



# 1 Carbon Dioxide and Methane Emissions from Red Sea Mangrove

- 2 Sediments
- 3

# 4 Mallory A. Sea<sup>1</sup>, Neus Garcias-Bonet<sup>1</sup>, Vincent Saderne<sup>1</sup>\* and Carlos M. Duarte<sup>1</sup>

5

6 [1] {King Abdullah University of Science and Technology (KAUST), Red Sea Research Center

7 (RSRC), Thuwal, 23955-6900, Saudi Arabia}

8

9 \*Correspondence to: V. Saderne (vincent.saderne@kaust.edu.sa)

10

# 11 Abstract

Mangrove forests are highly productive tropical and subtropical coastal systems that provide a 12 variety of ecosystem services, including the sequestration of carbon. While mangroves are 13 reported to be the most intense carbon sinks among all forests, their sediments can also support 14 15 large emissions of greenhouse gases (GHG), such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), 16 to the atmosphere. However, data derived from arid mangrove systems like the Red Sea are lacking. Here, we report emission rates of CO<sub>2</sub> and CH<sub>4</sub> from mangrove sediments along the 17 Saudi Arabian coast of the Red Sea, and assess the relative role of these two gases in supporting 18 total GHG emissions. Diel CO2 and CH4 emission rates in Red Sea mangrove sediments ranged 19 from -3452 to 7500  $\mu$ mol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> and from 0.9 to 13.3  $\mu$ mol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively. The 20 rates reported here fall within previously reported ranges for both CO<sub>2</sub> and CH<sub>4</sub>, but maximum 21 22 CO<sub>2</sub> and CH<sub>4</sub> flux rates in the Red Sea are 10 to 100-fold below those previously reported for 23 mangroves elsewhere. Based on the isotopic composition of the CO<sub>2</sub> and CH<sub>4</sub> produced by 24 mangrove sediments, we identified the origin of the organic matter that supports GHG emissions. 25 In most of the mangrove stands, GHG emissions were supported by organic matter from mixed





- 26 sources while only in one mangrove stand the GHG emissions were supported by organic matter 27 derived from mangrove tissues. Moreover, the organic matter derived from mangrove tissues 28 reduced CO<sub>2</sub> fluxes and enhanced CH<sub>4</sub> production, pointing out the importance of the origin of 29 the organic matter in GHG emissions. Methane was the main source of CO<sub>2</sub>-equivalents, despite 30 the comparatively low emission rates, in most of the sampled mangroves, and therefore deserves 31 careful monitoring in this region. Despite the mean net emission of CO<sub>2</sub> and CH<sub>4</sub> by Red Sea 32 mangroves reported here, these forests become net organic carbon sinks when taking into 33 account the existing carbon burial rates for the Red Sea mangroves. By further resolving GHG 34 fluxes in arid mangroves, we will better ascertain the role of these forests in global carbon 35 budgets.
- 36
- 37





### 38 1 Introduction

39 Mangrove forests, typically growing in the intertidal zones of tropical and subtropical coasts, are highly productive components of coastal ecosystems and adapted to high salinity and anoxic 40 conditions associated with waterlogged sediments. Mangrove forests cover a global estimated 41 area of 137,760 km<sup>2</sup> (Giri et al., 2011) and are typically constrained by temperature, with 42 43 greatest biomass and species diversity in the equatorial zone (Alongi, 2012). Mangroves rank 44 amongst the most threatened ecosystems in the biosphere, with losses estimated at 50% of their 45 global extent over the past 50 years (Giri et al., 2011). These losses affect all mangrove regions, except for the Red Sea, where mangrove coverage has increased by 13% over the past four 46 47 decades (Almahasheer et al., 2016).

48

49 Loss of mangrove forest represents a loss of valuable ecosystem services, including habitat and 50 nursery for marine species, coastal protection from erosion due to wave action, and the filtration 51 of harmful pollutants from terrestrial sources (Alongi, 2008), as well as loss of CO<sub>2</sub> sink capacity 52 and a source of emissions of greenhouse gases (GHG) from disturbed soil carbon stocks (Donato 53 et al., 2011; Alongi, 2014). Hence, mangrove conservation and restoration have been proposed as 54 important components of so-called Blue Carbon strategies to mitigate climate change (Duarte, et 55 al., 2013). Indeed, mangroves are reported to be the most intense carbon sinks among all forests, 56 supporting carbon sequestration rates and organic carbon stocks as much as five times higher 57 than those in terrestrial forests (Donato et al., 2011). While mangrove forests cover less than 1% 58 of total coastal ocean area, they contribute to almost 15% of total carbon sequestration in coastal 59 ecosystems (Alongi, 2012), making mangrove forests highly effective in terms of carbon 60 sequestration per unit area. The management of mangroves to maximize CO<sub>2</sub> removal and 61 subsequent storage is gaining momentum as a cost-effective strategy to mitigate climate change.

62

63 However, mangroves act as both carbon sinks and sources, as their sediments have been reported 64 to support large GHG emissions, in the forms of  $CO_2$  and  $CH_4$  (Allen et al., 2007; Kristensen et 65 al., 2008a; Chen et al., 2016). Whereas concerns are focused on GHG emissions following





mangrove disturbance, estimated at 0.02 - 0.12 Pg C yr<sup>-1</sup> globally (Donato et al., 2011), 66 67 undisturbed mangrove sediments also support GHG emissions (Purvaja and Ramesh, 2000; 68 Kristensen et al., 2008b; Chauhan et al., 2015). Previous studies on GHG emission rates from 69 mangrove sediments show highly variable fluxes, with mangroves reported to act from negligible 70 (Alongi, 2005) to considerable sources (Livesley and Andrusiak, 2012; Chen et al., 2016). Comparisons of carbon sequestration rates between mangrove stands have revealed that climatic 71 72 conditions play an important role, with mangroves in the arid tropics, such as those in the Red 73 Sea, supporting the lowest carbon sequestration rates (Almahasheer et al. 2017). Likewise, GHG 74 emissions from mangrove forests may vary with climate, with most reported rates to-date derived 75 from the wet tropics (Alongi et al., 2005; Chauhan et al., 2015; Chen et al., 2016). Whereas Red 76 Sea mangroves are considered to play a minor role as  $CO_2$  sinks, their role may be greater than 77 portrayed by low carbon burial rates if they also support very low GHG emissions, thereby 78 leading to a balance comparable to mangroves in the wet tropics.

