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1 Dissolved neodymium isotopes in the Mediterranean Sea

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24 25 26 **Abstract**

27 The neodymium isotopic composition (ϵ_{Nd}) of seawater is one of the most important geochemical
28 tracers to investigate water mass provenance, which can also serve as a proxy to reconstruct past
29 variations in ocean circulation. Nd isotopes have recently also been used to reconstruct past
30 circulation changes in the Mediterranean Sea on different time scales. However, the modern seawater
31 ϵ_{Nd} dataset for the Mediterranean Sea, which these reconstructions are based on, is limited and up to
32 now only 160 isotopic measurements are available for the entire basin. The lack of present-day data
33 also limits our understanding of the processes controlling the Nd cycle and Nd isotopic distribution
34 in this semi-enclosed basin. Here we present new ϵ_{Nd} data from 24 depth profiles covering all
35 Mediterranean sub-basins, which significantly increases the available dataset in the Mediterranean
36 Sea. The main goal of our study is to better characterize the relationship between the dissolved Nd
37 isotope distributions and major water masses in the Mediterranean Sea and to investigate the impact
38 and relative importance of local non-conservative modifications, which include input of riverine
39 particles and waters, aeolian-derived material and exchange with the sediments at continental
40 margins. This comprehensive ϵ_{Nd} data set reveals a clear ϵ_{Nd} – salinity correlation and a zonal and

41 depth gradient with ϵ_{Nd} systematically increasing from the western to the eastern Mediterranean basin
42 (average $\epsilon_{Nd} = -8.8 \pm 0.8$ and -6.7 ± 1 for the entire water column, respectively), reflecting the large-
43 scale basin circulation. We have evaluated the conservative ϵ_{Nd} behaviour in the Mediterranean Sea
44 and quantified the non-conservative components of the ϵ_{Nd} signatures by applying an Optimum
45 Multiparameter (OMP) analysis and results from the Parametric Optimum Multiparameter (POMP)
46 analysis of Jullion et al. (2017). The results of the present study combined with previously published
47 Nd isotope values indicate that dissolved ϵ_{Nd} behaves overall conservatively in the open
48 Mediterranean Sea and show that its water masses are clearly distinguishable by their Nd isotope
49 signature. However, misfits between measured and OMP- and POMP-derived ϵ_{Nd} values exist in
50 almost all sub-basins, especially in the eastern Levantine Basin and Alboran Sea at intermediate-deep
51 depths, which can be explained by the influence of detrital lithogenic ϵ_{Nd} signatures through
52 interaction with highly radiogenic Nile sourced volcanic fractions and unradiogenic sediments,
53 respectively.

54 The radiogenic signature acquired in the eastern Levantine Basin is carried by the Levantine
55 Intermediate Water and transferred conservatively to the entire Mediterranean at intermediate depths.
56 Our measured ϵ_{Nd} values and OMP- and POMP-derived results indicate that non-conservative
57 contributions originating from sediment sources are then propagated by water mass circulation (with
58 distinct preformed ϵ_{Nd}) along the Mediterranean Sea through advection and conservative mixing.
59 Mediterranean ϵ_{Nd} effectively traces the mixing between the different water masses in this semi-
60 enclosed basin and is a suitable water mass tracer.

61

62 **Keywords:** neodymium isotopes, seawater, Mediterranean Sea

63

64 **1. Introduction**

65 The Mediterranean Sea is a semi-enclosed and highly evaporative basin that is connected with the
66 Atlantic Ocean through the Strait of Gibraltar (sill depth ~ 300 m) and with the Black Sea through
67 the Strait of Dardanelles (sill depth ~ 100 m) and the Bosphorus Strait (sill depth ~ 65 m). The Atlantic
68 water that enters the Mediterranean Sea spreads throughout the entire basin and participates in the
69 formation of intermediate and deep waters that contribute to the Mediterranean thermohaline
70 circulation (Millot and Taupier-Letage, 2005). This vigorous basin-wide overturning cell is

