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1 **A comparison between water circulation and terrestrially-driven dissolved**
2 **silica fluxes to the Mediterranean Sea traced using radium isotopes**

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4 *Joseph Tamborski^{a*}, Simon Bejannin^a, Jordi Garcia-Orellana^{b,c}, Marc Souhaut^a, Céline*
5 *Charbonnier^d, Pierre Anschutz^d, Mireille Pujon-Pay^e, Pascal Conan^e, Olivier Crispin^e, Christophe*
6 *Monnin^f, Thomas Stieglitz^{g,h}, Valentí Rodellas^g, Aladin Andrisoa^g, Christelle Claude^g, Pieter van*
7 *Beek^a*

8 ^aLEGOS, Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (Université de
9 Toulouse, CNES, CNRS, IRD, UPS), Observatoire Midi Pyrénées, 14 Ave Edouard Belin, 31400
10 Toulouse, France

11 ^bICTA, Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona, 08193
12 Bellaterra, Catalunya, Spain

13 ^cDepartament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalunya, Spain

14 ^dEPOC, Environnements et Paléoenvironnements Océaniques et Continentaux, Université de
15 Bordeaux, CNRS, UMR 5805, Talence, France

16 ^eLOMIC, Laboratoire d'Océanographie Microbienne, Observatoire Océanologique, Sorbonne
17 Universités, CNRS, UPMC Univ Paris 06, UMR7621, 66650 Banyuls/Mer, France

18 ^fGET, Géosciences Environnement Toulouse (Université de Toulouse, CNRS, IRD, UPS),
19 Observatoire Midi Pyrénées, 14 Ave Edouard Belin, 31400 Toulouse, France

20 ^gAix-Marseille Université, CNRS, IRD, INRA, Coll France, CEREGE, Europôle de l'Arbois,
21 BP80, 13545 Aix-en-Provence, France

22 ^hCentre for Tropical Water & Aquatic Ecosystem Research, James Cook University, Townsville
23 QLD 4811, Australia

24 *Corresponding author: joseph.tamborski@legos.obs-mip.fr

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27

28 **Abstract**

29 The recirculation of seawater through permeable coastal sediments is increasingly
30 recognized as an important source of nutrients, including dissolved silica (DSi), to the coastal
31 ocean. Here, we utilized a Ra isotope (^{223}Ra , $^{224}\text{Ra}_{\text{ex}}$, ^{228}Ra) mass balance to quantify DSi fluxes
32 driven by water recirculation to a small shallow coastal lagoon (La Palme; French
33 Mediterranean) during June 2016, as compared to karstic groundwater spring inputs. The DSi
34 flux driven by lagoon water recirculation (derived from $^{224}\text{Ra}_{\text{ex}}$) was approximately one order of
35 magnitude greater ($1,930 \pm 1,650 \text{ mol d}^{-1}$) than the DSi load of the karstic groundwater spring
36 ($250 \pm 50 \text{ mol d}^{-1}$) and greater than molecular diffusion ($970 \pm 750 \text{ mol d}^{-1}$). Lagoon water
37 recirculation was a negligible source of ^{228}Ra , indicating that recirculation-driven DSi inputs
38 occur over a time-scale of days. Offshore transects were studied to quantify fluxes of marine-
39 derived submarine groundwater discharge (SGD) from the permeable sandy coastline adjacent to
40 the lagoon, into the Mediterranean Sea. Surface water transects revealed near-shore enrichments
41 of Ra and DSi, attributed to wave-setup and water exchange through the permeable beach
42 between the lagoon and the sea. Upscaling over the 9.5 km stretch of sandy beaches results in a
43 marine SGD-driven DSi flux of $2.3 \pm 1.3 * 10^4 \text{ mol d}^{-1}$, similar in magnitude to the Têt river
44 during November 2016 ($3.3 \pm 2.4 * 10^4 \text{ mol d}^{-1}$), the largest river in the region. A positive
45 relationship between DSi and $^{224}\text{Ra}_{\text{ex}}$ in lagoon water and seawater, but not ^{228}Ra , suggests that
46 $^{224}\text{Ra}_{\text{ex}}$ and DSi enrichments are derived from a similar source, the sediment (i.e. lithogenic
47 particle dissolution), operating on short time-scales. A marine SGD-driven DSi flux to the Gulf
48 of Lions ($3.8 \pm 2.2 * 10^5 \text{ mol d}^{-1}$) is likely continuous over time. The relatively constant DSi
49 inputs from water recirculation for the shallow lagoons and beaches along the French
50 Mediterranean Sea may sustain primary production in the coastal zone. In comparison, terrestrial

51 groundwater and rivers supply temporally variable nutrient (N, P, Si) inputs via changes in
52 regional precipitation, runoff and aquifer storage.

53 **Keywords:** recirculation; submarine groundwater discharge, pore water exchange, radium
54 isotopes, dissolved silica, Mediterranean Sea

55 **1. Introduction**

56 Dissolved silica (DSi) is a major nutrient which partly supports diatom primary
57 productivity in coastal oceans (Tréguer & De La Rocha, 2013). There is increasing evidence that
58 fluxes of DSi to the coastal ocean may be enhanced either by dissolution of biogenic particles
59 within permeable coastal sediments (Anschutz et al., 2009) or by dissolution of the permeable
60 sediment itself in the presence of seawater (Ehlert et al., 2016). In either scenario, the primary
61 mechanism behind DSi transport to the water column is from the advective movement of pore
62 water across the sediment-water interface or from the coastal aquifer, broadly defined as
63 submarine groundwater discharge (SGD), “regardless of fluid composition or driving force”
64 (Burnett et al., 2003). In the absence of terrestrial (i.e. fresh) groundwater inputs, this process
65 may be defined as water recirculation or marine SGD, which includes both large-scale and short-
66 scale (sometimes referred as pore water exchange; PEX) recirculation processes (Burnett et al.,
67 2003; Santos et al., 2012).

68 Pore waters obtain unique geochemical signatures in terms of carbon (Cyronak et al.,
69 2014), nutrients (Bernier, 1980; Slomp & Van Cappellen, 2004), trace metals (Beck et al., 2010;
70 Trezzi et al., 2017) and natural radionuclides (Garcia-Orellana et al., 2013; Moore, 1996) within
71 permeable coastal sediment (Moore, 1999). DSi enrichments in pore waters, which cannot be
72 explained by simple binary mixing between seawater and groundwater, have been observed in
73 various coastal water bodies throughout the world (Anschutz et al., 2016; Ehlert et al., 2016;

74 Kim et al., 2005; Ullman et al., 2003; Urquidi-Gaume et al., 2016; Weinstein et al., 2011). This
75 non-conservative DSi enrichment, combined with terrestrial inputs of DSi (rivers and
76 groundwater), may have a significant biogeochemical impact on the coastal ocean. For example,
77 SGD-driven DSi inputs were suggested to help maintain mixed-algal populations in a bay
78 surrounded by heavy industry (Lee et al., 2009) and have also lead to increased diatom
79 assemblages adjacent to coastal groundwater springs (Welti et al., 2015). SGD-driven nutrient
80 fluxes, including DSi, have been shown to impact primary production in a setting dominated by
81 diffuse SGD, while groundwater spring environments were more variable (Sugimoto et al., 2017;
82 Tovar-Sánchez et al., 2014). In karstic watersheds, DSi is generally enriched in terrestrial
83 groundwater and depleted in ocean waters, making DSi a useful tracer of terrestrial SGD,
84 particularly when combined with radium isotopes (El-Gamal et al., 2012; Garcia-Solsona et al.,
85 2010a; Garcia-Solsona et al., 2010b; Null et al., 2014).

86 Naturally occurring radium isotopes ($^{223,224,226,228}\text{Ra}$) have been widely used to estimate
87 volumetric water fluxes, as these tracers can spatially integrate different flow paths over large
88 areas (Swarzenski 2007). These radionuclides are enriched in pore water relative to surface
89 waters due to alpha recoil following production from the decay of their particle-associated Th
90 parent, and due to desorption from sediment solids via cation substitution and displacement in
91 high ionic strength solutions (Webster et al., 1995). Mass balances of Ra isotopes can be used to
92 quantify inputs of SGD in enclosed and semi-enclosed environments (Beck et al., 2007; Rodellas
93 et al., 2017). Shore-perpendicular surface water transects from the coast to the open sea are
94 commonly investigated to determine net exchange offshore, which in turn can be used to derive
95 SGD fluxes from long-lived ^{226}Ra and ^{228}Ra surface water gradients (Moore, 2000a). Short-lived
96 ^{223}Ra ($t_{1/2} = 11.4$ d) and ^{224}Ra ($t_{1/2} = 3.66$ d) can be used to trace short time-scale processes, while

97 longer-lived ^{226}Ra ($t_{1/2} = 1,600$ y) and ^{228}Ra ($t_{1/2} = 5.75$ y) may capture longer time-scale
98 discharge processes (Cai et al., 2014; Rodellas et al., 2017).

99 Total SGD-driven DSi inputs are comparable or higher than riverine inputs in the
100 Mediterranean Sea (Rodellas et al., 2015). There is little information to date in the Mediterranean
101 Sea comparing the flux of DSi from water recirculation or marine SGD, either via dissolution of
102 sediment or biogenic particles, to that of terrestrial groundwater and riverine inputs (Anschutz et
103 al., 2016). The Mediterranean Sea is, globally considered, an oligotrophic sea rich in oxygen and
104 deficient in nutrients such as silica, nitrogen and phosphorous; however, nutrient budget
105 calculations are based on non-synoptic and sometimes sparse data (Durrieu de Madron et al.,
106 2011). The release of DSi from lithogenic particle dissolution in the presence of seawater has
107 been experimentally (Anschutz et al., 2009; Morin et al., 2015; Techer et al., 2001) and
108 physically (Ehlert et al., 2016) observed, and has been invoked as a mechanism to explain the
109 DSi imbalance in the Mediterranean Sea (Jeandel & Oelkers, 2015). At a regional scale, the Gulf
110 of Lions (France) is a nutrient sink compared to other Mediterranean regions (Schroeder et al.,
111 2010). Major Mediterranean basin river fluxes over the last several decades have experienced an
112 increase in nitrogen and decrease in phosphorus loadings due to anthropogenic activity (Durrieu
113 de Madron et al., 2011), which has considerably modified the N:P stoichiometry (Ludwig et al.,
114 2009); however, information on nutrient inputs from water recirculation to coastal lagoons and
115 from marine SGD to the Gulf of Lions remain poorly known.

116 In this study, we utilize a Ra mass balance in a shallow coastal lagoon to assess the
117 relative importance of DSi inputs from a karstic groundwater spring compared to lagoon water
118 recirculation. In addition, we provide a first-order approximation of the marine SGD-driven DSi
119 flux (from wave-setup and water exchange across permeable sand barriers) to the Gulf of Lions,

120 as compared to riverine DSi inputs. The purpose of this study is to demonstrate the broad
121 importance of water recirculation in conveying DSi to the coastal ocean on a local and regional
122 scale, and its general biogeochemical impact.

123 **2. Methodology**

124 **2.1 Site description**

125 La Palme lagoon is a small, shallow lagoon located on the French Mediterranean
126 coastline (**Figure 1**). Tides have a minor influence on La Palme lagoon, as the tidal range in this
127 area of the Mediterranean Sea is approximately 20 – 30 cm. Water exchange between the lagoon
128 and the sea is confined to a small inlet in the southeast corner of the lagoon, and can be
129 seasonally opened from high-energy storm-events, which frequently occur during winter months.
130 Stream inputs vary seasonally with the local hydrologic conditions, and typically cease flow
131 during the summer. A karstic groundwater spring feeds into a former wash basin (lavoir), which
132 discharges into the northern basin of the lagoon via a small-stream. Groundwater discharge from
133 this spring (salinity 4 – 10) varies between 0.01 – 0.04 m³ s⁻¹ (Bejannin et al., 2017; Stieglitz et
134 al., 2013), and has been shown to maintain brackish ecosystem functioning in the lagoon during
135 the dry summer months (Stieglitz et al., 2013).

136 Previous estimates of lagoon water recirculation within La Palme lagoon vary from 0.29
137 – 2.1 m³ s⁻¹ during summer 2009, estimated from a ²²²Rn, water and salt balance, where strong
138 winds were hypothesized to drive recirculated water exchange (Stieglitz et al., 2013). Bejannin et
139 al. (2017) estimated a predominantly recirculation-driven flux between 0.56 – 1.7 m³ s⁻¹ during
140 July 2009, derived from a ²²³Ra and ²²⁴Ra_{ex} mass balance, while Rodellas et al. (2018) recently
141 estimated ²²²Rn and water balance-derived recirculation fluxes between 0.5 – 1.0 m³ s⁻¹ in the
142 northern basin of the lagoon, between June 2016 – June 2017. The northern, intermediate and
143 southern lagoon basins have limited water exchange due to long surface water residence times

144 (Bejannin et al., 2017) from constructed dikes and railways which impede surface exchange
145 between basins (**Figure 1**). The southern basin encompasses the area between the lagoon outlet
146 and the railway dike; the intermediate basin is defined as the area between the railway dike north
147 to the 0.4 m bathymetric contour (during June 2016), which separates the intermediate basin
148 from the northern basin (**Figure 1**).

149 Surficial sediments (upper 5 centimeters) vary in grain size throughout the lagoon; fine-
150 grained sediments ($\leq 50 \mu\text{m}$) dominate the deepest ($\leq 1.3 \text{ m}$) section of the northern basin of the
151 lagoon while fine-to-coarse grained sands ($\sim 100 - 500 \mu\text{m}$) make up the rest of the northern
152 basin (41 – 60 % of bottom-surface area). Fine-to-coarse grained sands ($\sim 100 - 500 \mu\text{m}$)
153 dominate the shallower intermediate ($\leq 0.6 \text{ m}$) and southern ($\leq 0.4 \text{ m}$) lagoon basins ($> 90\%$ of
154 bottom-surface area) (IFREMER, 2003). The permeable shoreline from the lagoon outlet north
155 toward Port-la-Nouvelle (**Figure 1**) is made up of fine-to-coarse sands ($\sim 200 - 500 \mu\text{m}$). There
156 are no river or stream inputs along this 9.5 km stretch of coastline.