Here we report emission rates of CO<sub>2</sub> and CH<sub>4</sub>, along with their carbon isotopic composition, from mangrove sediments along the Saudi coast of the Red Sea, and assess the relative role of these two gases in supporting total GHG emissions as well as their fluctuations along the daynight cycle.

83

# 84 2 Materials and Methods

### 85 2.1 Study area

86 We sampled seven mangrove forests along the eastern coast of the Red Sea (Fig. 1). We 87 collected triplicate sediment cores (translucent PVC tubes, 30.5 cm in height and 9.5 cm in 88 diameter) at each station in order to measure CO<sub>2</sub> and CH<sub>4</sub> fluxes. Additionally, we analyzed 89 sediment chlorophyll a and nutrient (organic carbon and nitrogen) content. Mangrove sediments 90 were sampled five to ten meters from the forest edge, typically in the center of the mangrove 91 belt. We sampled two stations (S1 and S2) in January and February 2017 and the other five 92 mangrove stations (S3-S7) in March on board the R/V Thuwal as part of a scientific cruise. The 93 sediment cores collected from S1 and S2 were immediately transported to the laboratory and





- placed in seawater baths and enclosed in environmental growth chambers (Percival Scientific
  Inc., Perry, IA, USA) with 12h-light:12h-dark cycles at a constant temperature of 26°C. The
  sediment cores collected during the scientific cruise were transported immediately on board and
  placed in open aquarium tanks with running seawater in order to keep them close to *in situ*temperature. Salinity and temperature were routinely recorded using a CTD.
- 99

### 100 2.2 Sediment characteristics

101 The chlorophyll a content of the sediment was measured by fluorometry. The surface layer of 102 each replicate core was collected and frozen until further analysis. Prior to chlorophyll a 103 extraction, the sediment samples were left at room temperature to thaw. The chlorophyll a was 104 extracted by adding 7 ml of 90% acetone to 2 ml of sediment sample. After a 24h incubation at 105  $4^{\circ}$  C in dark conditions, the samples were centrifuged and the chlorophyll *a* content in the 106 supernatant was measured on a Trilogy fluorometer. The nutrient (organic carbon and nitrogen) 107 content of the sediment was analyzed on an Organic Elemental Analyzer (Flash 2000) after 108 acidification of sediment samples.

109

### 110 **2.3** Measurement of greenhouse gas fluxes

We measured  $CO_2$  and  $CH_4$  fluxes in mangrove sediments using two different techniques. The CO<sub>2</sub> and  $CH_4$  fluxes from S1 and S2 were measured using the closed water circuit technique and the CO<sub>2</sub> and  $CH_4$  fluxes from the rest of the stations sampled during the scientific cruise (S3-S7) were measured using the headspace technique.

115

# 116 2.3.1 Measurement of CO<sub>2</sub> and CH<sub>4</sub> fluxes in sediment core incubations using 117 closed water circuit technique





118 We incubated mangrove sediment cores from stations S1 and S2 using a closed water circuit 119 technique in order to measure changes in CO<sub>2</sub> and CH<sub>4</sub> concentrations. Before starting the incubation, the seawater above the sediment from each core was replaced by fresh seawater 120 121 collected from the same location, avoiding disturbance of the sediment. Then, the seawater from 122 the core was recirculated by a peristaltic pump in an enclosed water circuit through a membrane 123 equilibrator (Liqui-cel mini module, 3M, Minnesota, USA). This setup enables the equilibration 124 of gases in dissolution with an enclosed air circuit. The air from the enclosed air circuit was then 125 passed through a desiccant (calcium sulfate, WA Hammond Drierite Co., LTD, Ohio, USA) 126 column and flowed into a cavity ring-down spectrometer (CRDS; Picarro Inc., Santa Clara, CA, 127 USA) to continuously measure the  $CO_2$  and  $CH_4$  concentration. We ran the incubations for at least 30 minutes under light (200 µmol photons m<sup>-2</sup> s<sup>-1</sup>) and dark conditions. 128

129 The concentration of  $CO_2$  in the water circuit (µmol ml<sup>-1</sup>) was calculated by Eq. (1):

130 
$$[CO_2] = Hcp x [HP_CO_2] x (1 - pH_20),$$
 (1)

where Hcp is the Henry constant (mol ml<sup>-1</sup> atm<sup>-1</sup>) calculated using R marelac package (Soetaert et al., 2016); [HP\_CO<sub>2</sub>] is the given concentration of CO<sub>2</sub> (ppm), and pH<sub>2</sub>0 is the water vapor pressure (atm).

The CO<sub>2</sub> fluxes were calculated from the change in CO<sub>2</sub> concentration over time during our incubations, correcting by the seawater volume present in each core. Then, the fluxes were transformed to an aerial basis ( $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>) by taking into account the core surface area. Finally, the daily fluxes ( $\mu$ mol m<sup>-2</sup> d<sup>-1</sup>) were calculated by multiplying the CO<sub>2</sub> flux obtained under light conditions by the number of light hours plus the CO<sub>2</sub> flux obtained under dark conditions by the number of dark hours.