71 characterized by a rapid mixing time of 75 to 150 years (Roether et al., 1996; Roether and Well, 2001)
72 and is mainly driven by internal advection of salt and heat, freshwater exchange, deep convection and
73 the external atmospheric forcing (Schroeder et al., 2012; Tanhua et al., 2013). The Mediterranean
74 thermohaline circulation exhibits large seasonal and interannual variations and its variability in the
75 past has been linked to major environmental changes that strongly modified the deep hydrology and
76 heavily affected the marine ecosystems of the Mediterranean basin, which includes episodes of deep-
77 sea oxygen starvation that led to the deposition of sapropels (Rohling et al., 2015). The reconstruction
78 of past variations in ocean circulation requires fingerprinting the different water masses to track their
79 origin and determine their relative exchange through time. One of the most useful tracers to
80 investigate water mass provenance is the dissolved neodymium (Nd) isotopic composition of
81 seawater (expressed as $\epsilon_{Nd} = \left(\frac{^{143}\text{Nd}/^{144}\text{Nd}}{^{143}\text{Nd}/^{144}\text{Nd}}_{\text{CHUR}} - 1 \right) \times 10^4$, where CHUR stands
82 for Chondritic Uniform Reservoir, an estimate of the average value of the Earth), which is considered
83 a direct water mass tracer as it “fingerprints” the different water masses as isotopically distinct entities
84 and its changes in the open ocean are mainly attributed to water mass mixing (e.g. Piepgras et al.,
85 1979; Albarede and Goldstein, 1992; Tachikawa et al., 2017).

86 The seawater ϵ_{Nd} signature is preserved in several natural archives, including Fe-Mn crusts (Frank et
87 al., 2002), to (e.g. Rutberg et al., 2000), foraminifera (e.g. Klevenz et al., 2008; Vance and Burton,
88 1999), cold-water corals (Copard et al., 2010; van de Flierdt et al., 2010; Montagna and Taviani,
89 2019) and fish teeth (Martin and Haley, 2000) and it has been widely employed in paleoceanographic
90 studies (Frank, 2002). This powerful tracer has also been used to reconstruct past circulation changes
91 in the Mediterranean Sea on different time scales (Osborne et al., 2010; Jiménez-Espejo et al., 2015;
92 Dubois-Dauphin et al., 2016, 2017a; Cornuault et al., 2018; Wu et al., 2019; Duhamel et al., 2020).

93 The seawater ϵ_{Nd} signature originates from the continental Nd supply through weathering of
94 surrounding source rocks of different ages (Goldstein and Hemming, 2003) and mainly reflects lateral
95 water mass advection and mixing. However, the use of ϵ_{Nd} as a water mass tracer is challenged by
96 non-conservative modifications that can impact its “quasi-conservative” behaviour, which includes
97 input of riverine particles and waters, aeolian-derived material, benthic fluxes of Nd, submarine
98 groundwater discharge and exchange with the sediments at continental margins (e.g. Frank, 2002;
99 Goldstein and Hemming, 2003; Lacan and Jeandel, 2005; Johannesson and Burdige, 2007; Abbott et
100 al., 2015; Morrison et al., 2019). This has been observed in several regions of the global ocean,
101 especially close to the continental margins, where seawater ϵ_{Nd} does not co-vary with other
102 conservative hydrographic parameters, such as salinity and temperature (e.g. Grenier et al., 2013;