157 2.2 Field sampling

158 La Palme lagoon surface waters were sampled between 14 and 16 June 2016. Surface
159 water samples were collected throughout the lagoon ($\sim 20 \text{ L}$) via submersible or hand pumps into
160 triple-rinsed plastic cubitainers for Ra analysis; water depth was simultaneously measured with a
161 leveling rod (**Figure 1**). Salinity and pH were measured *in-situ* using a WTW probe (Multi
162 3430), for all surface samples. Additional samples were taken from the groundwater spring to
163 determine the karstic groundwater endmember, as well as two salt evaporation ponds and a
164 sewage outlet. The discharge of the groundwater spring was directly measured using a flow-
165 meter (Hydreka BFM 801) during September 2016. Pore water samples were taken from select
166 locations (PZ1, PZ2 and PZ3; **Figure 1**) in the lagoon during March 2016 and June 2016 using a

167 stainless-steel drive-point piezometer for Ra isotopes; nutrient samples were collected during
168 June 2016 only. Pore waters were collected between 20 – 140 cm depth below the sediment
169 surface; depending on the station, this corresponded to specific sample depths of 20, 30, 40, 50,
170 75, 100 and 140 cm. Small volumes of pore water (<0.5 L) were sampled for Ra isotopes to
171 prevent mixing between different depth layers and with overlying lagoon waters.

172 A wide-diameter (22 cm) fine-grained sediment core ($D_{10} \sim 50 \mu\text{m}$) was collected in La
173 Palme Lagoon during November 2016 to determine the diffusive flux of Ra from the sediment to
174 the water column (**Figure 1**). Additional sediment cores (10 – 20 cm in length; 10 cm diameter)
175 were collected in May and September 2017 to define the vertical distribution of DSi at the
176 sediment-water interface, to assess the diffusive flux between the sediment and the water
177 column. Three to five stations were sampled for each basin of the lagoon (**Figure 1**); DSi core
178 sampling was carried out manually using 10-cm diameter PVC tubes. Sealed cores were
179 immediately brought to the shore for pore water extraction. A sub-sample of each core interval (1
180 – 2 cm thick slices) was immediately sealed in a pre-weighed vial for further water content
181 determination and porosity calculation. A second sub-sample was placed in a centrifuge vial (0.2
182 μm VIVASPIN20; Anschutz and Deborde, 2016) and pore waters were extracted by
183 centrifugation at 4000 rpm for 20 min. Waters were stored at 4°C until DSi analysis.

184 Five surface water transects (~100 L for Ra isotopes) were sampled offshore of La Palme
185 Lagoon, into the Mediterranean Sea, during November 2016 aboard the *R/V Nereis II* (**Figure 1**).
186 These profiles extend from 0.2 – 8.0 km offshore and cover over 7 km of the 9.5 km sandy
187 shoreline between the outlet of La Palme lagoon and Port-la-Nouvelle (**Figure 1**). Depth profiles
188 of salinity and temperature were measured at each station using a calibrated CTD (Sea-Bird SBE
189 19 SeaCat). Coastal surface waters and shallow (0.5 m) beach pore waters (dug from boreholes)

190 were sampled directly adjacent to the shoreline during the cruise (two northern beach stations;
191 **Figure 1**). Pore waters were sampled in June 2016 at the two southern endmember stations in a
192 shore-perpendicular transect between the lagoon and sea (**Figure 1**), from the shoreline to < 60
193 m distance from the sea across the beach (n = 3 samples per transect).

194 2.3 Analytical methods

195 Mediterranean surface water, karstic groundwater, lagoon surface water and pore waters
196 (taken from the drive-point piezometer) were immediately filtered in the field (using 0.45 μm
197 cellulose acetate filters) and stored in 20 mL polyethylene vials at $-20\text{ }^{\circ}\text{C}$ until analysis for DSi,
198 NO_3^- , NO_2^- , and PO_4^{3-} . In the laboratory, samples were analyzed by colorimetry on a Seal-Bran-
199 Luebbe autoanalyzer AA3 HR (Aminot and K erouel, 2007); analytical precision for DSi, NO_3^- ,
200 NO_2^- and PO_4^{3-} is $\pm 0.1\text{ }\mu\text{M}$, $0.05\text{ }\mu\text{M}$, $0.02\text{ }\mu\text{M}$ and $0.02\text{ }\mu\text{M}$, respectively. Samples were diluted
201 either 10x or 100x with deionized water and analyzed for Ba, Sr and Si via ICP-OES; analytical
202 precision is $\leq 10\%$ for all analytes. Lagoon water saturation states ($\log Q/K$) were calculated in
203 PHREEQC (Parkhurst and Appelo, 2013) using the THERMODDEM database (Blanc et al.,
204 2012).

205 Dissolved Ra was quantitatively adsorbed onto MnO_2 coated acrylic fiber by passing the
206 water through the fiber at a low flow rate ($< 0.5\text{ L min}^{-1}$); fibers were triple rinsed with Ra-free
207 deionized water and partially dried in a compressed air stream (Sun & Torgersen, 1998). Short-
208 lived ^{223}Ra and ^{224}Ra were counted using a radium delayed coincidence counting system
209 (RaDeCC) (Moore & Arnold, 1996). ^{223}Ra was determined from a second count approximately
210 10 days after the first count; ^{228}Th was determined from a third count ~ 4 weeks after sample
211 collection to determine supported ^{224}Ra activities that are used to determine excess ^{224}Ra
212 (denoted $^{224}\text{Ra}_{\text{ex}}$). Samples were counted again ≥ 6 months after collection to determine the

213 initial ^{228}Ra activity (Moore, 2008). Detector efficiencies were determined using ^{232}Th and ^{227}Ac
214 standards in secular equilibrium with their daughters. Analytical counting uncertainties were
215 estimated by standard rules of error propagation and are reported with a 1σ confidence interval
216 (Garcia-Solsona et al., 2008a).

217 The sediment core for Ra analysis was incubated following the methods of Beck et al.
218 (2007). The core was incubated in the laboratory with lagoon water (of a known Ra activity) for
219 various time intervals, after which the overlying water was extracted and replaced with new
220 lagoon water (of a known Ra activity), to determine the sediment Ra flux driven by diffusion and
221 bioirrigation (polychaetes found within the core). Suspended particle concentrations in the
222 lagoon surface waters were measured in February 2017 (during high winds) via vacuum filtration
223 using $0.45\ \mu\text{m}$ pore space filters. Additions of fine-grained dry-sediment (sieved to grain size \geq
224 $0.45\ \mu\text{m}$, $\leq 50\ \mu\text{m}$; sampled next to PZ1; **Figure 1**) were added to 20 L of Ra-free lagoon water,
225 shaken for 5 min, and measured following the methodology outlined above, to determine the Ra
226 flux driven by desorption of re-suspended sediments ($n = 6$; Luek & Beck, 2014).

227 DSi diffusive fluxes were calculated using Fick's first law for the May and September
228 2017 cores. The molecular diffusion coefficient value (Schultz and Zabel, 2006) was corrected
229 for *in-situ* temperature and porosity (Boudreau, 1996). Porosity was calculated from particle
230 density and water content determined by the weight difference between wet and freeze-dried
231 sediment, after sea salt correction. The density of particles was estimated at $2.65\ \text{g cm}^{-3}$ (Berner,
232 1980), i.e. mean density of alumino-silicate and calcium carbonate minerals. Sediment from the
233 southern basin ($\sim 200 - 250\ \mu\text{m}$) was incubated with *in-situ* lagoon water (**Figure 1**) in order to
234 assess the kinetics of DSi enrichment in pore water through lithogenic particle dissolution, for
235 two different water/particle ratios (Anschutz et al., 2009). In the first incubation, 7 g sand and 6

236 mL water were continuously stirred. The second experiment consisted of 2 g sand with 40 mL
237 water. One mL of water was regularly sampled and replaced by 1 mL *in-situ* lagoon water over
238 16 days.

239 3. Results

240 3.1 La Palme Lagoon

241 Four distinct geochemical endmembers were observed in La Palme Lagoon: i) the karstic
242 groundwater spring (salinity = 8.4 ± 0.7); ii) an evaporative, hyper-saline pore water (salinity >
243 38); iii) the salt evaporation ponds (salinity = 48 – 69) and iv) the open Mediterranean Sea
244 (salinity ~38) (**Figure 2; Figure 3**). Lagoon surface waters were brackish in the northern basin
245 (salinity = 33 ± 5), reflecting inputs from the karstic groundwater spring, with increasing salinity
246 in the intermediate (salinity = 40 ± 2) and southern (salinity = 42 ± 3) basins, both of which were
247 higher on average than the open Mediterranean Sea (38; **Table 1**). The karstic groundwater
248 spring exhibited Ra activities of 11 ± 3 dpm 100L⁻¹ for ²²³Ra, 710 ± 80 dpm 100L⁻¹ for ²²⁴Ra_{ex}
249 and 450 ± 30 dpm 100L⁻¹ for ²²⁸Ra (n = 4). Over the course of six different sampling events,
250 Bejannin et al. (2017) found ²²³Ra, ²²⁴Ra_{ex} and ²²⁸Ra activities between 16 – 43 dpm 100L⁻¹, 427
251 – 652 dpm 100L⁻¹ and 84 – 237 dpm 100L⁻¹, respectively, linked to the changing salinity of the
252 spring. Mean Ra activities (\pm STD) were greatest for lagoon pore waters and exhibited strong
253 vertical gradients, where deep samples (²²³Ra = 400 ± 270 dpm 100L⁻¹, ²²⁴Ra_{ex} = $5,500 \pm 3,900$
254 dpm 100L⁻¹, ²²⁸Ra = $2,800 \pm 1,900$ dpm 100L⁻¹; n = 7) were approximately 5 – 10 times greater
255 than shallow samples (²²³Ra = 70 ± 49 dpm 100L⁻¹, ²²⁴Ra_{ex} = $1,060 \pm 740$ dpm 100L⁻¹, ²²⁸Ra =
256 500 ± 450 dpm 100L⁻¹; n = 5; **Table 1**). The salt evaporation ponds (²²³Ra = 7 – 51 dpm 100L⁻¹,
257 ²²⁴Ra_{ex} = 287 – 676 dpm 100L⁻¹, ²²⁸Ra = 362 – 1,090 dpm 100L⁻¹) likely contributed little Ra to
258 La Palme lagoon, based on the measured Ra concentration and salinity (**Figure 2**); we found no
259 evidence of a connection between the salt ponds and the lagoon through visual inspection. There

260 was no evidence of a Ra isotope or nutrient (DSi, NO_3^-) source from samples taken adjacent to
261 the sewage outlet during June 2016 (**Figure 1**; **Figure 3**).

262 Lagoon waters in the northern basin showed high activities of Ra isotopes derived from
263 the groundwater spring, where Ra activities were elevated closest to the spring (**Figures 2 & 3**).
264 In the intermediate and southern basins of the lagoon, ^{223}Ra and $^{224}\text{Ra}_{\text{ex}}$ activities increased with
265 increasing salinity. Despite these general trends, there was observable spatial variability between
266 the three Ra isotopes. Lagoon waters adjacent to the groundwater spring outlet were highest in
267 $^{224}\text{Ra}_{\text{ex}}$ and ^{228}Ra . ^{223}Ra was greatest at the intersection between the intermediate and southern
268 basins, while $^{224}\text{Ra}_{\text{ex}}$ activities were lowest in the intermediate basin. In contrast, ^{228}Ra activities
269 were more uniform throughout the entire lagoon, but lowest in the southern basin, near the outlet
270 to the Mediterranean Sea (**Figure 3**). Lagoon waters were near equilibrium with respect to barite
271 in the northern and intermediate basins and under-saturated in the southern basin; all lagoon
272 basins were under-saturated with respect to celestine (**Table 2**). In the northern basin, we
273 observed lagoon water Ra activity distributions that reflected two-endmember linear mixing
274 between the groundwater spring and higher salinity lagoon waters (**Figure 2**); thus, barite (and
275 celestine) precipitation likely did not scavenge Ra and therefore did not impact the distribution of
276 dissolved Ra.

277 The spatial distribution of dissolved silica (DSi) was similar to that of $^{224}\text{Ra}_{\text{ex}}$ (**Figure 3**,
278 **Figure 4**), with higher concentrations adjacent to the groundwater spring outlet, lower
279 concentrations in the intermediate basin and elevated concentrations (above seawater) in the
280 southern basin. DSi was negatively correlated with salinity in the northern basin (p value <
281 0.001; $R^2 = 0.79$) and positively correlated with salinity in the intermediate (p value = 0.0346; R^2
282 = 0.34) and southern (p value = 0.001; $R^2 = 0.65$) basins. DSi was positively correlated with

283 $^{224}\text{Ra}_{\text{ex}}$ in the northern (p value < 0.001; $R^2 = 0.90$) and southern (p value = 0.0146; $R^2 = 0.42$)
284 basins (**Figure 5**). In the northern basin, DSi was positively correlated with ^{223}Ra (p value =
285 0.0021; $R^2 = 0.49$) and ^{228}Ra (p value = 0.0342; $R^2 = 0.35$), while there was no relationship
286 between DSi and ^{223}Ra or ^{228}Ra in the intermediate and southern basins (**Figure 5**). Quartz and
287 amorphous silica were under-saturated in the surface waters of the lagoon (**Table 2**).