140 The  $CH_4$  fluxes were calculated in the same manner as for the  $CO_2$  fluxes, with the exception 141 that the Henry constant was calculated using Eq. (2):

142 
$$\beta = \operatorname{Hep} x (RT),$$
 (2)





- 143 where Hcp is the Henry constant (mol ml<sup>-1</sup> atm<sup>-1</sup>), R is the ideal gas constant (82.057338 atm ml
- 144 mol<sup>-1</sup> K<sup>-1</sup>), T is standard temperature (273.15 K), and  $\beta$  is the Bunsen solubility coefficient of
- 145 CH<sub>4</sub>, extracted from Wiesenburg and Guinasso (1979).

# 146 2.3.2 Measurement of CO<sub>2</sub> and CH<sub>4</sub> fluxes in sediment core incubations using the 147 headspace technique

148 Mangrove sediment cores from stations S3 to S7 were incubated using a headspace technique in 149 order to measure changes in  $CO_2$  and  $CH_4$  concentrations. Before starting the incubation, the 150 seawater above the sediment from each core was replaced by fresh seawater from the running 151 seawater system, leaving a headspace of 200 ml. Each core was sealed with a stopper equipped 152 with a gas-tight valve serving as a headspace sampling port. The sealed core was left for 1 hour 153 before the first headspace sampling to allow equilibration between seawater and air phases. Each 154 core was sampled with a syringe, withdrawing 15 ml of air from the equilibrated headspace. 155 Headspace samples were periodically drawn from each sediment incubation over a 24-hour 156 incubation period. The CO<sub>2</sub> and CH<sub>4</sub> concentrations in the headspace samples along with their isotopic composition ( $\delta^{13}$ C-CO<sub>2</sub> and  $\delta^{13}$ C-CH<sub>4</sub>) were measured with a cavity ring-down 157 158 spectrometer (CRDS; Picarro Inc., Santa Clara, CA, USA) connected to a small sample isotopic 159 module extension (SSIM A0314, Picarro Inc., Santa Clara, CA, USA). We ran standards (730 160 ppm CO<sub>2</sub>, 1.9 ppm CH<sub>4</sub>) before and after every three samples.

161 The concentration of dissolved  $CO_2$  in the seawater after equilibrium was calculated from the 162 concentration in the equilibrated headspace (ppm) as described previously by Wilson et al. 163 (2012) for other gases:

164 
$$[CO_2]_w = 10^{-6} \beta m_a p_{dry},$$
 (3)

165 where  $\beta$  is the Bunsen solubility coefficient of CO<sub>2</sub> (mol ml<sup>-1</sup> atm<sup>-1</sup>),  $m_a$  is the given 166 concentration of CO<sub>2</sub> in the equilibrated headspace (ppm), and  $p_{dry}$  is atmospheric pressure (atm) 167 of dry air. The Bunsen solubility coefficient of CO<sub>2</sub> was calculated using Eq. (4):

168 
$$\beta = \text{Hep x}(RT)$$
 (4)





where Hcp is the Henry constant (mol ml<sup>-1</sup> atm<sup>-1</sup>) calculated using R marelac package (Soetaert et al., 2016), R is the ideal gas constant (82.057338 atm ml mol<sup>-1</sup> K<sup>-1</sup>) and T is standard

171 temperature (273.15 K). The atmospheric pressure of dry air ( $p_{dry}$ ) was calculated using Eq. (5):

172 
$$p_{dry} = p_{wet} (1 - \% H_2 0)$$
 (5)

- 173 where  $p_{wet}$  is the atmospheric pressure of wet air corrected by the effect of multiple syringe
- draws from the same core, applying Boyle's law.
- 175 The initial concentration of dissolved CO<sub>2</sub> in seawater before equilibrium was then calculated as:

176 
$$[CO_2]_{aq} = ([CO_2]_w V_w + 10^{-6} m_a V_a) / V_w$$
 (6)

where  $[CO_2]_w$  is the concentration of dissolved  $CO_2$  in the seawater after equilibrium,  $V_w$  is the volume of seawater (ml) and  $V_a$  is the headspace volume (ml) in the core. Finally, treating the

179 gas as ideal, the units were converted to nM using Eq. (7):

180 
$$[CO_2]_{aq} = 10^9 * p_{dry}[CO_2]_{aq}/(RT)$$
 (7)

181 where *R* is the ideal gas constant (0.08206 atm  $1 \text{ mol}^{-1} \text{ K}^{-1}$ ) and *T* is temperature (K).

182 The CO<sub>2</sub> fluxes were calculated from the change in CO<sub>2</sub> concentration over time during our 183 incubations, correcting by the seawater volume present in each core. Then, the fluxes were 184 transformed to an aerial basis ( $\mu$ mol m<sup>-2</sup> d<sup>-1</sup>) by taking into account the core surface area. Finally, 185 the day and night fluxes ( $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>) were calculated from the change in CO<sub>2</sub> concentration 186 between consecutive samplings during day and night time, respectively.

187 The CH<sub>4</sub> fluxes were calculated in the same manner as for the  $CO_2$  fluxes, with the exception 188 that the Bunsen solubility coefficient of CH<sub>4</sub> was calculated according to Wiesenburg and 189 Guinasso (1979).

190

#### 191 2.4 Isotopic composition of CO<sub>2</sub> ( $\delta^{13}$ C- CO<sub>2</sub>) and CH<sub>4</sub> ( $\delta^{13}$ C- CH<sub>4</sub>)





192	The isotopic signature of the CO <sub>2</sub> and CH <sub>4</sub> produced in the sediment incubations was estimated
193	by conducting keeling plots (Pataki et al. 2003; Thom et la. 2003; Garcias-Bonet and Duarte
194	2017). Briefly, the $\delta^{13}C$ of the $CO_2$ and $CH_4$ produced was extracted from the intercept of the
195	linear regression between the inverse of the gas partial pressure and the isotopic signature.