103 Stichel et al., 2015). The exchange between seawater and the sediments deposited on the continental
104 margins has been termed “boundary exchange” (BE) and results in a modification of seawater ϵ_{Nd}
105 without a net change in Nd concentration [Nd] (Lacan and Jeandel, 2005; Arsouze et al., 2007),
106 although recent studies have shown that sediment-water interactions can affect [Nd] (Abbott, 2019).
107 Local overprints from different Nd sources may strongly limit the use of ϵ_{Nd} as a conservative tracer
108 for oceanographic and paleoceanographic studies but can also provide additional information on
109 modern and past changes in ocean circulation. This can be especially the case in marginal and semi-
110 enclosed basins, such as the Mediterranean Sea, where the local influence of different Nd sources
111 may strongly modify the original ϵ_{Nd} signature of the water masses. Previous studies on the Nd budget
112 of the Mediterranean Sea have documented higher Nd concentrations and more radiogenic ϵ_{Nd} values
113 in most of the basin than in the surface Atlantic water entering through the Strait of Gibraltar, which
114 reflects sources of radiogenic Nd within the basin (Spivack and Wasserburg, 1988; Henry et al., 1994;
115 Tachikawa et al., 2004; Garcia-Solsona and Jeandel, 2020). In particular, the Atlantic Inflow shows
116 [Nd] < 20 pmol/kg and ϵ_{Nd} < -10, whereas the Mediterranean seawater has [Nd] > 20 pmol/kg and
117 ϵ_{Nd} values generally > -10.5, with the eastern basin showing a more radiogenic signature (i.e. higher
118 ϵ_{Nd} values) compared to the western basin (~ -9 vs. -7) (Censi et al., 2004; Tachikawa et al., 2004;
119 Garcia-Solsona and Jeandel, 2020). Results based on a high-resolution regional oceanic model also
120 indicate a strong E-W ϵ_{Nd} gradient and the importance of the BE process in controlling the Nd cycle
121 in the Mediterranean Sea (Ayache et al., 2016). However, our knowledge on the present-day seawater
122 ϵ_{Nd} distribution in the Mediterranean Sea is still fragmentary with only about 160 ϵ_{Nd} measurements
123 available for the entire basin. This strongly limits our understanding of the processes and sources that
124 control seawater Nd cycling in the Mediterranean and restricts the interpretation of ϵ_{Nd} -based
125 paleoceanographic reconstructions in this and other semi-enclosed basins.

126 Here we present dissolved ϵ_{Nd} compositions of 80 new seawater samples that were recovered at 24
127 stations covering different Mediterranean sub-basins, which significantly increases the available data
128 set in the Mediterranean Sea. Combined with published ϵ_{Nd} values the data support that dissolved ϵ_{Nd}
129 behaves overall conservatively in the open Mediterranean Sea and shows that most of the surface and
130 sub-surface water masses can be depicted based on their Nd isotopic composition. A mixing analysis
131 of the water masses has been performed to assess the degree of conservativeness of dissolved ϵ_{Nd}
132 when used as a water mass tracer. This comprehensive ϵ_{Nd} database helps to identify the most relevant

133 mechanisms and external sources driving the Nd isotopic composition of the different Mediterranean
134 water masses including water mass mixing and advection, riverine fluxes, atmospheric deposition
135 and water-sediment exchange along the continental margins in the different sub-basins.

136

137 **2. General hydrography of the Mediterranean Sea**

138 The Mediterranean Sea is characterized by two main basins, the western (WMED) and eastern
139 (EMED) Mediterranean, which are separated by the Sicily Channel (sill depth ~500 m). Since
140 evaporation exceeds precipitation and river runoff, the relatively fresh (salinity ~ 36.5) surface
141 Atlantic Water (AW) entering the Mediterranean Sea across the Strait of Gibraltar at the surface
142 becomes progressively saltier and denser during eastward advection, reaching values of 39.2 in the
143 Cretan Sea (Velaoras et al., 2015). AW salinity also increases by mixing with the surrounding surface
144 and underlying intermediate waters, leading to the gradual modification of this water mass, while it
145 flows along the basin at 50-200 m water depth following a general cyclonic path including several
146 eddies and meanders (Pinardi and Masetti, 2000). Evaporation and mixing together with intense
147 cooling and strong wind-induced heat loss in specific areas in winter (Gulf of Lion, Adriatic Sea,
148 Levantine and Aegean Seas) result in denser waters that sink via convection and form the intermediate
149 and deep waters in the Mediterranean Sea (Pinardi and Masetti, 2000; Schroeder et al., 2012). In
150 particular, the Levantine Intermediate Water (LIW) is formed by intermediate convection in the
151 Cyprus-Rhodes area and it spreads in the EMED and WMED at intermediate depths (~ 200-600 m)
152 (Fig. 1). LIW is the most abundant water mass in the Mediterranean Sea and is identifiable by its
153 subsurface salinity maximum (Lascaratos et al., 1993). It flows westwards generally following a basin
154 scale cyclonic circulation pattern and enters the Adriatic Sea through the Strait of Otranto and the
155 WMED through the Sicily Channel at depths between 200 and 350 m (Ben Ismail et al., 2012). Based
156 on transient tracer data and salinity anomalies, the transport time of LIW from the formation area to
157 the Sicily Channel has been estimated to be between 8 and 13 years (Roether et al., 1998; Gačić et
158 al., 2013). In the Adriatic Sea, LIW is involved in the formation of the Adriatic Deep Water (AdDW)
159 that sinks to the deep EMED and together with the Aegean Deep Water (AeDW) contributes to the
160 formation of the Eastern Mediterranean Deep Water (EMDW). After entering the WMED, the LIW,
161 or the Eastern Intermediate Water as named by Millot (2013), breaks into current segments that flow
162 across the Corsica Strait and the Algeria basin through the Sardinia Channel (Pinardi et al., 2015; Fig.
163 1). During advection in the WMED, LIW is gradually diluted with adjacent water masses thereby
164 becoming less salty and colder (Schroeder et al., 2012). In the Tyrrhenian Sea, the depth of the core
165 of LIW is observed between 350 and 550 m water depth (Wu and Haines, 1996) whereas in the

