deficit or excess 388 in the balance between fluxes entering and leaving the lagoon. By capturing the carbon 389 exchange rate at ecosystem boundaries, overall assessment of the net balance 390 between these processes is achieved. Our resultant analysis indicates whether the 391 ecosystem acts to balance the carbon budget as a net sink or source during the study 392 period.

393

# 394 **4.1 Lagoon system**

395 Changes in lagoon water parameters were observed from 08.00 to 19.30 BST, 396 during a complete spring tidal cycle. The mean lagoon water residence time is 397 estimated at 39 ± 6 hr calculated from simulated model channel throughput values 398 (Table 2). Seawater temperature increased linearly from 16.6°C to 19.8°C over the 399 course of the day, reaching a plateau during mid-afternoon while salinity remained 400 relatively constant at 34.01  $\pm$  0.02 ( $\pm$ 1 s.d, n = 24). During the flood period, the pH<sub>sws</sub> 401 varied between 8.05 and 8.13, while during the ebb tide it increased systematically 402 from 8.05 to 8.26. Total alkalinity initially decreased during flood tide from 2329 µmol kg<sup>-1</sup> to 2300 µmol kg<sup>-1</sup> and remained relatively constant for most of the ebb tide, with a 403

404 small step change of ~10  $\mu$ mol kg<sup>-1</sup> toward the end of the study period. The calculated 405 DIC and pCO<sub>2W</sub> exhibited similar behaviour with sinusoidal fluctuations. During the 406 flood tide, the DIC exhibited a short initial increase followed by a sustained systematic 407 decrease from 2092 to 1937 µmol kg<sup>-1</sup>. Over the same period, the pCO<sub>2W</sub> fluctuated 408 between 312 µatm and 394 µatm during flood and exhibited a systematic decrease 409 from 330 µatm to 220 µatm during ebb (Figures 7 and 8; Table 3).

410 The  $pCO_{2W}$  indicates that, throughout the study period,  $CO_2$  levels in the lagoon 411 were conducive to transfer of CO<sub>2</sub> from the atmosphere to seawater. Wind velocity 412 increased over the course of the day from 1.6 m s<sup>-1</sup> at the start of the study to almost 5 413 m s<sup>-1</sup> by the end (Figure 8). The  $F_{GAS}$  calculations were estimated to be negative 414 throughout the study period (Figure 9), indicating again that the air-sea exchange of 415 CO<sub>2</sub> occurred from atmosphere to seawater. There was an increase from a minimum 416 air-sea flux of -0.002 mmol C m<sup>-2</sup> hr<sup>-1</sup> to a maximum of -0.38 mmol C m<sup>-2</sup> hr<sup>-1</sup>, with a mean (± 1 s.d)  $F_{GAS}$  = -0.13 ± 0.26 mmol m<sup>-2</sup> hr<sup>-1</sup>. The mean NEP rate for this tidal 417 period Is estimated at 3.0  $\pm$  0.4 mmol C m<sup>-2</sup> hr<sup>-1</sup> (Table 3), with F<sub>GAS</sub> equivalent to 4.3% 418 419 of NEP DIC provision. 420

- 421
- 422 423

Table 2 Calculated water residence time based on cumulative modeled channel flow data over the mean ebb and flood period during sampling.

	Flood (m <sup>3</sup> hr <sup>-1</sup> )	Ebb (m <sup>3</sup> hr <sup>-1</sup> )	Water Residence			
			Time (hr)			
Min	3032258	1098513	33.4			
Max	3057142	823390	45.0			
Mean Period (hr)	4.5	7.6				



Figure 7. Lagoon carbonate system parameters of (a) pH (b) TA (c) DIC and (d)  $pCO_2$  on JD 232 (solid markers). DIC and  $pCO_2$  are derived from CO2Calc estimates of in-situ pH and TA observations. High and low water (blue lines) and non-daylight hours (grey areas) are also indicated.



Figure 8. Lagoon physical parameters of (a) water temperature (b) surface solar irradiance (c) salinity (d) and surface wind speed observed on JD 232. High and low water (blue lines) and non-daylight hours (grey areas) are also indicated.