196

# 197 **3 Results**

The mean ( $\pm$  SE) diel CO<sub>2</sub> and CH<sub>4</sub> emission rates for the seven sites were 372  $\pm$  1309 µmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> and 5.6  $\pm$  1.6 µmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively. We observed high variability among the seven mangrove forest sites studied, with net CO<sub>2</sub> and CH<sub>4</sub> diel emission rates ranging from -3452 to 7500 µmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> and from 0.9 to 13.3 µmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively (Table 1).

Mangrove sediments absorbed CO<sub>2</sub> during daytime and emitted CO<sub>2</sub> during night time, with means ( $\pm$  SE) of -54.6  $\pm$  37 µmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> and 86  $\pm$  120 µmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> respectively (Table 1, Fig. 2). However, in three out of seven sites, heterotrophic activities outbalanced photosynthesis on a 24h basis. At two sites, S3 and S6, we found an increase of the CO<sub>2</sub> emissions between day and night, contradictory to the classical daytime primary production– night-time respiration pattern, possibly indicative of a light mediated increase of heterotrophic processes.

209 Methane emissions did not show circadian patterns with linear increases in CH<sub>4</sub> concentration in 210 our incubations (Fig. 2) and with similar light and dark rates  $(0.26 \pm 0.08 \text{ and } 0.21 \pm 0.07 \mu \text{mol}$ 211 CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> (mean ± SE), respectively (Table 1)). In terms of total GHG contribution, the mean 212 CO<sub>2</sub>-equivalents (CO<sub>2</sub>e) emission was 564 ± 1284 µmol CO<sub>2</sub>e m<sup>-2</sup> d<sup>-1</sup> (mean ± SE); mangrove 213 sediments were net emitters of CO<sub>2</sub>e in three out of seven sites (Table 1), and in five out of seven 214 mangrove stands sampled, CH<sub>4</sub> was the main source of CO<sub>2</sub>e to the atmosphere.

While no overall trend was revealed through the relationship between day and night fluxes for CO<sub>2</sub> and CH<sub>4</sub> (Fig. 3), consistencies are evident at specific mangrove stations. For example, night CO<sub>2</sub> emissions are clearly visible at S2, while S3 appears to emit CO<sub>2</sub> during daylight hours. No relationship was apparent between GHG fluxes and the densities of organic carbon or





nitrogen in the sediment. There was no discernible trend between gas fluxes and chlorophyll *a*content in surface sediments.

- 221 The isotopic signatures of the produced CO<sub>2</sub> ( $\delta^{13}$ C-CO<sub>2</sub>) ranged from -11.21 to -25.72 ‰ as
- 222 derived from keeling plots (Fig. 4, Table 1). The  $\delta^{13}$ C-CO<sub>2</sub> was similar for almost all stations,
- 223 with the exception of S3 that had a  $\delta^{13}$ C-CO<sub>2</sub> of -25.72 ‰. The isotopic composition of the
- produced CH<sub>4</sub> ( $\delta^{13}$ C-CH<sub>4</sub>) ranged from -71.28 to -87.08 ‰, with a mean  $\delta^{13}$ C signature of -80.61
- 225 % (Fig. 4, Table 1). The data set is available from Sea et al. (2018).

226

### 227 **4 Discussion**

The CO<sub>2</sub> and CH<sub>4</sub> emissions reported in this study show that Red Sea mangrove sediments can 228 229 act as a source of GHG to the atmosphere. Values reported from this study fall within previously 230 reported ranges for both CH<sub>4</sub> and CO<sub>2</sub>, but maximum CH<sub>4</sub> and CO<sub>2</sub> flux rates in the Red Sea are 231 over 10 to 100 fold below those reported elsewhere (Table 2). The variability in GHG emission 232 rates reported here could be attributed to spatial differences, as cores were taken from different 233 parts of each forest. Previous studies report significant discrepancies in emission rates in fringe 234 versus forest positions (Allen et al., 2007), although this is likely to be a minor source of 235 variability provided the narrow belt Red Sea mangroves typically form, about 30 m, due to the 236 restricted tidal range of about 0.6 m in this region.

237 The uniformity of day and night emission rates for CH<sub>4</sub> we observed in Red Sea mangrove 238 stands is consistent with previous work reporting that emission rates for CH4 do not vary 239 significantly during light and dark hours in mangrove forests (Allen et al., 2007). It has been 240 suggested instead that variables such as sediment temperature are more significant in their 241 contributions to emission rates (Allen et al., 2007; Allen et al., 2011). Indeed, seasonal studies of 242 longer duration have reported increased emission rates during warmer seasons (Chen et al., 2016; 243 Livesley and Andrusiak, 2012). Methane concentrations typically remain low due to anaerobic 244 methane oxidation processes that take place near sediment surfaces (Kristensen et al., 2008a), 245 consistent with the low CH<sub>4</sub> emission rates from Red Sea mangrove sediments observed here. 246 Additionally, environments of high salinity like the Red Sea have been associated with decreased





247 CH<sub>4</sub> emissions, as sulfate-reducing bacteria are thought to outcompete methanogens
248 (Poffenbarger et al., 2011).