166 Sardinia Channel it is identified between 250 and 450 m depth (Gana et al., 2015). A fraction of the
167 LIW then flows into the Ligurian Sea and the Provençal basin and its salt content contributes to the
168 Western Mediterranean Deep Water (WMDW) formation in the Gulf of Lion during extreme
169 meteorological conditions in winter (Millot and Taupier-Letage, 2005). Most of the LIW finally exits
170 the Mediterranean through the Strait of Gibraltar as part of the Mediterranean Outflow Water (MOW).
171 The WMDW spreads southward and westward into the Balearic basin and the Tyrrhenian Sea
172 between ~ 2000 and 3000 m depth (Millot, 1999; Schroeder et al. 2012; Fig. 1) and also contributes
173 to MOW (Bryden, 2009). The depth range between ~ 700 and 2000 m in the WMDW is filled by the
174 Tyrrhenian Deep Water (TDW) (Millot et al., 2006), which results from the mixing between WMDW,
175 LIW and the upper part of the EMDW (Sparnocchia et al., 1999). In the WMED, the depth layer
176 between the AW and LIW (i.e. ~ 85-200 m) is occupied by the Winter Intermediate Water (WIW),
177 which is formed by intense cooling and downward mixing of AW (Millot, 1999).

178 3. Materials and methods

179

180 3.1. Seawater sampling

181

182 Seawater samples were collected during the oceanographic cruises Medcor (December 2009),
183 Arcadia (March-April 2010) and Record (November 2013) on the R/V *Urania*, Meteor 84/3 (April
184 2011) on the R/V *Meteor* and MedBlack GEOTRACES 64PE370 (May-June 2013) and 64PE374
185 (July-August 2013) on the R/V *Pelagia* (Fig. 1, Table 1). A total of 80 samples were recovered from
186 24 stations covering all Mediterranean sub-basins using either an ultraclean all-titanium frame CTD
187 rosette system (cruises GEOTRACES 64PE370 and 64PE374; Rijkenberg et al., 2015) or a CTD
188 rosette system equipped with 24 12L Niskin bottles. Four samples (Meteor 309-799m, 64PE374-17-
189 25m, 64PE374-17-1500m and 64PE374-17-2824m) were collected in duplicate to check intra and
190 inter-laboratory analytical reproducibility. At each station, continuous temperature and salinity were
191 obtained from a CTD system SBE19 Sea-Bird Electronics (Table 1). Seawater samples were also
192 collected for dissolved inorganic nutrient measurements. The analytical methods for nutrient
193 determination and results for phosphate and nitrate concentration are reported in Tanhua et al. (2013b),
194 and Tanhua (2013) for Meteor 84/3 cruise, Cruise reports 64PE370 (<http://geotraces.imev-mer.fr/library-88/scientific-publications/cruise-reports/823-ga04>)
195 and 64PE374
196 (<http://geotraces.imev-mer.fr/library-88/scientific-publications/cruise-reports/857-ga04-3>)
197 for MedBlack GEOTRACES cruise. The samples collected during the cruises Medcor, Arcadia and
198 Record were syringe-filtered through Whatmann® GF/F and cellulose acetate Albet® filters (0.45
199 µm), and immediately frozen at -20°C. The concentrations of nitrite, nitrate and phosphate were
200 determined by colorimetric methods using a Bran-Luebbe® autoanalyzer III at the Institute of Marine