426

Table 3 Measured seawater salinity, temperature, pH and TA along with calculated DIC, *p*CO<sub>2</sub>,
and air-sea CO<sub>2</sub> exchange rate (F<sub>GAS</sub>) in the Inland Sea. The NEP value is the overall estimated
daytime average. A net carbon sink is inferred from a positive NEP value and a negative F<sub>GAS</sub>
indicates a net transfer of CO<sub>2</sub> from the atmosphere to seawater. The mean water residence

432 433 time was derived from a validated 1-D MATLAB model of boundary volumetric flow, while DIC (± 8 µmol kg<sup>-1</sup>) and  $pCO_2$  (± 20 µatm) were derived from CO2Calc.

NEP							Mean Water Residence Time							
(mmol C m <sup>-2</sup> hr <sup>-1</sup> )									(	(hr)				
$3.0 \pm 0.4$									3	9±6				
Time (BST)	Time (BST) Salinity Temp (°C)		pН	sws	TA DIC		IC	pC	02	Fgas				
							(µmo	l kg <sup>-1</sup> )	(µmo	l kg <sup>-1</sup> )	(µa	tm)	(mmol C	m <sup>-2</sup> hr <sup>-1</sup> )
	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232
08:00	33.3	34.0	17.5	16.6	8.04	8.12	2323	2329	2089	2055	406	325	0.022	-0.020
08:30	33.4	34.1	17.5	16.6	8.04	8.05	2323	2319	2089	2082	405	391	0.020	-0.002
09:00	33.4	34.0	17.5	16.6	8.04	8.05	2326	2329	2092	2092	406	394	0.016	-0.002
09:30	33.5	33.8	17.5	16.7	8.04	8.05	2325	2326	2090	2090	405	394	0.017	-0.002
10:00	33.4	33.8	17.5	16.9	8.04	8.07	2330	2317	2095	2070	407	371	0.022	-0.015
10:30	33.0	33.9	17.6	17.0	8.04	8.08	2333	2307	2100	2054	409	359	0.020	-0.026
11:00	33.3	34.1	17.8	17.1	8.06	8.13	2333	2303	2082	2020	385	312	-0.017	-0.061
11:30	33.3	34.0	18.0	17.3	8.09	8.13	2331	2302	2067	2019	355	312	-0.054	-0.076
12:00	33.3	34.0	18.3	17.5	8.08	8.13	2327	2307	2064	2021	364	312	-0.040	-0.080
12:30	33.5	33.9	18.7	17.7	8.08	8.11	2316	2306	2051	2031	362	330	-0.044	-0.072
13:00	33.6	33.9	19.1	17.9	8.11	8.12	2308	2302	2023	2020	331	321	-0.083	-0.113
13:30	33.6	34.0	19.6	18.1	8.12	8.12	2309	2303	2014	2018	322	320	-0.081	-0.109
14:00	33.6	34.0	19.9	18.4	8.12	8.15	2310	2304	2012	1999	322	294	-0.086	-0.147
14:30	33.6	33.8	20.2	18.8	8.13	8.15	2314	2301	2007	1994	313	294	-0.093	-0.185
15:00	33.4	33.9	20.5	19.1	8.16	8.18	2317	2304	1988	1976	288	270	-0.121	-0.242
15:30	33.6	33.8	20.5	19.5	8.16	8.17	2319	2300	1991	1975	288	277	-0.090	-0.236
16:00	33.6	33.9	20.7	19.6	8.21	8.17	2322	2302	1955	1975	249	277	-0.166	-0.229
16:30	33.7	34.0	20.3	19.6	8.18	8.21	2317	2299	1973	1946	271	246	-0.143	-0.318
17:00		34.1		19.5		8.17		2313		1984		278		-0.251
17:30		34.0		19.7		8.22		2308		1947		240		-0.298
18:00		34.0		19.5		8.19		2310		1970		263		-0.260
18:30		34.1		19.6		8.23		2308		1941		233		-0.357
19:00		34.1		19.6		8.24		2311		1937		227		-0.369
19:30		34.2		19.2		8.25		2317		1939		221		-0.380



Figure 9. Air-sea CO<sub>2</sub> exchange, wind velocity,  $pCO_{2W}$  and temperature normalized partial pressure of CO<sub>2</sub>,  $pCO_{2,NT}$  for the study period on JD 232. Outgassing inferred from  $pCO_{2,NT}$  values early in the study period is prevented by low water temperature that increases gas solubility and lowers  $pCO_{2W}$  preventing transfer of CO<sub>2</sub> from lagoon to atmosphere.