249 There were no relationships between GHG fluxes and sediment properties, such as chlorophyll a, 250 nitrogen density, and organic carbon density, suggesting that other factors have greater influence 251 on GHG flux rates in this region. Since mangroves can receive large contributions of organic 252 carbon from other sources (Newell et al., 1995), such as algal mats, seagrass and seaweed, the 253 examination of the isotopic composition of emitted carbon provides insights into the origin of the 254 organic carbon supporting GHG fluxes in mangrove sediments. The isotopic signature of the 255  $CO_2$  ( $\delta^{13}C-CO_2$ ) produced by mangrove sediments in four out of the five mangrove stands with 256 available isotopic data was heavier (from  $-11.2 \pm 0.6$  to  $-15.9 \pm 1.1$  % (Table 1)) than the 257 isotopic signature of mangrove tissues, suggesting the decomposition of organic matter from 258 mixed sources (Kennedy et al. 2010). Specifically, the isotopic signature of the mangroves found in the central Red Sea has been recently reported as  $\delta^{13}C_{leaves} = -26.98 \pm 0.15$  ‰,  $\delta^{13}C_{stems} = -$ 259  $25.75 \pm 0.16$  ‰ and  $\delta^{13}C_{roots} = -24.90 \pm 0.17$  ‰ for mangrove leaves, stems and roots while the 260 261 mean isotopic signature of other primary producers in the central the Red Sea has been reported 262 as  $\delta^{13}C_{seaweed} = -12.8 \pm 0.5$  ‰ and  $\delta^{13}C_{seagrass} = -8.2 \pm 0.2$  ‰ for seaweed and seagrass tissues, respectively (Almahasheer et al. 20170). However, in one mangrove stand (S3) the  $\delta^{13}$ C-CO<sub>2</sub> 263 264 was much lighter (-25.72  $\pm$  0.21 ‰), indicative of mangrove tissues. Thus, according to the 265 isotopic signature, the CO<sub>2</sub> produced in mangrove sediments would be supported by mangrove 266 biomass in only one mangrove stand out of the five sampled sites with available isotopic data. 267 Moreover, the mean isotopic signature of the CH<sub>4</sub> produced in mangrove sediments ( $\delta^{13}$ C-CH<sub>4</sub>= 268 -80.6 ‰) confirms its biogenic origin, which normally ranges from -40 to -80 ‰, depending on 269 the isotopic signature of the organic compounds being biologically decomposed (Reeburgh, 2014). The lowest  $\delta^{13}$ C-CH<sub>4</sub> was detected in S3, coinciding with the lowest  $\delta^{13}$ C-CO<sub>2</sub> value, 270 271 suggesting that the organic matter being decomposed by methanogens came from mangrove 272 tissues as well.

Interestingly, the mangrove with the lightest  $\delta^{13}$ C-CO<sub>2</sub> and  $\delta^{13}$ C-CH<sub>4</sub> (S3), showed the lowest daily CO<sub>2</sub> flux (-1524 ± 686 µmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) but the highest CH<sub>4</sub> emission rate (13.3 ± 9.5 µmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>), compared to the fluxes detected in the rest of mangrove stands with available isotopic data. Part of the variability in the CO<sub>2</sub> (R<sup>2</sup>=0.42) and CH<sub>4</sub> (R<sup>2</sup>=0.40) emission rate seems





to be explained by the origin of the organic matter being decomposed, estimated here as the  $\delta^{13}$ C-CO<sub>2</sub> and  $\delta^{13}$ C-CH<sub>4</sub>. Organic matter with lighter isotopic composition would enhance CO<sub>2</sub> emissions; whereas organic matter with heavier isotopic composition would enhance CH<sub>4</sub> emissions (Fig. 5), suggesting a different preferential use of organic matter by different microbial groups in mangrove sediments. This corroborates the importance of the origin of the organic carbon stored in mangrove sediments on their GHG emissions.

283 This study is first in reporting CO<sub>2</sub> and CH<sub>4</sub> fluxes from Red Sea mangrove sediments, 284 contributing to the scant data on arid mangrove systems (Atwood et al. 2017, Almahasheer et al. 285 2017) essential to establish a solid baseline on GHG emissions for future studies. Seasonal 286 variation should be considered in future studies on GHG emissions by Red Sea mangroves to 287 better determine annual emission rates from this system, which reaches some of the warmest 288 temperatures experienced by mangrove forests worldwide. Similarly, a wider spatial coverage 289 within the mangrove forest should be considered to confidently determine net GHG fluxes that 290 can be upscaled to the entire stock of Red Sea mangroves. While many studies use the static 291 chamber technique to determine concentrations of methane and carbon dioxide, the highly 292 sensitive CRDS was able to detect trace gases at very low concentrations, making this device 293 useful in future flux studies. However, it is recognized that inherent differences in reported 294 emissions exist as a result of two different sampling techniques used in this study. Establishing a 295 unified GHG sampling technique for mangrove sediments will aid future researchers in 296 establishing total carbon budgets and accurately informing policymakers of their findings.

297 Methane emission rates from Red Sea mangrove sediments, although quite low, become more 298 substantial when considered in terms of global warming potential. In this study, CH<sub>4</sub> was, despite 299 the comparatively low emission rates, the main source of  $CO_2e$  in the majority of sampled 300 mangroves, and therefore deserves careful monitoring in this region. Reported organic carbon burial rates of Red Sea mangroves of 3.42 mmol C m<sup>-2</sup> d<sup>-1</sup> (Almahasheer et al. 2017), are 10 301 302 times larger than the combined average CO<sub>2</sub> and CH<sub>4</sub> emission rates reported here (0.37 mmol C  $m^{-2} d^{-1}$ ), identifying mangrove sediments as net carbon sinks. The balance is lower when 303 computed in terms of CO2e, the relevant metric in terms of radiative forcing, but still resulted in 304 a net CO<sub>2</sub>e removal rate of about 2.9 mmol C m<sup>-2</sup> d<sup>-1</sup> by Red Sea mangrove sediments. Whereas 305 306 our results show that, despite sizeable CH<sub>4</sub> and CO<sub>2</sub> emissions, Red Sea mangrove sediments are





307 net sinks for organic carbon; their contribution to climate change, by either promoting it or 308 mitigating it is not reflected on this balance. The role of Red Sea mangrove sediments in climate 309 change depends on the changes experienced. In contrast to mangrove forests elsewhere around 310 the world, Red Sea mangroves are not in decline and, rather, have expanded 12% from the 120 Km<sup>2</sup> occupied in 1972 to 132 Km<sup>2</sup> in 2013 (Almhasheer et al. 2016). Hence, Red Sea mangroves 311 312 would have had a modest, but measurable contribution to climate change mitigation. Moreover, 313 protection measures and further reforestation efforts are being deployed along the Red Sea that 314 will further expand the area of mangroves (Almhasheer et al. 2016). The rationale for conserving 315 mangroves, in the climate change context, is not adequately represented by their net carbon sink 316 capacity when undisturbed, but rather by the emissions resulting from their disturbance. Indeed, 317 previous studies analyzing anthropogenic impacts on methane emission rates from mangrove 318 sediments have shown that disturbance significantly increases methane emissions (Purvaja and 319 Ramesh, 2001; Chen et al., 2011). This provides an additional rationale to conserve, and 320 continue to expand, Red Sea mangroves. 321 Data availability. All data will be accessible in the repository Pangea pending manuscript 322 acceptance.