288 3.2 Offshore Transects

289 Surface water transects sampled offshore of La Palme lagoon during November 2016
290 (**Figure 1**) displayed elevated $^{223,224,228}\text{Ra}$ and DSi near the coastline that decreased with
291 increasing distance offshore (**Figure 6**). Pore waters sampled from shallow (0.5 m) beach pits
292 next to the shoreline were significantly enriched in ^{223}Ra (44 – 65 dpm 100L⁻¹), $^{224}\text{Ra}_{\text{ex}}$ (1,030 –
293 1,730 dpm 100L⁻¹), ^{228}Ra (58 – 62 dpm 100L⁻¹) and DSi (5.8 – 24.2 μM); mean pore water
294 salinity (37.0 ± 0.5) was slightly lower than coastal Mediterranean seawater (n = 8). Short-lived
295 $^{224}\text{Ra}_{\text{ex}}$ was significantly correlated with DSi in surface water samples (**Figure 5**). There are no
296 external input sources (i.e. rivers or streams) along the 9.5 km investigated shoreline to cause the
297 observed geochemical gradients, aside from molecular diffusion from the sediment, such that
298 surface enrichments were likely derived from marine SGD (exchange between permeable sand
299 barriers and wave-setup). Assuming that advection is negligible and the system is in steady-state,
300 we estimated horizontal eddy diffusivity (K_h ; Moore, 2000a) between 18 – 70 m² s⁻¹ for ^{223}Ra
301 and 14 – 219 m² s⁻¹ for $^{224}\text{Ra}_{\text{ex}}$, for the five-surface water transects (≥ 200 m offshore).

302 3.3 Sediment: Diffusive Fluxes & Dissolution Experiments

303 Ra fluxes from fine-grained sediments (J_{Ra}) were estimated for each individual
304 incubation time point as:

$$305 J_{\text{Ra}} = \frac{(Ra_t - Ra_o) * V}{A * t} \quad (1)$$

306 Where Ra_t is the measured Ra activity at time t , Ra_o is the initial Ra activity of the overlying
307 water, V is the water volume overlying the core and A is the sediment core surface area. Burrow
308 structures were apparent on the sides of the core; therefore, we assume that the measured Ra flux
309 was supported by both molecular diffusion and bioirrigation. Mean (\pm SD) ^{223}Ra and ^{224}Ra fluxes
310 equal 3.6 ± 1.4 and 75 ± 50 dpm $\text{m}^{-2} \text{d}^{-1}$, respectively ($n = 5$). We use an average of the first two
311 incubation time points for ^{228}Ra , which have the lowest analytical uncertainties, with an assumed
312 uncertainty of 50% (15 ± 8 dpm $\text{m}^{-2} \text{d}^{-1}$). Mean (\pm SD) fine-grained sediment (grain size ≥ 0.45
313 μm , $\leq 50 \mu\text{m}$) available for desorption was 0.24 ± 0.05 dpm g^{-1} sediment dry weight for ^{224}Ra
314 and 0.008 ± 0.007 dpm g^{-1} for ^{223}Ra ($n = 6$).

315 Lagoon pore waters showed gradients of DSi at the sediment-water interface during June
316 2016, May 2017 and September 2017. The concentration of DSi in sandy sediments was between
317 10 and 100 μM at 10 cm depth (**Figure 7**). In muddy sediments of the northern basin and in sites
318 with sea-grass in the southern basin, DSi concentrations reached 400 μM at the bottom of the
319 cores ($\sim 10 - 20$ cm depth). Permeable sandy sediments have relatively low and constant DSi vs
320 depth concentrations, unlike DSi profiles from muddy sediments which exhibit strong vertical
321 DSi gradients. The small DSi concentration gradient in permeable sandy sediments suggests that
322 DSi concentrations are homogenized through advective flows. Mean (\pm SD) diffusive fluxes of
323 DSi to the water column in May and September 2017 were 56 ± 51 and 188 ± 173 $\mu\text{mol m}^{-2} \text{d}^{-1}$,
324 respectively ($n = 12$), considering both muddy and sandy sediments. The hydrologic conditions
325 in September 2017 were close to those of June 2016, with low water level and high salinities in
326 the water column; therefore, we assume that the gradient of DSi in June 2016 was in the range of
327 what was measured in September 2017 (**Figure 7**). DSi fluxes were highest in the northern and

328 the southern basins. Accordingly, the total diffusive DSi flux, assessed from the addition of
329 fluxes for each basin, equaled $970 \pm 750 \text{ mol d}^{-1}$ in September 2017 (**Table 3**).

330 The release of DSi from lithogenic particle (i.e. sediment) dissolution in the presence of
331 lagoon water from the incubation experiments showed a constant increase in DSi of $100 \mu\text{M}$ for
332 the first several days until a stable, saturated equilibrium concentration was reached (**Figure 8**).
333 DSi increased with a slope of $82 \mu\text{M d}^{-1}$ in the experiment with a water/rock ratio (W/R) of 6 mL
334 water/7 g sand. After 3 days DSi remained below $200 \mu\text{M}$, close to the concentration at
335 equilibrium with quartz. DSi increased for 10 days at a rate of $12 \mu\text{M d}^{-1}$ in the incubation with a
336 higher W/R (40 mL water/2 g sand; **Figure 8**).

337 **4. Discussion**

338 **4.1 Ra isotope distributions in La Palme lagoon**

339 Ra isotope activity distributions in the lagoon waters are influenced by inputs from the
340 groundwater spring and the lagoon bottom-sediments (**Figure 2**), in addition to decay and
341 mixing. The mean $^{224}\text{Ra}_{\text{ex}}/^{223}\text{Ra}$ and $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ activity ratio of the groundwater spring was 84
342 ± 21 and 1.7 ± 0.3 , respectively (**Figure 9**). Lagoon surface waters closest to the mouth of the
343 groundwater spring have relatively high $^{224}\text{Ra}_{\text{ex}}/^{223}\text{Ra}$ and $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ activity ratios; the
344 activity ratios quickly decreased with increasing distance away from the groundwater spring
345 (distance from spring measured using current high-resolution imagery in Google Earth; assumed
346 10% uncertainty). $^{224}\text{Ra}_{\text{ex}}/^{223}\text{Ra}$ activity ratios of the lagoon waters reached a relatively constant
347 value near the boundary between the northern and intermediate basins, reflective of either the
348 underlying pore waters ($\sim 10 - 25$; **Figure 9a**) or rapid mixing and homogenizing of surface
349 waters between basins. At the interface between the northern and intermediate basin, there was a
350 pulse in the $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ activity ratio, most likely reflecting inputs from pore water (**Figure**
351 **9b**). $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ activity ratios between the intermediate and southern basins began to increase

352 with increasing distance from the groundwater spring. This increase possibly reflects the
353 changing grain-size of the surficial bottom sediments (less ^{228}Ra present due to smaller sediment
354 surface-area of the larger grains), where the bottom-sediment transitioned from finer-grained
355 sediment in the north to increasingly coarser-grained surficial sediment in the intermediate and
356 southern basins (i.e. **Figure 7**), in addition to increased water recirculation likely as a
357 consequence of higher sediment hydraulic conductivities. The bottom-sediment was clearly the
358 source controlling the distribution of short-lived Ra isotopes in the overlying waters of La Palme
359 lagoon, while the groundwater spring influenced the Ra distribution closest towards the
360 groundwater spring outlet in the northern basin.

361 The apparent Ra age of the lagoon waters may be estimated using $^{224}\text{Ra}_{\text{ex}}/^{223}\text{Ra}$ and
362 $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ activity ratios (Moore et al. 2006). The use of Ra activity ratios to derive apparent
363 ages considers a principal source of Ra at a set activity ratio, which will decrease as a function of
364 the distance from the input source due to radioactive decay and mixing (Moore et al., 2006).
365 Surface water samples taken within several hundred meters of the karstic groundwater spring
366 may be dated (Bejannin et al., 2017); however, the strong influence of pore waters and bottom-
367 sediment prevents us from accurately using Ra activity ratios to estimate water ages between
368 lagoon basins at the scales considered here (several km). Thus, we cannot combine the lagoon
369 water age and the basin water volume to derive a surface water exchange rate between basins and
370 with the sea.

371 4.2 Ra mass balance for La Palme lagoon: Estimation of water recirculation fluxes

372 A one-box mass balance is constructed to assess the inventory of dissolved Ra in La
373 Palme lagoon during June 2016 (Equation 2),

$$374 J_{out} + J_{decay} = J_{spring} + J_{sediment} + J_{desorp} + J_{recirculation} \quad (2)$$

375 where J_{out} is the Ra water flux lost from the lagoon to the Mediterranean Sea, J_{decay} is the Ra lost
376 from radioactive decay, J_{spring} is the brackish groundwater Ra input from the karstic groundwater
377 spring in the northern basin, $J_{sediment}$ is the Ra input from the bottom sediments which includes
378 both molecular diffusion and bioirrigation, J_{desorp} is the Ra input from desorption of re-suspended
379 sediments and $J_{recirculation}$ is the Ra exchanged from water recirculation. Ra inputs from molecular
380 diffusion and bioirrigation, determined from the sediment core incubation experiments, are
381 explicitly separated from Ra inputs driven by lagoon water recirculation. Terms used in the mass
382 balances are summarized in **Table 4**.

383 The groundwater spring Ra flux is estimated as the mean endmember Ra activity
384 multiplied by the discharge of the groundwater spring (**Table 1**), which was manually measured
385 at its outlet using a flow-meter in September 2016 ($0.025 \pm 0.005 \text{ m}^3 \text{ s}^{-1}$). Here we assume that
386 the flow of the groundwater spring was relatively constant during the dry season, between June
387 and September. The small streams in the northern basin were not flowing during the June 2016
388 sampling campaign and therefore are not considered.

389 Ra isotopes released from re-suspended sediments were quantified following the methods
390 of Luek and Beck (2014). The amount of ^{223}Ra and ^{224}Ra available for desorption (X_{desorp}) from
391 fine-grained sediment (**Section 3.3**) equal $0.008 \pm 0.007 \text{ dpm g}^{-1}$ and $0.21 \pm 0.05 \text{ dpm g}^{-1}$
392 sediment dry weight, respectively, whereas desorption for ^{228}Ra and coarse-grained sediment is
393 assumed to be negligible. A maximum suspended sediment concentration (C_{sed} ; $40 \pm 10 \text{ mg L}^{-1}$)
394 measured during a high-wind event (max wind gust speed = 20 m s^{-1} ; February 2017) is used to
395 represent the maximum potential input of Ra desorbed from re-suspended sediments; we assume
396 a maximum concentration of new sediments are re-suspended once per day. The Ra flux driven
397 by the desorption of re-suspended sediment (J_{desorp}) was estimated with respect to the volume of

398 water within the lagoon (V), and represents the smallest input source of Ra by an order of
399 magnitude. Ra inputs from molecular diffusion and bioirrigation are estimated using the results
400 from the sediment incubation experiment, which contained visible burrow structures, indicative
401 of bioirrigation (**Section 3.3**). For coarse-grained sediment, we assume that the Ra sediment
402 fluxes are ~50% lower than the fine-grained sediment fluxes, as observed in coastal sediments
403 from Long Island Sound (Garcia-Orellana et al., 2014). Diffusive fluxes are multiplied by the
404 surface area of the lagoon with respect to the distribution of fine (~25%) and coarse-grained
405 (~75%) surficial sediments. Experimental diffusive fluxes (**Table 4**) are in relative agreement
406 with previous estimates for shallow water basins using the same technique, including Venice
407 lagoon ($^{223}\text{Ra} = 1.1 \text{ dpm m}^{-2} \text{ d}^{-1}$; $^{224}\text{Ra} = 32 \text{ dpm m}^{-2} \text{ d}^{-1}$; $^{228}\text{Ra} = 27 \text{ dpm m}^{-2} \text{ d}^{-1}$ in Garcia-
408 Solsona et al., 2008b) and Jamaica Bay, NY ($^{223}\text{Ra} = 1.1 \text{ dpm m}^{-2} \text{ d}^{-1}$; $^{224}\text{Ra} = 28 \text{ dpm m}^{-2} \text{ d}^{-1}$; in
409 Beck et al., 2007).

410 During June 2016 the inlet between the lagoon and the Mediterranean Sea was only
411 partially open, with visibly minor surface water exchange. Therefore, the mass balance is
412 simplified by assuming that the net surface water exchange between the lagoon and the sea (J_{out})
413 was only significant in the area of the southern basin between the culvert and lagoon outlet
414 (**Figure 1**), based on the observed surface water salinity distribution (~38; **Figure 3**). Surface
415 water exchange farther north of this location is primarily restricted by constructed railway dikes
416 (**Figure 1**). Ra surface water exchange fluxes are calculated by subtracting the coastal
417 Mediterranean surface water Ra activity from the mean Ra activity in this section of the lagoon
418 ($^{223}\text{Ra} = 11.4 \pm 3.5 \text{ dpm } 100\text{L}^{-1}$; $^{224}\text{Ra}_{ex} = 197 \pm 41 \text{ dpm } 100\text{L}^{-1}$; $^{228}\text{Ra} = 156 \pm 52 \text{ dpm } 100\text{L}^{-1}$; n
419 = 5), and are multiplied by the volume of lagoon water in this section ($4.0 \cdot 10^4 \text{ m}^3$), with an
420 assumed flushing rate of 1.0 d (Stieglitz et al., 2013). The ^{228}Ra deficit from exchange with the

421 Mediterranean Sea is equal to $6.0 \pm 2.0 * 10^7$ dpm d⁻¹, approximately in balance with the ²²⁸Ra
422 inputs from diffusion and bioirrigation ($4.3 \pm 3.0 * 10^7$ dpm d⁻¹) and the groundwater spring (1.0
423 $\pm 0.2 * 10^7$ dpm d⁻¹). The export flux of ²²³Ra and ²²⁴Ra_{ex} to the Mediterranean Sea is
424 approximately $0.4 \pm 0.1 * 10^7$ dpm d⁻¹ and $7.4 \pm 1.6 * 10^7$ dpm d⁻¹, respectively.