# 436 **5. Discussion**

### 437 **5.1 Thermal effects**

438 Temperature change affects the solubility of  $CO_2$  in water, whereby an increase 439 in temperature by 1°C causes approximately 4% pCO<sub>2W</sub> increase as the dissolved gas 440 dissociates (Gazeau et al., 2005; Jiang et al., 2011; De Carlo et al., 2013). Using 441 CO2Calc to assess the maximum possible change of  $pCO_{2W}$  ( $\Delta pCO_{2,T}$ ) from the 442 temperature variation observed over the full tidal cycle on JD232 by fixing DIC and TA 443 values at the lowest observed diel temperature and allowing pH to vary with inputs of 444 minimum and maximum recorded temperature, we found that  $\Delta pCO_{2,T} = 46 \mu atm$ . This 445 is the maximum extent to which the temperature change within the lagoon can affect 446 the  $pCO_{2W}$  of the system ( $pCO_{2,T}$ ) during the study period. This value was confirmed by 447 isolating the thermally forced  $pCO_{2W}$  changes to reveal only the change due to  $pCO_{2,T}$ 448 using the approach of Takahashi et al. (1993).

449

$$pCO_{2,T} = pCO_{2,mean} \times e^{0.0423 \times (Tobs - Tmean)}$$
(9)

450

Here  $pCO_{2,T}$  and  $pCO_{2,mean}$  are the  $pCO_{2W}$  values from thermal forcing alone and the insitu average, respectively, while  $T_{mean}$  and  $T_{obs}$  are the in-situ mean and observed water temperature, respectively. This thermally isolated change reveals a similar 40 µatm change for the 3.2°C temperature increase observed in the lagoon water, resulting in only a 3.8% difference in value. A maximum diel range in  $pCO_{2W}$  of approximately 172 µatm as observed on JD 232 (Figure 9) can be attributed to a combination of the remaining physical and biogeochemical processes within the lagoon, which have over three times the influence that temperature effects alone can explain. We used a similar approach in order to isolate the influences of the non-thermal processes of mixing, gas exchange and biological activity from the temperature effect on  $pCO_{2W}$  by normalizing to the mean temperature during empirical observations ( $pCO_{2,NT}$ ) using the following formula:

464

$$pCO_{2,NT} = pCO_{2,Tobs} \times e^{0.0423 \times (Tmean - Tobs)}$$
(10)

465 where  $pCO_{2,NT}$  and  $pCO_{2,Tobs}$  are the  $pCO_{2W}$  values from temperature normalized and 466 actual observation calculations, respectively. The normalized values along with  $pCO_{2W}$ 467 can be compared to reveal the time-based influence of temperature on the system.

468 The relative importance of thermal contribution over the course of the study 469 period is highlighted by the lower temperatures in the lagoon at the start of the study 470 due to low solar irradiance and the influence of incoming seawater. These factors 471 promote greater solubility of CO<sub>2</sub> and act to prevent the system from outgassing to 472 atmosphere during this time. As the day progresses and the absorbed radiant energy 473 peaks, the thermal contribution predictably acts to increase  $pCO_{2W}$ . Given an assumed 474 constant pCO<sub>2A</sub> (396.7 ppm, NOAA, 2013), the air-sea flux drives CO<sub>2</sub> into the water 475 column due to the increasing  $pCO_2$  gradient, aided by an increase in wind velocity as 476 the study period progressed, thus promoting aquatic CO<sub>2</sub> uptake (Takahashi et al., 477 2002). It should also be noted that the influence of processes acting to reduce  $pCO_{2W}$ 478 appear to have greater impact in the lagoon than that of air-sea exchange influenced 479 by wind speed (Figure 9).