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

324

### 325 Author contribution

MAS, NG-B, VS and CMD designed the study. MAS and NG-B performed the measurements
and calculations. MAS, NG-B, VS and CMD interpreted the results. All authors contributed
substantially to the final manuscript.

329

### 330 Acknowledgements

This research was funded by King Abdullah University of Science and Technology (KAUST)
through baseline funding to C.M.D. We thank D. Krause-Jensen, Nabeel Massoudi, and





- 333 Kimberlee Baldree for help during sampling, and the captain and crew of KAUST R/V Thuwal
- 334 for support. M.A.S. was supported by King Abdullah University of Science and Technology
- through the VRSP program. We thank P. Carrillo de Albornoz for lab instrument support, and
- 336 Mongi Ennasri for help with sediment analysis.

337

### 338 References

339 Allen, D. E., Dalal, R. C., Rennenberg, H., Meyer, R., L., Reeves, S., Schmidt, S.: Spatial and

340 temporal variation of nitrous oxide and methane flux between subtropical mangrove sediments

and the atmosphere, Soil Biology and Biochemistry, 39, 622-631, 2007.

342 Allen, D. E., Dalal, R.C., Rennenberg, H., and Schmidt, S.: Seasonal variation in nitrous oxide

343 and methane emissions from subtropical estuary and coastal mangrove sediments, Australia,

- 344 Plant Biology, 13, 126-133, 2011.
- Almahasheer, H., Aljowair, A., Duarte, C. M., Irigoien, X.: Decadal stability of Red Sea
  mangroves, Estuarine, Coastal and Shelf Science, 169, 164-172, 2016.
- Almahasheer, H., Serrano, O., Duarte, C. M., Arias-Ortiz, A., Masque, P., and Irigoien, X.: Low
  carbon sink capacity of Red Sea mangroves, Scientific Reports, 7, 9700, doi:10.1038/s41598017-10424-9, 2017.
- 350 Alongi, D. M.: Mangrove forests: Resilience, protection from tsunamis, and responses to global
- 351 climate change, Estuarine, Coastal, and Shelf Science, 76, 1-13, 2008.
- 352 Alongi, D. M.: The energetics of mangrove forests, Springer Press, London, England, 2009.
- Alongi, D. M.: Carbon sequestration in mangrove forests, Carbon Management, 3, 313-322, doi:
- 354 10.4155/cmt.12.20, 2012.
- Alongi, D. M.: Carbon cycling and storage in mangrove forests, Annu. Rev. Mar. Sci., 6, 195-
- 356 219, doi: 10.1146/annurev-marine-010213-135020, 2014.





- 357 Alongi, D. M., Pfitzner, J., Trott, L. A., Tirendi, F., Dixon, P., and Klumpp, D. W.: Rapid
- 358 sediment accumulation and microbial mineralization in forests of the mangrove Kandelia candel
- in the Jiulongjiang Estuary, China, Estuarine, Coastal, and Shelf Science, 63, 605-618, 2005.
- 360 Atwood, T.B., Connolly, R.M., Almahasheer, H., Carnell, P., Duarte, C. M., Ewers, C., Irigoien,
- 361 X., Kelleway, J., Lavery, P. S., Macreadie, P. I., Serrano, O., Sanders, C., Santos, I., Steven, A.,
- 362 and Lovelock, C. E.: Global patterns in mangrove soil carbon stocks and losses, Nature Climate
- 363 Change, doi:10.1038/nclimate3326, 2017.
- 364 Chauhan, R., Datta, A., Ramanathan, A. L., Adhya, T. K.: Factors influencing spatio-temporal
- 365 variation of methane and nitrous oxide emission from a tropical mangrove of eastern coast of
- 366 India, Atmospheric Environment, 107, 95-106, 2015.
- 367 Chen, G., Tam, N. F. Y., Wong, Y. S., and Ye, Y.: Effect of wastewater discharge on greenhouse
- 368 gas fluxes from mangrove soils, Atmospheric Environment, 45, 1110-1115, 2011.
- 369 Chen, G., Chen, B., Yu, D., Tam, N. F. Y., Ye, Y., and Chen, S.: Soil greenhouse gas emissions
- 370 reduce the contribution of mangrove plants to the atmospheric cooling effect, Environmental
- 371 Research Letters, 11, 1-10, doi:10.1088/1748-9326/11/12/124019, 2016.
- 372 Duarte, C. M., Losada, I. J., Hendriks, I. E., Mazarrasa, I., and Marbà, N.: The role of coastal
- plant communities for climate change mitigation and adaptation, Nature Climate Change, 3, 961968, doi: 10.1038/NCLIMATE1970, 2013.
- 375 Donato, D. C., Kauffman, J. B., Murdiyarso, D., Kurnianto, S., Stidham, M., and Kanninen, M.:
- 376 Mangroves among the most carbon-rich forests in the tropics, Nature Geoscience, 4, 293-297,
- doi: 10.1038/NGEO1123, 2011.
- Garcias-Bonet, N. and Duarte, C. M.: Methane production by seagrass ecosystems in the Red
  Sea, Frontiers in Marine Science, 4, 340 doi: 10.3389/fmars.2017.00340, 2017.
- 380 Giri, C., Ochieng, E., Tieszen, L. L., Zhu, Z., Singh, A., Loveland, T., Masek, J., and Duke, N.:
- 381 Status and distribution of mangrove forests of the world using earth observation satellite data,
- 382 Global. Ecol. Biogeogr., 20, 154-159, 2011.