425 From the mass balance (Eq. 2), the ²²⁴Ra_{ex} flux supplied by water recirculation is equal to
426 $6.4 \pm 1.9 * 10^8$ dpm d⁻¹; the ²²³Ra flux is highly uncertain ($4.4 \pm 6.6 * 10^6$ dpm d⁻¹) and inputs of
427 ²²⁸Ra are negligible. Differences in Ra-derived water recirculation fluxes are interpreted to
428 reflect the time-scale length of water recirculation through the lagoon sediment (Rodellas et al.,
429 2017). The water recirculation flux drives significant inputs of ²²⁴Ra_{ex} but not ²²⁸Ra, suggesting
430 that recirculation is operating on a time-scale of days. The ²²⁴Ra_{ex} flux is divided by the average
431 shallow pore water ²²⁴Ra_{ex} activity (20 – 40 cm depth; **Table 1**) to estimate a volumetric water
432 recirculation flux, assuming the ²²⁴Ra_{ex} deficit is balanced by inputs of water recirculation
433 through the lagoon sediment.

434 The volume flux of water recirculation to La Palme lagoon during June 2016 is $0.70 \pm$
435 0.51 m³ s⁻¹ for ²²⁴Ra_{ex}; uncertainties are propagated throughout each term in Equation 2. If the
436 “true” ²²⁴Ra_{ex} pore water endmember is from a shallower depth (< 20 cm), then the water
437 recirculation flux will be larger (Cook et al., 2018). In comparison, Stieglitz et al. (2013)
438 estimated a water flux between $0.4 - 2.1$ m³ s⁻¹ during summer 2009 from a combined ²²²Rn,
439 water and salt balance, which was hypothesized to be driven by wind-forcing, while Bejannin et
440 al. (2017) estimated a predominantly recirculation-driven flux between $0.56 - 1.7$ m³ s⁻¹. It is
441 important to note the Ra mass balance calculations in Bejannin et al. (2017) used the karstic
442 groundwater spring as the Ra endmember (opposed to pore water collected from permeable
443 sediments), while the diffusive flux of Ra from the sediments was underestimated; further, the

444 study was conducted under different seasonal conditions (July 2009), in which the lagoon was
445 completely closed off to the sea. As noted by Rodellas et al. (2018), water recirculation in the
446 northern basin of La Palme lagoon varies over time. The $^{224}\text{Ra}_{\text{ex}}$ -derived water recirculation flux
447 ($0.70 \pm 0.51 \text{ m}^3 \text{ s}^{-1}$), divided by the volume of water within the lagoon ($2.28 * 10^6 \text{ m}^3$) during the
448 time of sampling (**Table 4**), suggests that 2.6 % of the lagoon volume was recirculated through
449 the sediment per day, in agreement with previous summer-time estimates (1.4 – 7.0 %; Stieglitz
450 et al., 2013). The $^{224}\text{Ra}_{\text{ex}}$ -derived water recirculation flux, normalized to the lagoon basin surface
451 area (**Table 4**), is therefore $1.3 \pm 1.0 \text{ cm d}^{-1}$. The physical mechanisms that may drive water
452 recirculation through permeable sediments are summarized in Santos et al. (2012). Drivers such
453 as density gradients (temperature and/or salinity), flow- and topography-induced advection, and
454 shear-stress may recirculate water through the permeable sediment of La Palme lagoon. During
455 the five days preceding the lagoon surface water sampling, mean wind speed was approximately
456 6.3 m s^{-1} with mean wind gusts of 16.0 m s^{-1} (www.weatherunderground.com); we speculate that
457 wind may be an adequate driver of water recirculation in La Palme lagoon during this time
458 period, as hypothesized by Stieglitz et al. (2013). Cook et al. (2018) found that pore water ^{222}Rn
459 profiles in La Palme lagoon were consistent with wave action-driven recirculation, locally
460 generated by winds.

461 4.3 DSi fluxes: terrestrial vs. marine sources

462 4.3.1 La Palme lagoon

463 There is an enrichment of DSi in the hyper-saline (> 38) lagoon waters of the
464 intermediate and southern basins, which cannot be explained by external inputs (e.g. salt ponds,
465 offshore Mediterranean seawater; **Figure 3F**, **Figure 4**, **Figure 5**). Intermediate and southern
466 basin surface waters increased in DSi with increasing salinity, reflecting underlying pore waters.
467 DSi may be added to overlying lagoon waters from bottom-sediments through both molecular

468 diffusion and water recirculation; in addition, DSi in lagoon waters can be concentrated by
469 evaporation, which we do not quantitatively take into account here. In La Palme lagoon, the DSi
470 enrichment is not likely associated with biogenic Si dissolution (Loucaides et al., 2008), as
471 bottom sediments in the intermediate and southern basins are dominated by fine-sand (**Figure 7**).
472 A similar result was concluded in a sandy barrier island subterranean estuary, where diatom
473 dissolution within the sediment was unable to support enriched DSi concentrations in pore
474 waters, which was primarily driven by sediment dissolution from seawater recirculation (Ehlert
475 et al., 2016). Longer recirculated water residence times permit a longer contact period of pore
476 fluid with sediment, which in turn increases pore water DSi concentrations via lithogenic particle
477 dissolution, until a saturated equilibrium concentration is reached (**Figure 8**).

478 Experimental sediment dissolution rates conducted with sandy La Palme lagoon sediment
479 (from the southern basin; ~200 – 250 μm) showed very high dissolution rates with the two-
480 different water/rock ratios tested (82 and 12 $\mu\text{M DSi d}^{-1}$; **Figure 8**). These values are much
481 higher than previously reported rates of 1.18 $\mu\text{M DSi d}^{-1}$ for 50 g of sediment (170 μm grain
482 size) in 27 mL seawater (Ehlert et al., 2016) and of 0.23 $\mu\text{M DSi d}^{-1}$ for 50 g of sediment (300
483 μm grain size) in 50 mL seawater (Anschutz et al., 2009). From the $^{224}\text{Ra}_{\text{ex}}$ mass balance, $1.3 \pm$
484 1.0 cm d^{-1} of lagoon water is recirculated through the bottom-sediment; this relatively low rate of
485 pore water advection is in agreement with the relatively low concentration of pore water DSi in
486 sandy sediments (**Figure 7**), despite the high rate of DSi dissolution obtained experimentally
487 (**Figure 8**).

488 Pore water DSi is high only in sediment with high porosity, i.e. muddy and low
489 permeable sediments, where recirculation is likely restricted (**Figure 7**). In sandy permeable
490 sediments (porosity below 50%), pore waters of the top cm below the sediment-water interface

491 have mean DSi concentrations below 100 μM , suggesting that the residence time of pore waters
492 is between 1 and 8 days (**Figure 8**). The DSi flux driven by water recirculation is estimated as
493 the mean concentration difference between the shallow pore water within the top 10 cm of sandy
494 sediments and the lagoon water overlying the sediment. We do not observe significant seasonal
495 variability in the shallow pore water DSi endmember concentration (**Figure 7**); therefore, we
496 take a mean pore water DSi concentration equal to $32 \pm 14 \mu\text{M}$ ($n = 17$) from June 2016, May
497 2017 and September 2017 (0 – 10 cm depth). The mean DSi endmember concentration is
498 multiplied by the $^{224}\text{Ra}_{\text{ex}}$ -derived recirculated water flux ($0.7 \pm 0.5 \text{ m}^3 \text{ s}^{-1}$) to derive a DSi flux
499 equal to $1,930 \pm 1,650 \text{ mol d}^{-1}$ ($0.42 \pm 0.36 \text{ mmol m}^{-2} \text{ d}^{-1}$ over the entire lagoon), at least a factor
500 of two greater than inputs from molecular diffusion alone (**Table 5**). If the “true” Ra endmember
501 is from a shallower depth ($< 20 \text{ cm}$; Cook et al., 2018), then the water recirculation flux will be
502 larger; this would effectively increase the DSi flux driven by water recirculation, and therefore
503 the flux calculated above is a conservative estimate. The significant relationship between short-
504 lived $^{224}\text{Ra}_{\text{ex}}$ and DSi, but not with ^{228}Ra , indicates that the water recirculation-driven DSi flux
505 operates over a time-scale of days. ^{224}Ra is regenerated daily in the sediment from its longer-
506 lived (surface-bound) parent ^{228}Th , such that continuous recirculation inputs can be easily traced.
507 Longer-term studies in La Palme lagoon indicate significant water recirculation in the northern
508 basin, between $0.5 - 1.0 \text{ m}^3 \text{ s}^{-1}$ regardless of the season (Rodellas et al., 2018), signifying that
509 various forcing mechanisms (wind, waves, density-gradients) continuously drive lagoon water
510 recirculation and therefore supply DSi to La Palme lagoon. The groundwater spring is enriched
511 in DSi, with a mean concentration of $114 \pm 0.2 \mu\text{M}$ (**Figure 4**) and a resultant DSi flux equal to
512 $250 \pm 50 \text{ mol d}^{-1}$ (**Table 5**). The sediment contribution of DSi through water recirculation (and
513 molecular diffusion) is an order of magnitude greater than the DSi flux from the groundwater

514 spring, indicating that water recirculation through the lagoon sediment is significant in
515 controlling the DSi inventory within La Palme lagoon.

516 4.3.2 Offshore transects

517 On the seaward side of the lagoon, wind and wave action drive seawater into the sandy,
518 permeable beach face. Additionally, a hydraulic gradient exists between the lagoon and the sea
519 when lagoon water levels are high, driving lagoon water through the beach toward the sea; this
520 gradient may cease or reverse direction when lagoon water levels are low or when wind blows
521 from the sea towards the beach. We will broadly define flow paths which enter the
522 Mediterranean Sea from these two separate processes as marine SGD (Burnett et al., 2003);
523 being synonymous with the term “water recirculation” used for La Palme lagoon (Section 4.2).
524 Shallow pore waters sampled between the lagoon and sea were slightly reduced in salinity (37.0
525 ± 0.5 ; $n = 8$) compared to Mediterranean seawater; therefore, these samples likely reflect a
526 combination of a wave-setup endmember and an endmember driven by the hydraulic gradient
527 between the lagoon and sea, as traced by elevated ^{228}Ra activities (**Figure 6**).

528 Pore water can become enriched in DSi from lithogenic particle dissolution, depending
529 on the subsurface residence time (**Figure 8**). The DSi inventory of coastal surface waters
530 represents inputs from molecular diffusion (e.g. **Table 3**), bioturbation, lateral/onshore
531 advection, upwelling and marine SGD. We explicitly subtract coastal surface water DSi
532 concentrations from the shallow pore water samples collected along the beach to derive a non-
533 conservative DSi enrichment; this non-conservative DSi enrichment must be derived from
534 lithogenic particle dissolution from both wave-setup and exchange between the permeable sand
535 barrier. Beach pore water DSi concentrations were enriched over seawater concentrations ($1.6 \pm$
536 $0.1 \mu\text{M}$, $n = 36$, ≥ 100 m offshore), with an average non-conservative pore water DSi enrichment

537 of $18 \pm 7 \mu\text{M}$ during June and November 2016 ($n = 8$), after correcting for seawater. The
538 observed Ra and DSi surface water enrichments must be driven by marine SGD inputs, as there
539 are no other solute sources in this area to drive the observed gradients, aside from the partially
540 open outlet of La Palme lagoon, adjacent to transect N4 (**Figure 1**).

541 ^{223}Ra -derived horizontal eddy diffusivity was slightly lower than estimates derived from
542 $^{224}\text{Ra}_{\text{ex}}$ (**Section 3.2**). $^{224}\text{Ra}_{\text{ex}}$, with respect to ^{223}Ra , is typically less sensitive to onshore
543 advection of Ra-depleted offshore waters and the advection of Ra in the longshore direction, due
544 to the shorter half-life of ^{224}Ra (Colbert and Hammond, 2007). We therefore use $^{224}\text{Ra}_{\text{ex}}$ -derived
545 horizontal eddy diffusivity in the ensuing analysis. Multiplying the ^{228}Ra surface water gradients
546 (transects N1, N2 and N3 ≥ 200 m offshore; **Figure 6**) and the $^{224}\text{Ra}_{\text{ex}}$ -derived horizontal eddy
547 diffusivity, integrated over a 2.5 m thick impacted water column and distributed over the 9.5 km
548 long shoreline, results in a ^{228}Ra flux driven by marine SGD between $3.7 - 13.5 * 10^8$ dpm d^{-1} for
549 the three transects. Transect N4 is not included here, as it may be influenced by surface water
550 exchange from the outlet of La Palme lagoon (**Figure 1**); ^{228}Ra uncertainties for transect N5 are
551 relatively high and is therefore excluded from this analysis. Dividing the ^{228}Ra flux by the mean
552 shallow beach pore water ^{228}Ra endmember ($60 \text{ dpm } 100\text{L}^{-1}$) results in a marine SGD flux
553 between $0.6 - 2.2 * 10^6$ $\text{m}^3 \text{d}^{-1}$. Multiplying the marine SGD flux by the shallow beach pore water
554 DSi enrichment ($18 \pm 7 \mu\text{M}$) yields a DSi flux of $2.3 \pm 1.3 * 10^4$ mol d^{-1} ($2.4 \pm 1.4 \text{ mol d}^{-1} \text{ m}^{-1}$ of
555 shoreline). The ^{228}Ra marine SGD-derived DSi flux here is within the range of the DSi flux
556 driven by brackish SGD to the entire Mediterranean Sea, between $1 - 28 \text{ mol d}^{-1} \text{ m}^{-1}$ of shoreline
557 (Rodellas et al., 2015).