480 Using CO2Calc (section 3.1) we compute  $pH_{25}$  from the recorded salinity, TA 481 and DIC values (Table 3) and compare this with the in-situ pH data. As temperature 482 has a significant impact on this parameter, the temperature corrected value highlights 483 the biological influence in the signal. The corrected 25°C value is warmer than in-situ 484 measurements, therefore we expect to see lower pH<sub>25</sub> values. A clear reduction in the 485 signal difference over time can be seen in Figure 10 as the lagoon system warms. The 486 difference in the two pH values has a scale corrected range from 88.0% (08.30 to 487 09.00) to 93.4% (17.30) that can be attributed to biological activity alone.



Figure 10. The  $pH_{25}$  was computed using CO2SYS from measured salinity, TA, and DIC values (Table 3), using a constant temperature of 25°C.

#### 489 **5.2 Biogeochemical effects**

490 Using the stoichiometry of potential contributing biogeochemical processes that 491 could affect the CO<sub>2</sub> system of the lagoon, the fractional contribution of each to the TA-492 DIC mass balance can be assessed. This is achieved by examining the distribution of 493 salinity-normalized values of lagoon TA against DIC concentration relative to the 494 equivalent incoming seawater concentration from outside the basin. Photosynthesis will 495 cause a slight increase in TA due to nutrient uptake and will reduce the DIC 496 concentration due to its uptake by primary producers within the system, whereas 497 respiration will have the opposite effect. Both processes result in a low ratio of TA to 498 DIC concentration change, with  $\Delta A_T$ :  $\Delta C_T = -0.16$  (Lazar and Loya, 1991; Wolf-Gladrow 499 et al., 2007). The ratio of TA to DIC concentration change during calcification and 500 CaCO<sub>3</sub> dissolution is 2, while for benthic anaerobic respiration via sulphate reduction 501 with sulphide accumulation in sediment pore waters,  $\Delta A_T: \Delta C_T = 1$  (Wang & Cai 2004; 502 Wolf-Gladrow et al., 2007; Soetaert et al., 2007; Zhai et al., 2017).

503 The dominance of each of these processes to the biogeochemistry of the 504 lagoon depends on a number of factors and could be overridden by external forces, 505 such as freshwater input, lagoon stratification, and water residence time (Gupta et al., 506 2008; Kone et al., 2009; Muduli et al., 2012; Zhai et al., 2017). Their magnitude and 507 seasonal variability will affect the biogeochemistry of the lagoon and the net air-sea 508 CO<sub>2</sub> exchange. The trend in the current salinity-normalized TA versus DIC data over 509 the study period suggests that the carbonate system in the lagoon at full insolation was 510 influenced by photosynthesis and  $CO_2$  transfer from the atmosphere (Figure 11). The 511 sustained increase of pH with temperature and stable TA throughout the heightened 512 solar period, combined with an increased air-sea flux gradient suggests that maximum 513 utilization of  $CO_2$  occurs within the lagoon. Some moderate fluctuation in the normally 514 conservative TA parameter (Figure 7) suggests that it was affected somehow during

515 the study, but no water mass mixing occurs and CaCO<sub>3</sub> precipitation-dissolution 516 appears to be negligible as a  $\Delta A_T$ : $\Delta C_T$  = 2 in the salinity-normalized values would be

- 517 expected (Figure 11).
- 518



Figure 11. TA versus DIC concentrations in lagoon water observed during (a) JD 213 and (b) JD 232 normalized to S = 35, plotted relative to the inflowing seawater on each day. This is considered to be the baseline matrix altered by the physical-biogeochemical processes in the lagoon. The solid, colour coded lines indicate data distribution when individual physical-biogeochemical reactions dominate the carbonate system.

519

520 In studies of deeper coastal environments where only pelagic communities 521 dominate, temperature drives short-term changes in the carbonate system (Dai et al., 522 2009). This study suggests that, in agreement with Jiang et al. (2011), within shallow 523 nearshore systems, alterations driven by autotrophic benthic organisms may contribute 524 most to ecosystem change.