- 383 Kanninen, M.: Mangroves among the most carbon-rich forests in the tropics, Nature Geoscience,
- 384 4, 293-297, doi:10.1038/ngeo1123, 2011.
- 385 Kennedy, H., Beggins, J., Duarte, C. M., Fourqurean, J. W., Holmer, M., Marbà, N., and
- 386 Middelburg, J. J.: Seagrass sediments as a global carbon sink: isotopic constraints, Global
- 387 Biogeochemical Cycles, 24, GB4026, doi: 10.1029/2010GB003848, 2010.
- Kristensen, E., Bouillon, S., Dittmar, T., and Marchand, C.: Organic carbon dynamics in
  mangrove ecosystems: A review, Aquatic Botany, 89, 201-219,
  doi:10.1016/j.aquabot.2007.12.005, 2008a.
- 391 Kristensen, E., Flindt, M. R., Ulomi, S., Borges, A. V., Abril, G., Bouillon, S.: Emissions of CO<sub>2</sub>
- 392 and CH<sub>4</sub> to the atmosphere by sediments and open waters in two Tanzanian mangrove forests,
- 393 Marine Ecology Progress Series, 370, 53-67, doi: 10.3354/meps07642, 2008b.
- Livesley, S. J., and Andrusiak, S. M.: Temperate mangrove and salt marsh sediments are a small
  methane and nitrous oxide source but important carbon store, Estuarine, Coastal, and Shelf
  Science, 97, 19-27, 2012.
- Myhre, G., Shindell, D., Bréon, F. M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D.,
  Lamarque, J. F., Lee, D., Mendoza, B., and Nakajima, T.: Anthropogenic and natural radiative
  forcing, Climate Change, 423, 2013.
- Newell, R. I. E., Marshall, N., Sasekumar, A., Chong, V. C.: Relative importance of benthic
  microalgae, phytoplankton, and mangroves as sources of nutrition for penaeid prawns and other
  coastal invertebrates from Malaysia, Marine Biology, 123, 595-606, 1995.
- Pataki, D., Ehleringer, J. R., Flanagan, L. B., Yakir, D., Bowling, D. R., Still, C. J., Buchmann,
  N., Kaplan, J. O., and Berry, J. A.: The application and interpretation of Keeling plots in
  terrestrial carbon cycle research, Global Biogeochemical Cycles, 17, 1022, doi:
  10.1029/2001GB001850, 2013.
- 407 Poffenbarger, H. J., Needelman, B. A., and Megonigal, J. P.: Salinity influence on methane
  408 emissions from tidal marshes, Wetlands, 31, 831-842, doi: 10.1007/s13157-011-0197-0, 2011.





- 409 Purvaja, R. and Ramesh, R.: Human impacts on methane emission from mangrove ecosystems in
- 410 India, Regional Environmental Change, 1, 86-97, doi: 10.1007/PL00011537, 2000.
- 411 Purvaja, R. and Ramesh, R.: Natural and anthropogenic methane emission from wetlands of
- 412 south India, Environmental Management, 27, 547-557, doi: 10.1007/s002670010169, 2001.
- 413 Reeburgh, W. S.: Global Methane Biogeochemistry Treatise on Geochemistry (Second Edition),
- Holland, H. D., and Turekian, K. K., Oxford, Elsevier, 71-94, 2014.
- 415 Sea, M. A., Garcias-Bonet, N., Saderne, V., and Duarte, C. M.: Data set on methane emissions
- 416 from Red Sea mangrove sediments. Pangea DOI: [data set will be published in the Pangea open
- 417 data repository at the acceptance of paper], 2018.
- 418 Soetaert, K., Petzoldt, T., and Meysman, F.: Marelac: A tool for aquatic sciences (R package),
- 419 available at: https://cran.r-project.org/web/packages/marelac/marelac.pdf, 2016.
- Thom, M., Bosinger, R., Schmidt, M., and Levin, I.: The regional budget of atmospheric
  methane of a highly populated area, Chemosphere, 26, 143-160, doi: 10.1016/00456535(93)90418-5, 1993.
- Wiesenburg, D. A. & Guinasso, N. L.: Equilibrium solubilities of methane, carbon monoxide,
  and hydrogen in water and sea water, Journal of Chemical and Engineering Data, 24, 356-360,
  1979.
- 426 Wilson, S. T., Böttjer, D., Church, M. J., and Karla, D. M.: Comparative assessment of nitrogen
- fixation methodologies, conducted in the oligotrophic north Pacific Ocean, Applied andEnvironmental Microbiology, 78, 6516-6523, 2012.







Fig. 1. Mangrove stands sampled along the Saudi coast of the Red Sea. Numbers indicate
positions of sampling sites from this study. S1 and S2: King Abdullah University of Science and
Technology; S3: Duba; S4 and S5: Al Wahj; S6 and S7: Farasan Banks.







Fig. 2. Change in  $CO_2$  (left panels) and  $CH_4$  (right panels) concentrations over time in triplicated mangrove sediment cores from mangrove stations S3-S7. Shaded areas represent night time and each replicate is coded by different symbols.

443







445 Fig. 3. Relationship between day and night fluxes for CO<sub>2</sub> (top panel) and CH<sub>4</sub> (bottom panel) at
446 all mangrove stations.













- 448 Fig. 4. Keeling plots for mangrove stations S3-S7, showing the linear regression of the inverse of
- 449 CO<sub>2</sub> concentration (left panels) and CH<sub>4</sub> concentration (right panels) versus  $\delta^{13}$ C–CO<sub>2</sub> and  $\delta^{13}$ C–
- 450 CH<sub>4</sub>. Y-intercepts were used to estimate the isotopic signatures of produced gases.