558 To assess the relevance of marine SGD-driven DSi fluxes, we will compare with DSi
559 inputs from the largest river in the region, the Têt river (Sadaoui et al. 2016). The marine SGD

560 flux calculated above ($0.6 - 2.2 * 10^6 \text{ m}^3 \text{ d}^{-1}$) is significantly higher than the discharge of the Têt
561 river during November 2016 ($2.69 \pm 1.86 * 10^5 \text{ m}^3 \text{ d}^{-1}$). The DSi flux from the Têt river is
562 calculated from the monthly mean discharge of the river gauging station (Station Y0474030;
563 hydro.eaufrance.fr) and the mean DSi concentration of the river (Station 06172100;
564 sierm.eaurmc.fr). Riverine DSi samples are not available after 2013; therefore, we take an
565 average DSi concentration of $122 \pm 25 \text{ } \mu\text{M}$ ($n=48$) from January 2010 – December 2013. The
566 amount of DSi supplied by the Têt river during November 2016 is estimated as $3.3 \pm 2.4 * 10^4$
567 mol d^{-1} ; therefore, the marine SGD-driven DSi flux is on the same order of magnitude as the DSi
568 flux from the Têt river during November 2016 (**Table 5**). The Têt river varies in response to
569 regional precipitation; the average monthly discharge for 2016 was $3.1 \pm 1.6 * 10^5 \text{ m}^3 \text{ d}^{-1}$ with a
570 maximum during May ($7.3 \pm 6.3 * 10^5 \text{ m}^3 \text{ d}^{-1}$; DSi flux = $9.0 \pm 2.9 * 10^4 \text{ mol d}^{-1}$). The relative
571 significance of marine SGD in supplying DSi to the coastal Mediterranean Sea is thus seasonally
572 dependent with respect to the terrestrial DSi load supplied by coastal rivers and terrestrial
573 groundwater.

574 Coastal lagoons and sandy beaches dominate the French Mediterranean coastline, from
575 Perpignan to Montpellier, buffered on each end by impermeable rock. The shoreline length of
576 sandy beaches within this region is approximately 160 km (**Figure 1**). If we assume that the
577 marine SGD flux measured here, driven by wave-setup and water level differences between
578 permeable sand barriers, affects the 160 km long shoreline in a similar manner, and that the
579 derived $^{224}\text{Ra}_{\text{ex}}$, ^{228}Ra and DSi gradients offshore of La Palme lagoon are similar between each of
580 these sandy beaches, then we may be able to provide a first-order approximation of the marine
581 SGD-driven DSi flux to the sandy shoreline of the Gulf of Lions. Extrapolation of the DSi flux
582 of $2.4 \pm 1.4 \text{ mol DSi d}^{-1} \text{ m}^{-1}$ of shoreline for La Palme, over the 160 km sandy shoreline of the

583 Gulf of Lions, results in a marine SGD-driven DSi flux of $3.8 \pm 2.2 * 10^5$ mol d⁻¹. This DSi flux
584 is between one and two orders of magnitude lower than the Rhône River ($\sim 2 * 10^7$ mol DSi d⁻¹;
585 depending on the season), the largest river which discharges into the Gulf of Lions and the
586 Mediterranean Sea (Billen and Garnier, 2007; Ludwig et al., 2009). In contrast, Rodellas et al.
587 (2015) showed that total SGD-driven DSi inputs (terrestrial + marine flow paths) to the
588 Mediterranean can be comparable or higher than riverine inputs. Differences between the marine
589 SGD-driven DSi flux estimated here to the DSi flux supplied by the Rhône River is likely a
590 function of scale-length (only 160 km shoreline length) and the fact that the Rhône River is the
591 largest river in the Mediterranean Sea. The relative role of marine SGD as a source of DSi is
592 likely more significant in Mediterranean coastal areas which receive limited riverine inputs
593 (Trezzi et al., 2016).

594 4.4 Potential nutrient limitation

595 The relationship between short-lived ²²⁴Ra_{ex} and DSi for La Palme lagoon and the coastal
596 Mediterranean Sea (**Figure 5**) suggests that these dissolved constituents are derived from a
597 similar source, the sediment (**Figure 8**), operating over a time-scale of days. The constant wind
598 and wave action along the permeable shoreline of the investigated study area provides a
599 mechanism in which sediment is consistently exposed to seawater (or lagoon water), and
600 therefore, by this process, carries a distinct geochemical signature upon discharge back into the
601 sea or lagoon. A water recirculation-driven DSi flux derived from lithogenic particle dissolution
602 is likely a continuous DSi source over long time-scales, aside from minor variations in
603 recirculated water residence times within the permeable coastal sediment, as for example, due to
604 seasonally variable winds and storms. The relatively constant DSi inputs from water
605 recirculation for the shallow lagoons along the French Mediterranean Sea may sustain primary
606 production in the coastal zone. In comparison, terrestrial groundwater and rivers supply

607 temporally variable nutrient (N, P, Si) inputs via changes in regional precipitation, runoff and
608 aquifer storage (Michael et al., 2005; Slomp & Van Cappellen, 2004). For example, Rodellas et
609 al. (2018) estimated karstic groundwater discharge to La Palme lagoon during November 2016
610 that was approximately one order of magnitude higher than June 2016; such temporal variability
611 drives temporally variable nutrient loads that may impact primary production.

612 Analysis of La Palme lagoon water, Mediterranean seawater and pore water nutrient
613 ratios (DSi:DIN, DSi:DIP, DIN:DIP) reveals stark differences in the potential limiting nutrient of
614 La Palme lagoon and the coastal Mediterranean Sea (Garcia-Solsona et al., 2010b; Justic et al.,
615 1995). Here, DIN is equal to the sum of NO_3^- , NO_2^- and NH_4^+ ; DIP is equal to PO_4^{3-} . Surface
616 waters from the coastal Mediterranean Sea were limited in DIP (**Figure 10**), similar to other
617 karstic areas impacted by SGD along the Mediterranean Sea (Garcia-Solsona et al., 2010a;
618 Garcia-Solsona et al., 2010b) and the eastern Mediterranean basin (Krom et al., 2010).
619 Considering a mean beach pore water concentration of $0.18 \pm 0.07 \mu\text{M}$ DIP (after subtracting
620 surface seawater concentrations; $n = 8$), the marine SGD-driven DIP flux (derived from the ^{228}Ra
621 surface water gradient calculations; Section 4.3.2) to the Mediterranean Sea is $0.02 \pm 0.01 \text{ mol d}^{-1}$
622 m^{-1} of shoreline ($230 \pm 130 \text{ mol DIP d}^{-1}$ over the 9.5 km long shoreline), which is
623 approximately 5 – 23 % of the DIP load from the Têt river ($\sim 1 - 5 * 10^3 \text{ mol P d}^{-1}$). In
624 comparison, the marine SGD-driven NO_3^- flux to the Mediterranean Sea is $5.7 \pm 3.2 \text{ mol d}^{-1} \text{ m}^{-1}$
625 of shoreline ($5.4 \pm 3.0 * 10^4 \text{ mol N d}^{-1}$), considering a mean beach pore water concentration of 43
626 $\pm 28 \mu\text{M}$ NO_3^- (after subtracting surface seawater concentrations; $n = 8$). Therefore, marine SGD
627 along the Mediterranean shoreline drives a DIN:DSi flux ratio of approximately 2.4, higher than
628 Redfield ratio (0.8). This flux is at least a factor of two times greater than the NO_3^- load of the
629 Têt river ($\sim 1 - 3 * 10^4 \text{ mol N d}^{-1}$).

630 La Palme lagoon surface waters were primarily DIN limited, with the exception of three
631 samples taken closest to the karstic groundwater spring, which were limited in DIP (**Figure 10**).
632 The NO_3^- load of the groundwater spring to La Palme lagoon during June 2016 (220 mol N d^{-1} ;
633 Rodellas et al., 2018) is likely the primary driver limiting nutrient utilization in the northern-most
634 section of the lagoon (**Figure 3e**), in addition to DIN inputs (in the form of NH_4^+) from lagoon
635 water recirculation ($1,900 \pm 900 \text{ mol N d}^{-1}$ during June 2016). In comparison, the recirculation-
636 driven DIP flux estimated for June 2016 was relatively minor ($71 \pm 36 \text{ mol DIP d}^{-1}$; Rodellas et
637 al., 2018). The water recirculation-driven DIN:DSi flux ratio to La Palme lagoon is
638 approximately 0.98 ($1,900 \text{ mol DIN}/1,930 \text{ mol DSi}$), slightly higher than Redfield ratio (0.8). An
639 increase in recirculation-driven DSi inputs by lithogenic particle dissolution may not impact
640 diatom coastal zone primary production here.

641 Primary production of diatoms is dependent upon DSi loading; shifting DIN and DIP
642 loads over time, with respect to DSi, may shift coastal zone primary production from diatoms to
643 non-siliceous algae (Billen and Garnier, 20007; Ludwig et al., 2009). DSi limitation can occur
644 for diatoms in Mediterranean rivers, a persistent phenomenon between the 1970's and 1990's
645 due to reductions in DIP loadings (Ludwig et al., 2009). The sandy beaches subject to wave-
646 setup driven recirculation may transfer DIP to the coastal ocean as a remineralized nutrient
647 product (Anschutz et al., 2009). However, DIP may be removed from groundwater and adsorbed
648 onto the beach sediment in settings where sediment surfaces are coated with Fe-oxides (Charette
649 and Sholkovitz, 2002). Future work studying coastal zone nutrient limitation should therefore
650 carefully consider DSi loads driven by water recirculation, with respect to DIP and DIN loads.

651 **5. Summary & Conclusions**

652 In this study, we have quantified water recirculation through the permeable sediment of a
653 coastal lagoon and along its adjacent sandy shoreline using Ra isotopes as tracers of water
654 recirculation. We observed significant relationships between short-lived Ra isotopes and
655 dissolved silica (DSi), which point toward a common source, the sediment. DSi enrichment from
656 lithogenic particle (i.e. sediment) dissolution is supported by experimental dissolution rate
657 calculations, which suggests that the DSi enrichments were not derived from diatom (i.e.
658 biogenic) dissolution. The DSi flux from lagoon water recirculation is an order of magnitude
659 greater than a local karstic groundwater spring and at least a factor of two greater than inputs
660 from molecular diffusion. In comparison, the DSi flux from marine SGD along the 9.5 km sandy
661 shoreline into the Mediterranean Sea, driven by wave-setup and water level differences between
662 permeable sand barriers, is similar to the DSi flux from the nearby Têt River, the largest river in
663 the region. Upscaling this flux to the permeable sandy shoreline of the Gulf of Lions results in a
664 DSi flux that is one to two orders of magnitude lower than the Rhône River; however, the
665 importance of recirculation-driven DSi inputs may be significant for Mediterranean shoreline
666 segments that are not impacted by terrestrial (riverine and groundwater) DSi inputs. Despite
667 these large recirculation-driven DSi fluxes, coastal-zone primary production is limited by inputs
668 of DIN to the lagoon and DIP to the coastal Mediterranean Sea.

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907 **Tables**

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909 **Table 1.** Mean (\pm STD) lagoon water (northern, intermediate and southern), karstic groundwater
 910 spring and lagoon pore water salinity, ^{223}Ra , $^{224}\text{Ra}_{\text{ex}}$, ^{228}Ra and DSi during June 2016. Shallow
 911 PW = shallow lagoon pore water samples. DSi concentrations are from <10 cm depth, used in
 912 the flux calculation (June 2016, May 2017 and September 2017). Shallow pore water DSi
 913 concentrations are corrected for overlying lagoon water DSi. Shallow Ra activities are from 20 –
 914 40 cm depth. Deep PW = lagoon pore water samples between 50 – 140 cm depth from the drive-
 915 point piezometers; DSi concentrations are for 50 cm depth only (June 2016).

Endmember	Salinity	^{223}Ra dpm 100L ⁻¹	$^{224}\text{Ra}_{\text{ex}}$ dpm 100L ⁻¹	^{228}Ra dpm 100L ⁻¹	DSi μM	n
Northern	33 \pm 5	6 \pm 2	180 \pm 120	270 \pm 70	15 \pm 21	Ra=27; DSi=24
Intermediate	40 \pm 2	9 \pm 4	140 \pm 30	280 \pm 40	4 \pm 4	Ra=15; DSi=15
Southern	42 \pm 3	12 \pm 4	230 \pm 80	190 \pm 90	9 \pm 7	Ra=15; DSi=14
Spring	8.4 \pm 0.7	11 \pm 3	710 \pm 80	450 \pm 30	114.0 \pm 0.2	Ra=4; DSi=3
Shallow PW	38 \pm 8	70 \pm 49	1,060 \pm 740	500 \pm 450	32 \pm 14	Ra=5; DSi=17
Deep PW	59 \pm 16	400 \pm 270	5,500 \pm 3,900	2,800 \pm 1,900	129 \pm 23	Ra=7; DSi=3

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932 **Table 2.** Summary of lagoon water pH and relevant saturation state indices (\pm STD), determined
 933 using PHREEQC. Negative values indicate under-saturation conditions, positive values indicate
 934 saturation conditions.

	pH	Barite	Celestine	Quartz	Amorphous Silica	n
				log SI		
Northern	8.41 \pm 0.23	0.09 \pm 0.02	-0.84 \pm 0.06	-1.3 \pm 0.3	-2.3 \pm 0.3	23
Intermediate	8.35 \pm 0.03	0.12 \pm 0.03	-0.76 \pm 0.01	-1.6 \pm 0.2	-2.6 \pm 0.2	7
Southern	8.35 \pm 0.15	-0.10 \pm 0.20	-0.75 \pm 0.03	-1.3 \pm 0.3	-2.3 \pm 0.3	11

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957 **Table 3.** Diffusive DSi fluxes to La Palme lagoon (May and September 2017) at the sediment
 958 water interface, arranged by lagoon basin.