525

# 526 5.3 Tidal influence

527 Overlaying the eularian carbonate system analyses during sampling periods 528 highlights the tidal influence on the biological signal (Figure 12). The ebbing tide 529 sampled on JD 213 exhibits a maximum lagoon DIC concentration of around 2090 530 umol kg<sup>-1</sup> at the start of observations (09.30) likely due to the overnight predominance 531 of CR. The DIC concentration systematically decreases from that point throughout the day to around 1950 µmol kg<sup>-1</sup> with an approximate linear trend of -20 µmol kg<sup>-1</sup> hr<sup>-1</sup> 532 533 driven by autotrophic activity linked with increasing solar irradiance, which had a mean 534 value of 580  $\pm$  42 W m<sup>-2</sup> ( $\pm$  1s.d, n = 18) over the period.



Figure 12. Lagoon tidal regime and observed inlet DIC concentration for both JD213 and JD232. A distinct pattern of diurnal biological production during the semi-diurnal tidal cycle fluctuation is present, indicating nutrient availability from tidal ebb and flood and daytime biology utilisation.

536 By comparison, during JD 232 when sampling started (08.00) on a flood tide, 537 the DIC concentration within the lagoon initially increased from 2050 µmol kg<sup>-1</sup> to 2090 538 umol kg<sup>-1</sup> due to a proportion of lagoon water that had earlier vacated the lagoon being 539 forced back by the tide. Mixing of water carried back into the lagoon initially attenuates 540 any biologically driven DIC concentration decrease. Net DIC loss becomes apparent 541 after 09.30 when a sharp concentration drop was observed. The overall linear trend is 542 approximately  $-13 \mu$ mol kg<sup>-1</sup> hr<sup>-1</sup> for a mean solar irradiance of 334 ± 35 W m<sup>-2</sup> (± 1s.d. 543 n = 25). As the sampling occurred during daylight hours, primary production appears to 544 be the driver of DIC concentration change over time at this site. In contrast, community 545 respiration would be expected to dominate at night (Frankignoulle and Bouquegneau, 546 1990) and during winter periods (Delille, Borges and Delille, 2009).

547

535

#### 548 5.4 Diel NEP rate

549 The contribution of atmospheric carbon via CO<sub>2</sub> transfer from atmosphere to the 550 lagoon during the sampling period was estimated to be 4.3% of NEP. Conceivably, this 551 is as a direct result of the photosynthetic uptake in the Inland Sea. Jiang et al. (2011) 552 and Muduli et al. (2013) report similar findings, with CO<sub>2</sub> transfer from the atmosphere 553 playing a significant role in the latter study. In this study we determined a positive NEP of 3.0  $\pm$  0.4 mmol C m<sup>-2</sup> hr<sup>-1</sup>, which indicates a net carbon sink due to primary 554 555 production during daytime. This is the average ecosystem metabolism during the 556 photic semi-diurnal period of study (12.12 hr). Therefore, approximately 96% of the 557 daytime carbon NEP budget in the lagoon was supported by DIC availability from 558 advected nutrients while the remainder came from surface interface atmospheric CO<sub>2</sub> transfer. The estimated time-integrated metabolic rate for the 13.5 hr total daylight period is then equivalent to  $40.5 \pm 5.4$  mmol C m<sup>-2</sup>.

561 We lack site-specific information on CR, however, Hopkinson and Smith (2005) 562 report pelagic respiration rates in shallow inshore waters of between 58 and 114 mmol C m<sup>-2</sup> d<sup>-1</sup>. Thus, assuming an overnight CR range of 2.42 – 4.75 mmol C m<sup>-2</sup> hr<sup>-1</sup> NEP 563 564 estimates during our study period would yield values between 15.23 and -9.24 mmol C 565  $m^{-2} d^{-1}$ . Whereas using a CR value of 279 ± 184 mmol O<sub>2</sub>  $m^{-2} d^{-1}$  (*n* = 7) measured in Z. noltii meadows in the Thau lagoon, France, and a photosynthetic quotient of 1 (Duarte 566 567 et al., 2010), a time-integrated CR of  $122 \pm 81$  mmol C m<sup>-2</sup> can be calculated over the 568 10.5 hr respiration-dominated night-time period. This then suggests a diel NEP rate of approximately  $-82 \pm 81$  mmol C m<sup>-2</sup> d<sup>-1</sup> for our study site; the former range of estimates 569 being more consistent with the median NEP value of 20.6 mmol C m<sup>-2</sup> d<sup>-1</sup> reported in 570 571 seagrass ecosystem studies (Johnson et al., 2017).