201 Sciences (ICM-CSIC) in Barcelona. For the calibration, standards were run along with the samples
202 after every set of 20 samples.

203 All seawater samples for Nd isotopes were filtered on board using AcroPak 500 (0.8–0.45 μ m) capsule
204 filters connected to the spigot of the Niskin bottles through a Tygon tubing into acid-cleaned 5-liter
205 and 20-liter LDPE-collapsible cubitainers. The filters had previously been cleaned with 1N ultra-
206 clean HCl, rinsed with MilliQ water and flushed with seawater prior to sample collection. The same
207 capsule filters were repeatedly used for similar depth ranges (i.e. surface, intermediate and deep).
208 Upon recovery, all the samples from cruises Medcor, Arcadia, Record and Meteor 84/3 were
209 immediately acidified to pH \leq 2 with ultra-clean HCl and mixed with ca. 20 mg of ultra-pure FeCl₃
210 solution for pre-concentration of REEs. After one day of equilibration the samples were treated with
211 NH₄OH (Optima grade) to induce Fe(OH)₃ precipitation by adjusting the pH between 7.5 and 8.5.
212 After precipitation of the Fe and the REEs, the supernatant was siphoned off and the cubitainers were
213 sealed with Parafilm[®] and stored in double plastic bags for further processing in the home
214 laboratories. Samples from cruise 64PE370 and 64PE374 were treated similarly but the entire
215 procedure was conducted in the home laboratory. Seawater sampling followed established protocols
216 for GEOTRACES cruises (Cutter et al., 2010).

217 **3.2 Laboratory procedures**

218 The cubitainers containing the Fe-REEs co-precipitated fraction were transferred to the Lamont-
219 Doherty Earth Observatory (LDEO) of Columbia University (samples from cruises Medcor and
220 Arcadia) and to the Laboratoire GEOsciences Paris-Sud (GEOPS), University of Paris-Saclay
221 (samples from cruises Record and Meteor 84/3, and 17 samples from cruise 64PE374), whereas
222 samples from cruise 64PE370 (and eleven samples from cruise 64PE374) were sent to GEOMAR
223 Helmholtz Centre for Ocean Research in Kiel.

224 At LDEO, the samples were transferred to 250 mL acid-cleaned containers, centrifuged and dissolved
225 in 3N HNO₃. The solutions were then transferred to Teflon beakers, dried down at \sim 120°C and re-
226 dissolved in ultra-clean 1N HNO₃ before loading the samples into 100 μ L columns containing
227 Eichrom RE-resin to separate the rare earth elements (REEs) from the major and trace elements. Nd
228 was subsequently isolated from the other REEs using 0.15M α -HIBA acid and a cation resin (Dowex
229 AG50-X4, 100-200 mesh size). The Nd isotopes were analyzed as Nd-oxide on a VG Sector 54-30
230 thermal ionization mass spectrometer by dynamic multicollection in June 2010. The samples were
231 analysed at ¹⁴⁴Nd¹⁶O signal intensities between 160 and 360 mV for 250-300 ratios using 10¹¹ ohm
232 resistors on the amplifiers. The instrumental mass fractionation was corrected using a ¹⁴⁶Nd/¹⁴⁴Nd
233 value of 0.7219. The external error, calculated as the standard deviation (2 σ) of replicates of the