Basin	Surface area *10 ⁶ m ²	Diffusive flux May mol d ⁻¹	Diffusive flux Sept. mol d ⁻¹
Northern	2.48	145 ± 176	817 ± 747
Intermediate	1.55	23 ± 20	48 ± 25
Southern	0.53	32 ± 23	106 ± 61
Total	4.56	201 ± 179	972 ± 750

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982 **Table 4.** Summary of the terms used in the Ra mass balance. The groundwater spring inflow has
 983 an assumed uncertainty of 20%.

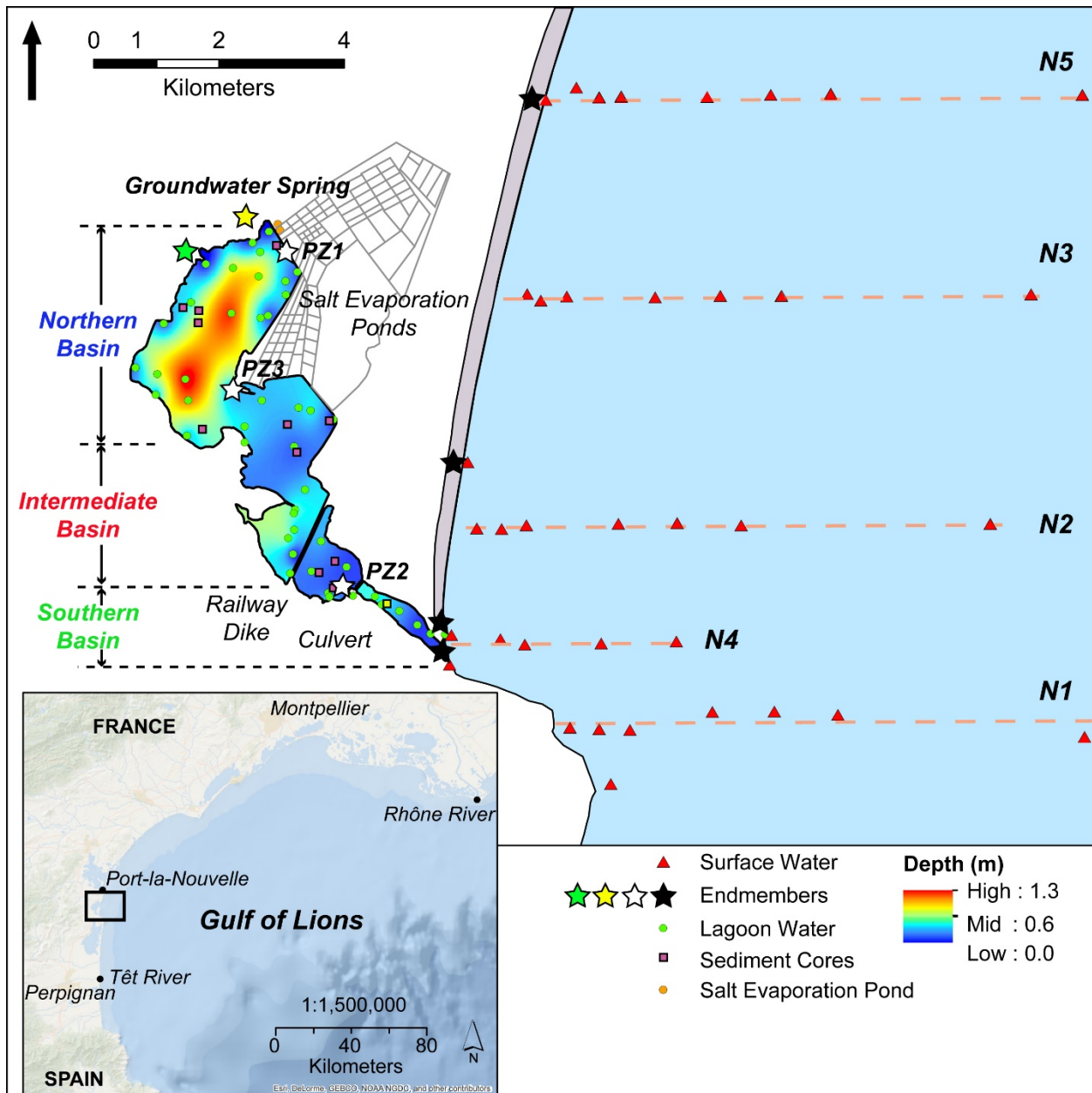
Term	Description	Value	Units
<i>A</i>	Lagoon Surface Area	4.56 ± 0.23	*10 ⁶ m ²
<i>V</i>	Lagoon Volume	2.28 ± 0.11	*10 ⁶ m ³
<i>Q_{spring}</i>	Groundwater Spring Inflow	0.025 ± 0.005	m ³ s ⁻¹
<i>C_{sed}</i>	Suspended Solids	40 ± 10	mg L ⁻¹
<i>X_{desorp}</i>	²²³ Ra available for desorption	0.008 ± 0.007	dpm g ⁻¹
<i>X_{desorp}</i>	²²⁴ Ra available for desorption	0.24 ± 0.05	dpm g ⁻¹
<i>J_{sediment}</i>	²²³ Ra diffusive flux from fine sediment	3.6 ± 1.4	dpm m ⁻² d ⁻¹
<i>J_{sediment}</i>	²²⁴ Ra diffusive flux from fine sediment	75 ± 50	dpm m ⁻² d ⁻¹
<i>J_{sediment}</i>	²²⁸ Ra diffusive flux from fine sediment	15 ± 8	dpm m ⁻² d ⁻¹

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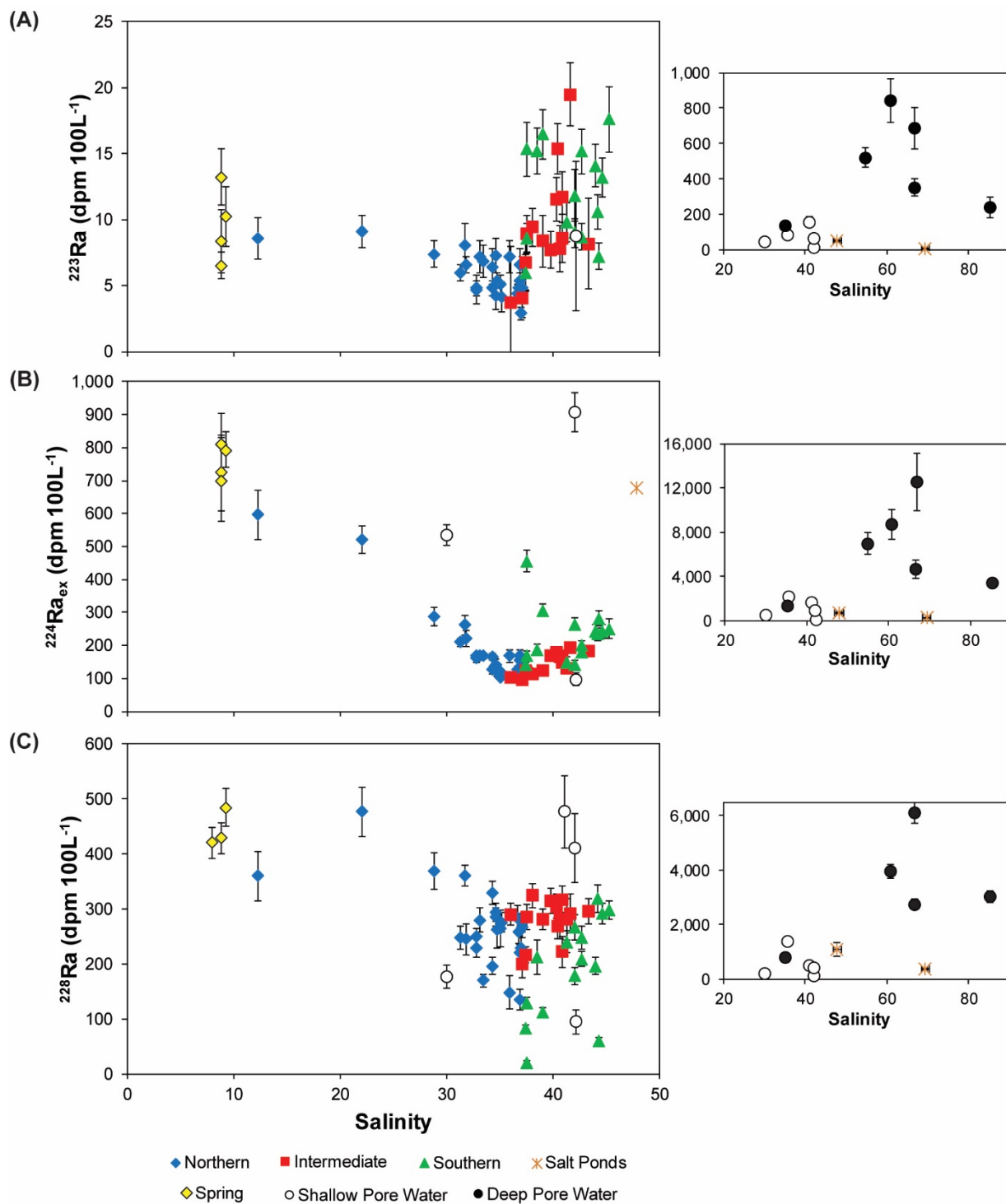
1002 **Table 5.** Summary of DSi fluxes to La Palme lagoon (June 2016) and the coastal Mediterranean
 1003 Sea (November 2016). The marine SGD flux to the coastal Mediterranean Sea is for the 9.5 km
 1004 long stretch of shoreline from the outlet of La Palme lagoon to Port-la-Nouvelle (Figure 1).

	DSi Flux
	* 10 ³ mol d ⁻¹
<i>Lagoon</i>	
Groundwater spring	0.25 ± 0.05
Water recirculation	1.93 ± 1.65
Molecular diffusion	0.97 ± 0.75
<i>Mediterranean Sea</i>	
Marine SGD	23 ± 13
Têt river	33 ± 24

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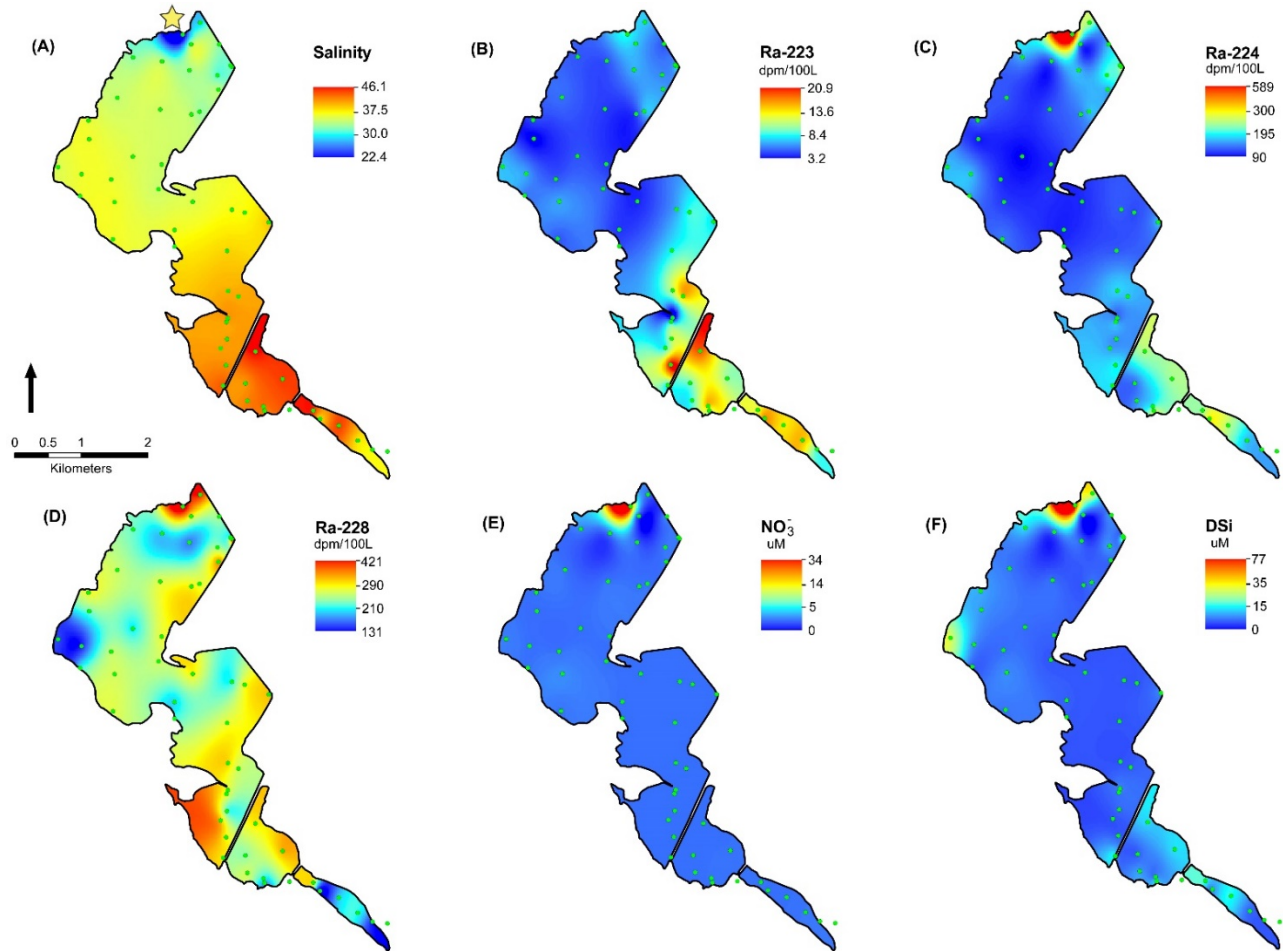


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 1027 **Figure 1.** La Palme lagoon, located in southern France, adjacent to the Mediterranean Sea (inset;
 1028 black square). Lagoon surface waters were collected during June 2016 (green circles), open
 1029 surface water transects were collected during November 2016 (red triangles). Sediment cores
 1030 (purple squares) were collected during May and September 2017. The sediment core for the DSi
 1031 incubation experiment is indicated by a yellow square. The sediment core for the Ra diffusion
 1032 experiment was collected next to PZ2. Lagoon water depth is specific to the June 2016 sampling
 1033 period. Endmember samples are indicated by stars, including the sewage outlet (green),
 1034 groundwater spring (yellow), lagoon pore waters (white) and beach pore waters (black). The
 1035 gray shaded area indicates the sandy 9.5 km long shoreline (not to scale).