572 Tokoro et al. (2014) presented global seagrass ecosystem NEP rates of 27 ± 6 mmol C m<sup>-2</sup> d<sup>-1</sup> converted from oxygen-based units. NEP estimates and errors may 573 574 vary dependent upon applied method and location. For example, Gazeau et al. (2005) 575 found that measured NEP rates fluctuated between 7 ± 1 mmol C m<sup>-2</sup> d<sup>-1</sup> and 41 ± 3 mmol C m<sup>-2</sup> d<sup>-1</sup>, with a mean of 22 ± 12 mmol C m<sup>-2</sup> d<sup>-1</sup>. Estimates of water residence 576 times, which are difficult to quantify in open embayment's, contributed most to 577 578 uncertainty. Ribas-Ribas et al. (2011) found NEP values between 10 and 60 mmol C m<sup>-</sup> 579 <sup>2</sup> d<sup>-1</sup> neglecting the influence of water residence time. Other studies have assessed 580 whether net autotrophic or heterotrophic behavior dominates in coastal systems based 581 on longer studies of NEP, estimated from rates of GPP and CR, with GPP known to 582 vary inter-annually by as much as 35% and NEP by 87% (Champenois and Borges, 583 2012).

584 The intertidal beds of the Inland Sea are colonized by the seagrass Zostera 585 noltii, which contribute to primary production in the study area. Papadimitriou et al. 586 (2006) estimated an increase in the above-ground seagrass biomass equivalent to 18 587 - 27 mmol C m<sup>-2</sup> d<sup>-1</sup> and in the below-ground biomass (roots and rhizomes) equivalent to 22 – 28 mmol C m<sup>-2</sup> d<sup>-1</sup> during growth periods in spring and summer. Duarte et al. 588 589 (2005) reported on GPP, CR, and NEP for seagrass species and found that, in general, 590 seagrass meadows with GPP  $\geq$  180 mmol C m<sup>-2</sup> d<sup>-1</sup> were net autotrophic. Specifically, 591 for Z. noltii, ~66% of the meadows included in the Duarte et al. (2010) study had GPP 592 values of this magnitude, attesting to the potential for carbon sequestration for this 593 species of seagrass. Based on the limited daytime NEP data and assumed night-time 594 CR of Duarte et al. (2010), the seagrass community in our study site may be net 595 heterotrophic on an annual time scale but more detailed investigation is required to 596 validate this indication. Thus, future modelling of lagoon systems would benefit from

diurnal and seasonal sampling of the CO<sub>2</sub> system to obtain annual estimates of netcarbon gain or loss to the atmosphere and to the adjacent Irish Sea waters.

#### 600 **5.5 Residence time**

599

601 The box model approach utilized here allows us to quantify the input and output 602 of CO<sub>2</sub> in the system from both advective lateral fluxes and surface transfer regimes, 603 which is crucial in shallow nearshore ecosystems. However, it requires the ability to 604 accurately predict water flow through the channels, because large uncertainties are 605 introduced into calculations over short time scales (Borges et al., 2008). By considering 606 an integrated approach over a tidal period, the uncertainty is somewhat attenuated. 607 The integrated mean used to derive mass balance calculations are based on 608 polynomial fits of the plotted observational data, with 95% confidence intervals of the 609 standard deviation of the slope used to constrain NEP calculations.