451

**Fig. 5.** Relation between the carbon isotopic signature of the produced CO<sub>2</sub> ( $\delta^{13}$ C–CO<sub>2</sub>) and CO<sub>2</sub> fluxes (top panel) and carbon isotopic signature of the produced CH<sub>4</sub> ( $\delta^{13}$ C–CH<sub>4</sub>) and the CH<sub>4</sub> fluxes (bottom panel) in Red Sea mangroves. Error bars indicate standard error of the mean.

455





**Table 1.** Summary of greenhouse gas fluxes and sediment characteristics from studied mangrove forests. CH<sub>4</sub> fluxes in brackets represent CO<sub>2</sub> equivalents in terms of global warming potential for a time horizon of 100 years (GWP<sub>100</sub>), taking into account climate-carbon feedback as suggested by the AR5 of IPCC (Myhre et al., 2013). Data represent the mean  $\pm$  SEM and nd means no data available.

Station	$\begin{array}{c} CO_2 \ Day \ Flux \\ (\mu mol \ m^{-2} \ hr^{-1}) \end{array}$	CH <sub>4</sub> Day Flux (µmol m <sup>-2</sup> hr <sup>-1</sup> )	$\begin{array}{c} CO_2 \ Night \ Flux \\ (\mu mol \ m^{-2} \ hr^{-1}) \end{array}$	$\begin{array}{c} CH_4 \ Night \ Flux \\ (\mu mol \ CH_4 \ m^{-2} \ hr^{-1}) \end{array}$	$\begin{array}{c} \text{Daily CO}_2 \ Flux \\ (\mu mol \ m^{-2} \ d^{\cdot 1}) \end{array}$	$\begin{array}{c} Daily \ CH_4 \ Flux \\ (\mu mol \ m^{-2} \ d^{\cdot 1}) \end{array}$	$\overset{\delta^{13}C\text{-}CO_2}{(\%)}$	δ <sup>13</sup> C-CH <sub>4</sub> (‰)	Nitrogen Density (mg cm <sup>-3</sup> )	Corg Density (mg cm <sup>-3</sup> )	Chl a (µg Chl a g <sup>-1</sup> sediment)
1	$\textbf{-188} \pm 25$	$0.30 \pm 0.17$ [10.2]	$\textbf{-99} \pm 18$	$0.19 \pm 0.04$ [6.46]	$-3452\pm271$	5.9 ± 1.3 [201]	nd	nd	nd	nd	nd
2	$-157\pm89$	$0.05 \pm 0.02$ [1.7]	$782\pm 66$	$0.03 \pm 0.01$ [1.02]	$7500\pm894$	$0.9 \pm 0.25$ [31]	nd	nd	nd	nd	nd
3	$49\pm37$	0.69 ± 0.4 [23.46]	$\text{-}176\pm23$	$0.42 \pm 0.39$ [14.28]	$\text{-}1524\pm686$	13.3 ± 9.5 [452]	$\textbf{-25.7} \pm 0.2$	$\textbf{-87.1} \pm 2.3$	$1.03\pm0.05$	$13.33 \pm 1.01$	nd
4	$-86\pm79$	$0.28 \pm 0.1$ [9.52]	$29\pm19$	$0.01 \pm 0.03$ [0.34]	$\textbf{-684} \pm 1038$	$3.5 \pm 0.8$ [119]	$\textbf{-}11.1\pm0.6$	$\textbf{-71.3} \pm 2.3$	$0.80\pm0.03$	$8.98\pm0.86$	$1.02\pm0.05$
5	$-22 \pm 11$	0.09 ± 0.03 [3.06]	$24\pm20$	$0.13 \pm 0.10$ [4.42]	$23\pm331$	2.6 ± 1.6 [88]	$\textbf{-15.6} \pm 2.3$	$\textbf{-83.6} \pm 2.3$	$1.12\pm0.05$	$13.34\pm0.98$	$1.03\pm0.04$
6	$73\pm10$	$0.27 \pm 0.10$ [9.18]	$35\pm17$	$0.45 \pm 0.18$ [15.30]	$1289\pm280$	8.7 ± 3.4 [296]	$\textbf{-12.9}\pm0.5$	$\textbf{-82.5} \pm 1.7$	$1.51\pm0.14$	$10.58\pm0.82$	$0.43\pm0.14$
7	$-51\pm28$	$0.13 \pm 0.05$ [4.42]	$5\pm3$	$0.26 \pm 0.03$ [8.84]	$-547\pm363$	$4.6 \pm 1.0$ [156]	$\textbf{-15.9}\pm1.1$	$\textbf{-78.6} \pm 0.6$	$3.30\pm0.55$	$33.43 \pm 6.69$	$1.86\pm0.12$







**Table 2.** Comparison of GHG fluxes from global mangrove forests and Red Sea mangroves. Literature values converted from reported form for comparison purposes.

		(mmol	O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup> )	$\begin{array}{c} CH_4 \\ (\mu mol \ m^{-2} \ d^{-1}) \end{array}$		
		Minimum	Maximum	Minimum	Maximum	
Kristensen, 2008a	Global	2	373	0	5000	
Kristensen, 2008b	Tanzania	28	115	0	87.6	
Livesley & Andrusiak, 2012	Australia	50	150	50	749	
Alongi, 2005	China	17	121	5	66	
Alongi, 2014	Global	49	69	0	5100	
Chen, 2016	China	-16.9	279.2	-2.1	8015.1	
Allen, 2007	Australia	-	-	4.5	25974	
Allen, 2011	Australia	-	-	70.3	2348	
Chuang, 2015	Mexico	-	-	12	11000	
This Study	Red Sea	-3.5	7.5	0.9	13.3	