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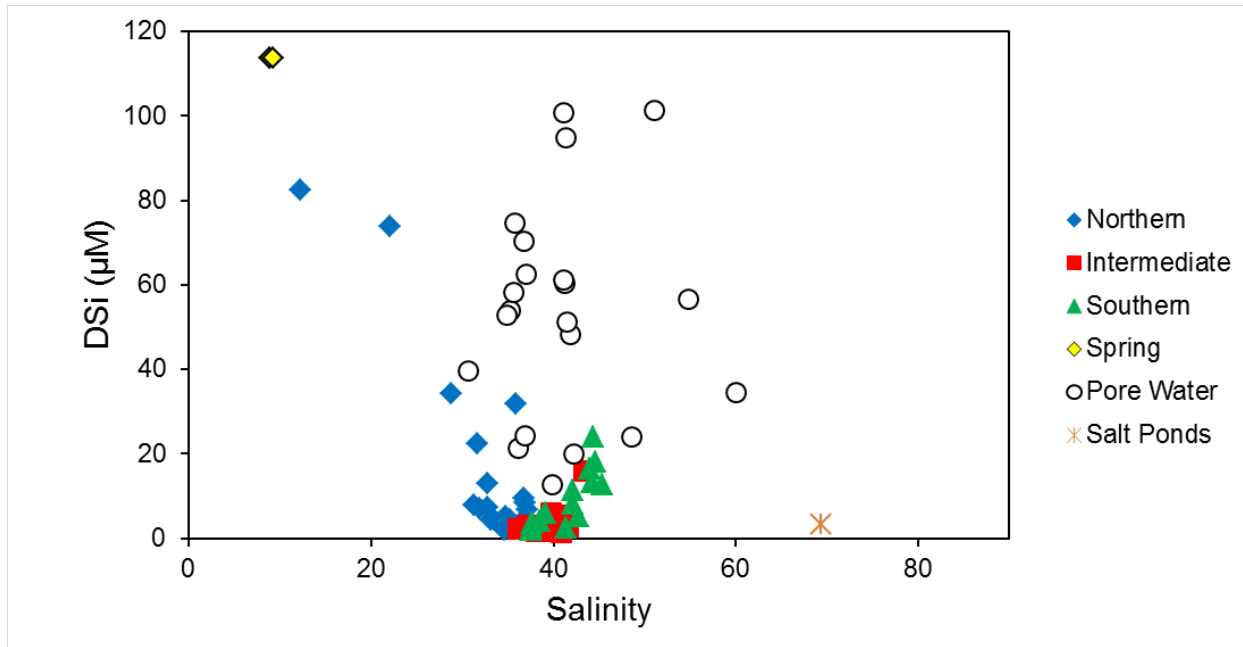
1037 **Figure 2.** ^{223}Ra (A), $^{224}\text{Ra}_{\text{ex}}$ (B) and ^{228}Ra (C) activity vs. salinity for La Palme lagoon surface
 1038 waters and pore waters. Lagoon surface water samples are grouped by basin (northern,
 1039 intermediate and southern). Pore water and salt pond samples are presented on the right-hand
 1040 side for improved visualization. Note that most of these points are out of range on the left-hand
 1041 panels. Shallow pore waters (20 – 40 cm) are indicated by hollow circles; deep pore waters (50 –
 1042 140 cm) are indicated by filled circles.



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1044 **Figure 3.** Interpolated surface water distributions of (A) salinity, (B) ²²³Ra, (C) ²²⁴Ra_{ex}, (D)
 1045 ²²⁸Ra, (E) NO₃⁻ and (F) DSi in La Palme lagoon, during June 2016. The green dots represent the
 1046 sampling locations. Note the interpolation color scale is not linear and differs between plots to
 1047 improve visualization. The yellow star in (A) marks the location of the karstic groundwater
 1048 spring.

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1051 **Figure 4.** DSi vs. salinity for La Palme lagoon surface waters and pore waters collected during
 1052 June 2016. Lagoon surface water samples are grouped by basin (northern, intermediate and
 1053 southern). Pore water samples were taken from drive-point piezometers within the lagoon
 1054 (Figure 1).

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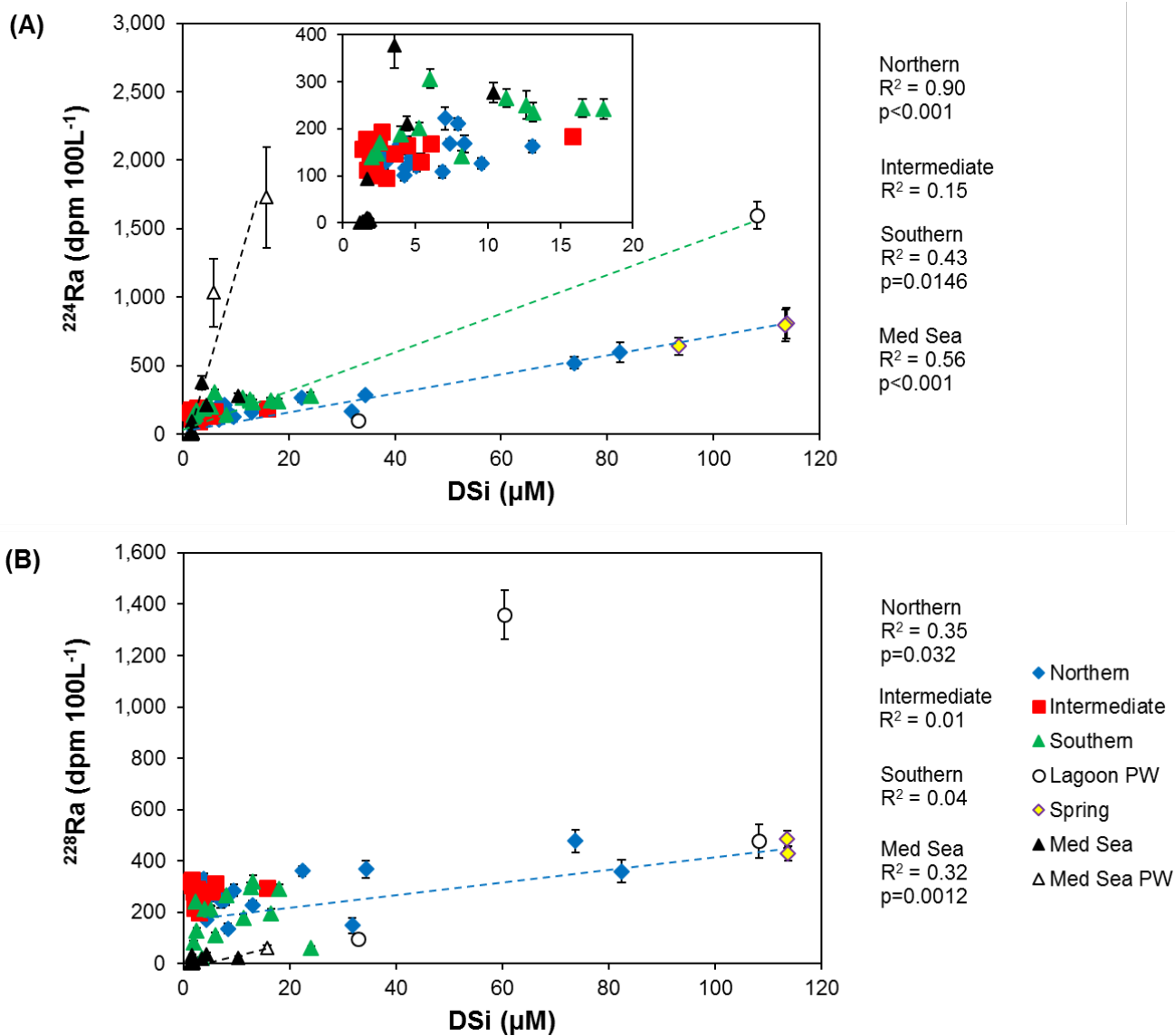
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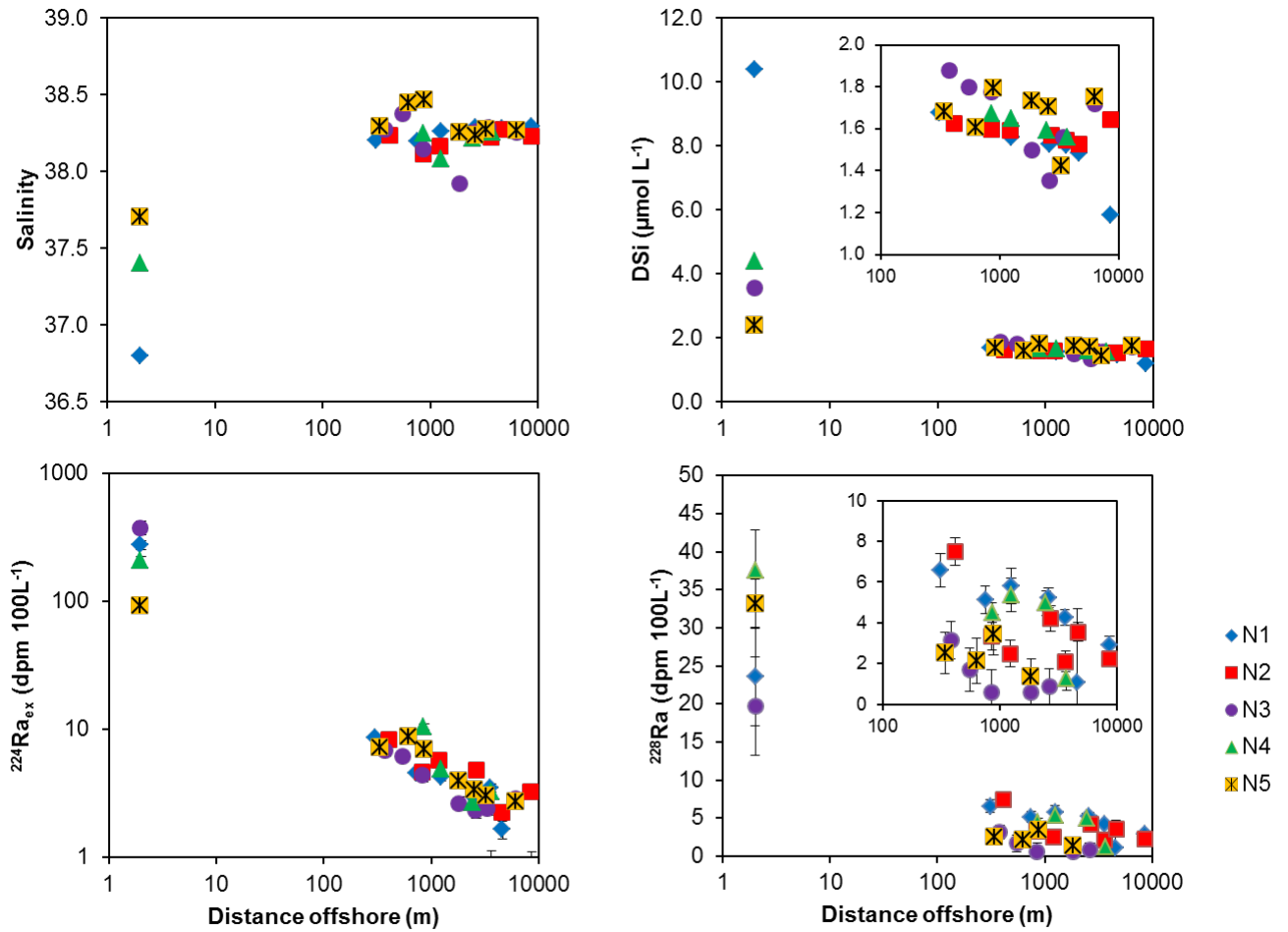
1069 **Figure 5.** $^{224}\text{Ra}_{\text{ex}}$ (A) and ^{228}Ra (B) vs. DSi. Lagoon surface water samples are grouped by basin
 1070 (northern, intermediate and southern). Lagoon pore waters (PW) are for shallow (20 – 40 cm)
 1071 depths only, during June 2016. P-values and trend lines are only shown for statistically
 1072 significant correlations.