610 Based on simplified unidirectional, unforced and hydrostatically balanced 611 channel flow calculations (0.5  $u^2 = -g d\eta/dx$ ) the contribution to error from uncertainty in 612 harmonic boundary forcing in the MATLAB simulations causes a maximum elevation 613 uncertainty of approximately 10 cm. This yields a maximum potential flow uncertainty 614 of around 0.14 m s<sup>-1</sup> in a channel of 100 m length (this error reduces for longer 615 channels). However, validation data resolution was of the same order of magnitude, 616 therefore this was ignored for NEP error estimate. The largest contribution to 617 uncertainty for this study came from the estimated lagoon phase error of  $0.11 \pm 0.09$  hr 618 (n = 9). Assuming an average flow through the channel over the error phase period of 619 0.5 m s<sup>-1</sup> (i.e. around slack water), a maximum difference in  $\Delta F_{MIX}$  of approximately 0.15 620 mmol C m<sup>-2</sup> Is possible. Therefore, greatest uncertainty is derived from the change in 621 water residence time with phase shift. This results in an increase in the cumulative 622 error estimation from  $\pm$  0.03 mmol C m<sup>-2</sup> hr<sup>-1</sup> to  $\pm$  0.4 mmol C m<sup>-2</sup> hr<sup>-1</sup> for a calculated 623 difference in mean residence time of approximately 6 hours.

624 Based on a fixed tidal period and using the methods of this study, water 625 residence time will increase if mean lagoon capacity increases or if the change in 626 channel volumetric flow decreases (effectively a decrease in tidal range). An increase 627 in residence time subsequently reduces NEP as the nutrients within the system take 628 longer to be replenished and may result in a loss of seagrass habitat (Orfila et al., 629 2005). Delhez et al. (2014) report that the total time spent within the control domain 630 may be significantly underestimated in oscillating flow regimes using the approach 631 presented. It should be noted that calculation of residence time based on eq (6) utilizes 632 the simple assumption that all of the water is exchanged through the channel, when in 633 reality some of the water exiting or entering the lagoon returns immediately. A better 634 approach may be to consider the fractional return of some of the water to avoid

overestimation of NEP (Sheldon and Alber, 2006; Rynne et al., 2016). Future work
should focus on constraining the parameters critical to estimating the time taken for
water to be replenished within the lagoon. Increased understanding of the lagoon
bathymetry, channel dimensions and substrate type would all conceivably contribute to
a reduction in modelled phase error.

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# 641 6. Conclusion

642 Restricted lagoons such as the Inland Sea offer the ability to examine the 643 variation in NEP from DIC utilization and water residence period due to the nature of 644 their water exchange regimes. Increased high-resolution temporal monitoring using 645 autonomous techniques may be beneficial, as would constraining spatial distribution of 646 carbonate system concentrations. It has been shown that the overall net carbon 647 productivity of the Inland Sea ecosystem can be assessed over a complete tidal period 648 by conducting measurements of carbonate system parameters from water advected 649 through the channels, in combination with post observation, bulk parameterization 650 analysis. Development of methods should include autonomous measurements, 651 improved geophysical evaluation, enhanced validation and numerical hydrodynamic 652 modelling of boundary exchange, in order to further constrain estimates. Extrapolation 653 of calculated values for increased spatial and temporal assessment should also be a 654 future objective.

655 The overall net autotrophic balance of the seagrass containing system studied 656 suggests a potential sink for inorganic carbon during summer periods. An estimated NEP of 40.5 ± 5.4 mmol C m<sup>-2</sup> during the 13.5 hr daytime study period is equivalent to 657 658 a diel range of between 15.23 and -9.24 mmol C m<sup>-2</sup> d<sup>-1</sup> based on assumptions using 659 reported shallow water pelagic respiration rates. However, it is crucial to include 660 measurements of actual overnight respiration rate during studies, as a potential source of inorganic carbon is calculated (-82  $\pm$  81 mmol C m<sup>-2</sup> d<sup>-1</sup>) when literature values for 661 662 Zostera noltii meadows based on  $O_2$  utilization is assumed. Furthermore, the former 663 approach suggests that approximately 4% of DIC is provided by CO<sub>2</sub> transfer from 664 atmosphere to ocean during the study period. Similar methodology may provide an 665 opportunity to assess the atmospheric carbon sequestration potential of planned 666 nearshore lagoon constructions. From the MRE perspective, there exists the potential 667 of enhancing the financial feasibility of tidal range lagoon energy schemes through 668 consideration of carbon offsetting. In particular when such structures are designed to 669 accommodate colonies of productive autotrophic flora.

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