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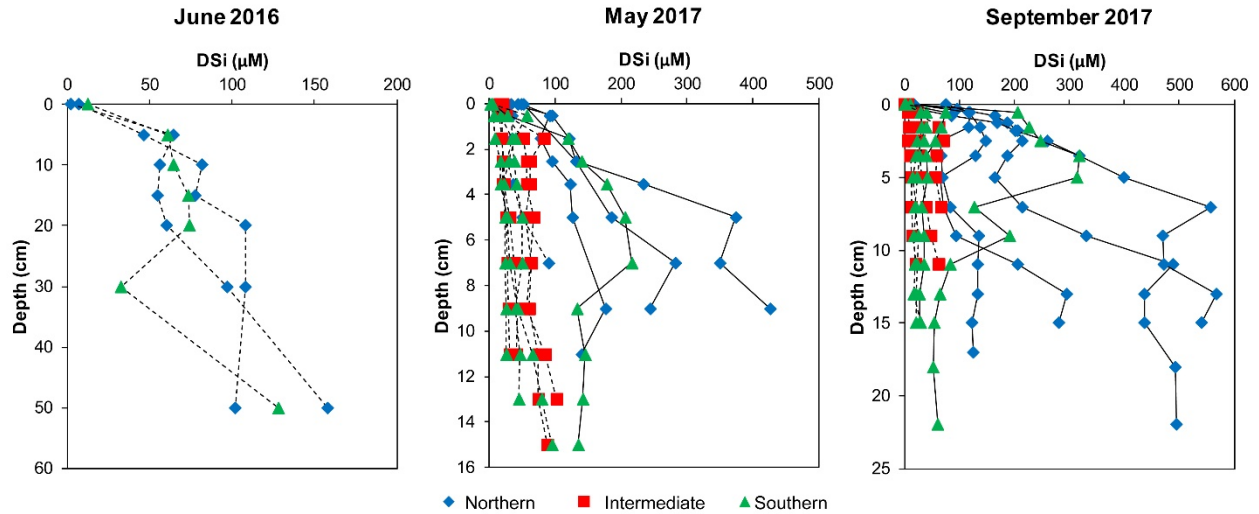


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1078 **Figure 6.** Surface water transects of salinity, DSi, $(\log) ^{224}\text{Ra}_{\text{ex}}$ and ^{228}Ra off the coast of La
 1079 Palme lagoon into the coastal Mediterranean Sea, during November 2016.

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1083 **Figure 7.** DSi concentration profiles in sediment cores collected in La Palme lagoon during June
 1084 2016, May 2017 and September 2017, grouped by lagoon basin (northern, intermediate and
 1085 southern). Cores collected in permeable, sandy sediments are depicted by a dashed-line (mean
 1086 down-core porosity ≤ 0.5); cores collected in impermeable, muddy sediments are depicted by a
 1087 solid-line (mean down-core porosity > 0.5). Note the x- and y-axes differ between plots. June
 1088 2016 pore waters were taken by drive-point piezometer; May 2017 and September 2017 pore
 1089 waters were extracted from sediment cores. Note that there is no sample for the intermediate
 1090 basin during June 2016.

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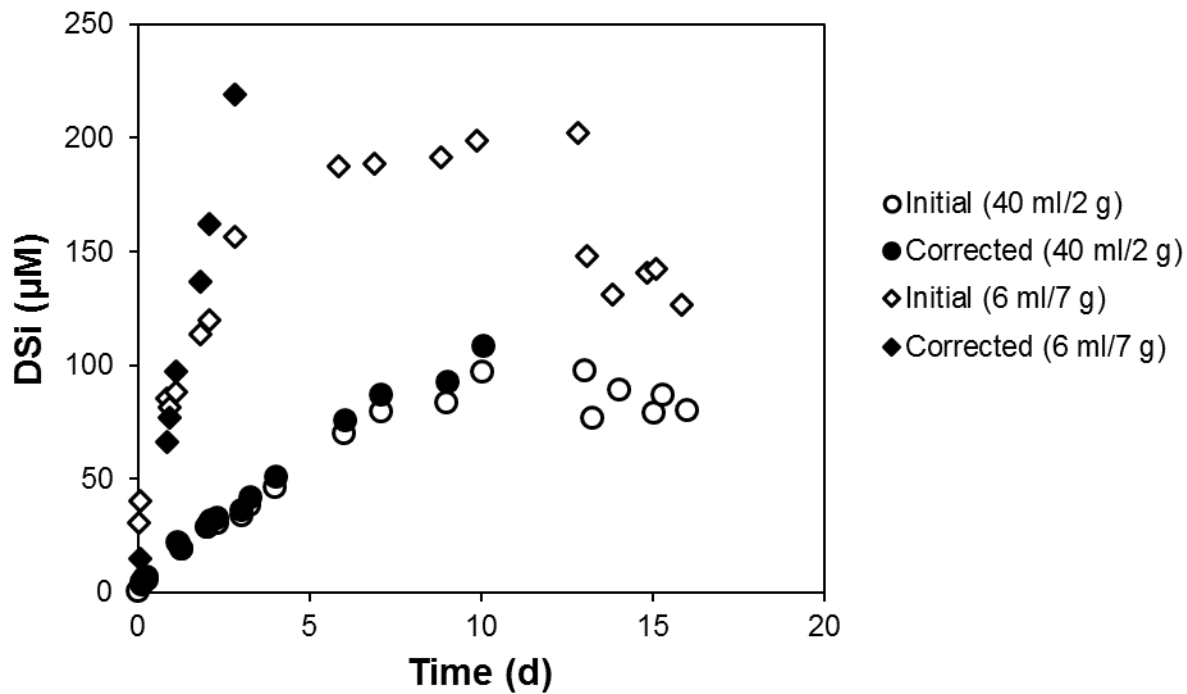
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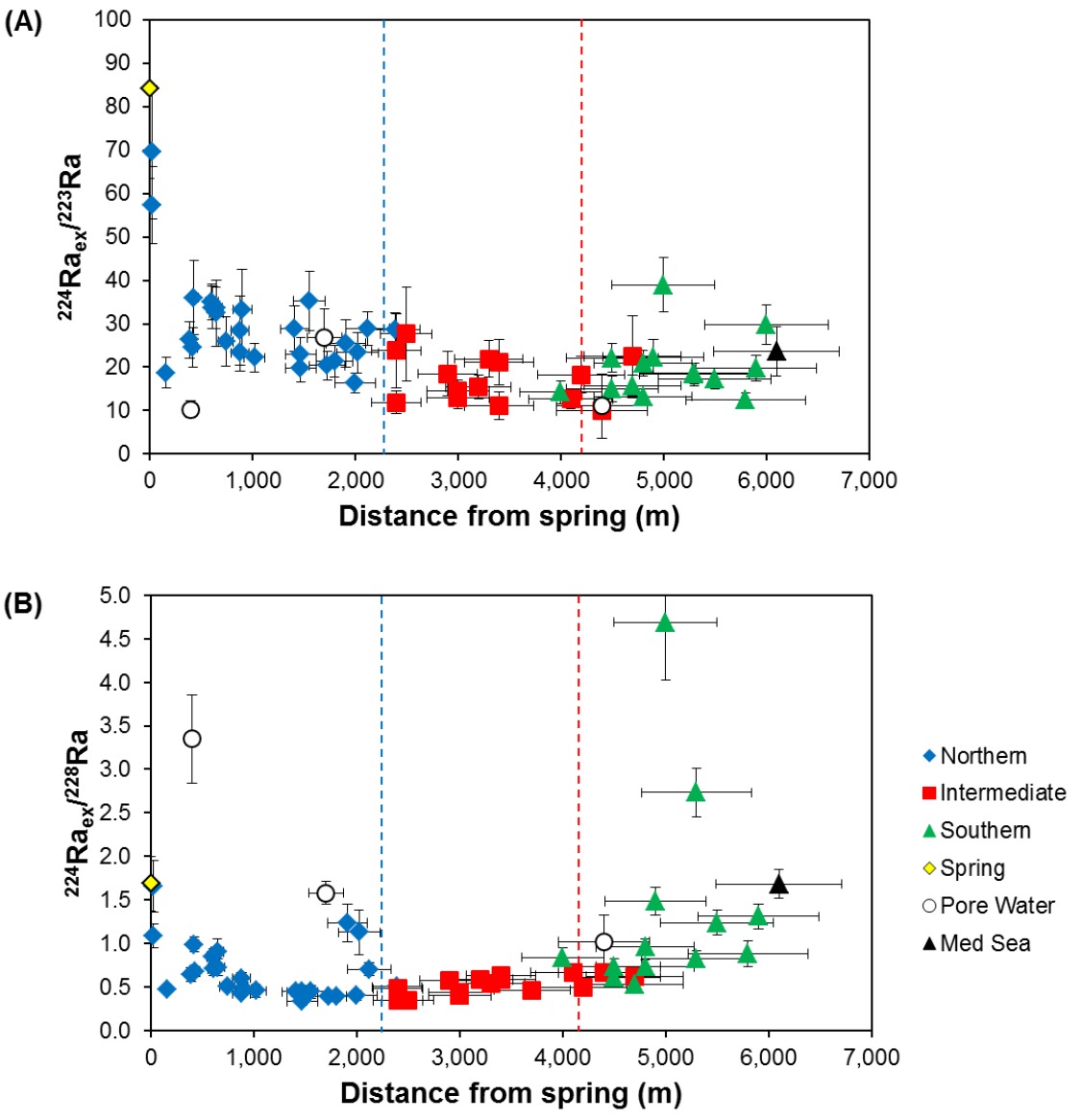
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 1101 **Figure 8.** Evolution of DSi concentration during experimental incubations of La Palme lagoon
 1102 sandy sediments for a water/rock ratio = 40 mL/2 g (circles) and a water/rock ratio = 6 mL/7 g
 1103 (diamonds). Hollow symbols represent the measured DSi concentration; filled symbols represent
 1104 the DSi concentration after correcting for sea water addition after water sampling.

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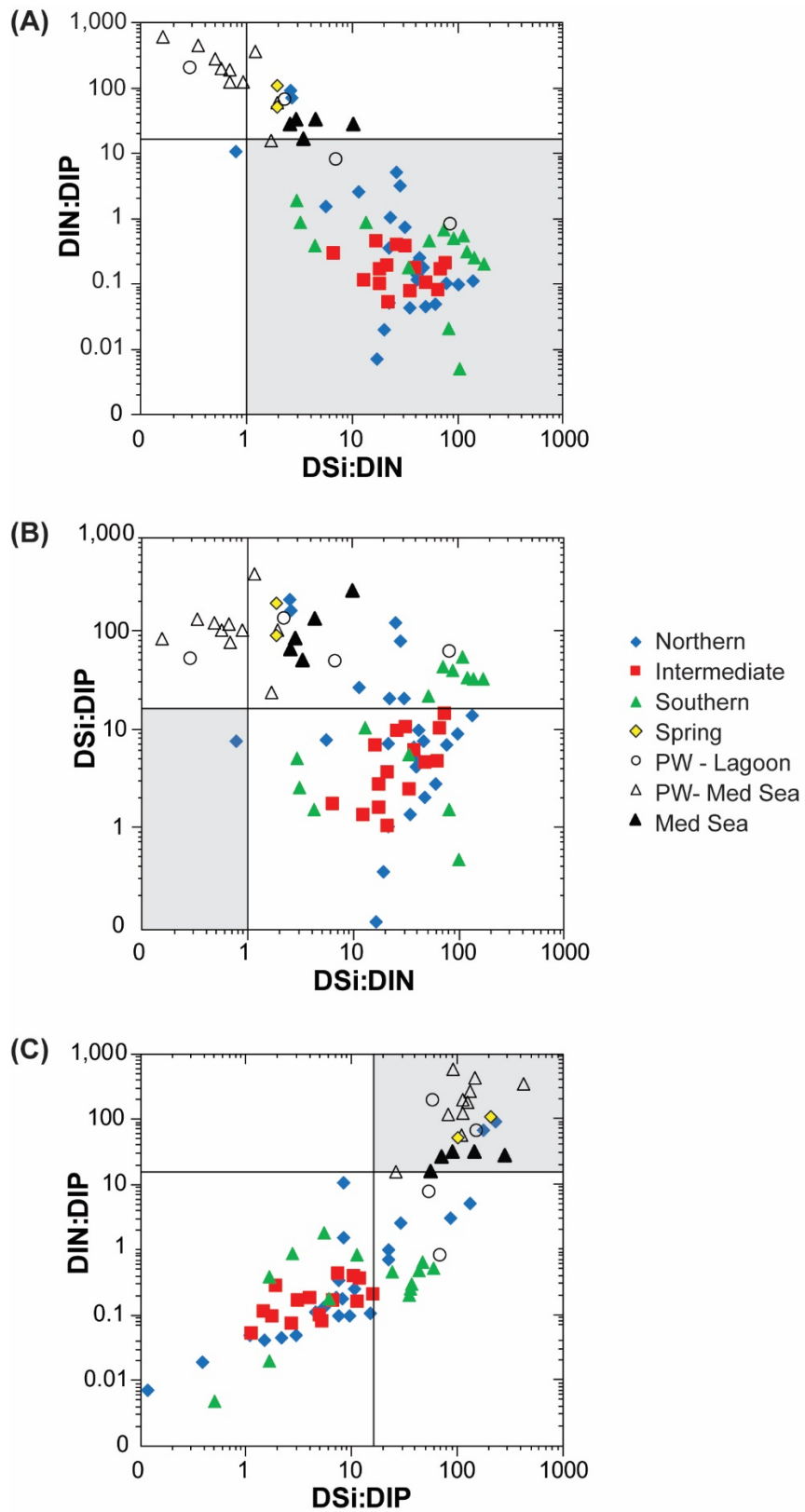


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1116 **Figure 9.** Lagoon surface water $^{224}\text{Ra}_{\text{ex}}/^{223}\text{Ra}$ (A) and $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ (B) activity ratios as a
 1117 function of distance from the groundwater spring, during June 2016. Distances were measured
 1118 using high resolution visible light imagery in Google Earth and assume a 10% measurement
 1119 uncertainty. Shallow pore water endmember activity ratios (20 – 40 cm depth) are indicated by
 1120 hollow circles (June 2016). The approximate interface between the northern and intermediate
 1121 basin is indicated by a blue dashed line, and between the intermediate and southern basin by a
 1122 red dashed line.

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1125 **Figure 10.** Stoichiometric ratios of DIN:DIP, DSi:DIN and DSi:DIP. Nutrient limitation is
 1126 indicated by a shaded gray box for DIN (A), DSi (B) and DIP (C).