234 international standard JNdi-1 performed during a 3-days analytical session, was ± 0.000017 (average
235 $^{143}\text{Nd}/^{144}\text{Nd} = 0.512076$, $n=9$). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio for all the samples was corrected for
236 instrumental bias to a JNdi-1 value of 0.512115 (Tanaka et al., 2000) and ϵNd was calculated using
237 a $^{143}\text{Nd}/^{144}\text{Nd}$ CHUR value of 0.512638 (Jacobsen and Wasserburg, 1980). Three procedural blanks
238 were analysed during the processing of the Medcor and Arcadia samples, with Nd concentration
239 ranging between 40 and 70 pg, which represents $< 2\%$ of the typical concentration of the
240 Mediterranean seawater samples (Tachikawa et al., 2004).

241 At GEOPS, the samples were transferred to 50 mL acid-cleaned Falcon tube, centrifuged, dissolved
242 in 3N HNO_3 and transferred into Teflon beakers. After total evaporation, the samples were re-
243 dissolved in 6N HCl and solutions were loaded onto anion exchange columns to remove Fe (AG1-
244 X8 resin, 100-200 μm mesh-size resin). REEs were separated from the matrix using Eichrom TRU-
245 spec resin (100-150 μm mesh-size) and finally Nd was purified using Eichrom Ln-spec resin (100-
246 150 μm mesh-size), following the procedure reported in Copard et al. (2010). The Nd isotopes of the
247 purified fractions were measured on a Thermo Scientific Neptune^{Plus} Multi-Collector Inductively
248 Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Laboratoire des Sciences du Climat et de
249 l'Environnement (LSCE) in Gif-sur-Yvette. For the Nd isotope analyses, sample and standard
250 concentrations were matched at 5 ppb. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for mass-dependent
251 fractionation using a $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (O'Nions et al., 1977) and an exponential law. The La
252 Jolla standard was analysed after every two samples (sample-standard bracketing method). Multiple
253 measurements of La Jolla standard during the analytical sessions yielded average $^{143}\text{Nd}/^{144}\text{Nd}$ values
254 of 0.511844 ± 0.000025 (2σ , $n = 14$). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of all the samples were normalized to
255 the generally accepted La Jolla value of 0.511858 (Lugmair et al., 1983). The internal reproducibility
256 ranged from 0.2 and 0.5 ϵNd units (2σ) and the external reproducibility was 0.5 ϵNd units (2σ).
257 Procedural blanks corresponding to all analytical procedures after preconcentration of Nd from
258 seawater matrix were < 25 pg, which represents $< 1\%$ of the typical concentration of the
259 Mediterranean seawater samples (Tachikawa et al., 2004)

260 At GEOMAR, the Fe-REEs co-precipitated fraction were centrifuged, rinsed with MilliQ water and
261 transferred into Teflon beakers. The samples were dissolved in 6N HCl and dried down at 80°C .
262 Afterwards, the samples were treated with aqua regia to destroy organic components, evaporated to
263 dryness and dissolved in 6N HCl . A back extraction method using a diethyl ether phase was applied
264 (Stichel et al., 2012) to remove the large amounts of Fe while keeping Nd dissolved in the acid phase.
265 Finally, the samples were evaporated again and dissolved in 1N HCl and 0.05N HF . Solutions were
266 loaded onto cation exchange columns (AG50W-X8, 200-400 μm mesh-size resin) to separate Nd

267 from the main matrix. Nd was finally separated from Sm and the other REEs using Eichrom Ln-spec
268 resin (50-100 μm mesh-size), following a slightly modified procedure by Pin and Santos Zalduegui
269 (1997). The Nd isotopes of the purified fractions were analyzed on a Thermo Scientific Neptune^{Plus}
270 MC-ICP-MS matching concentrations of the analysed solutions and standards. The mass fractionation
271 correction for the measured Nd isotopic compositions was carried out using a $^{146}\text{Nd}/^{144}\text{Nd}$ to 0.7219
272 (O’Nions et al., 1977) and applying an exponential fractionation law. The external reproducibility of
273 $^{143}\text{Nd}/^{144}\text{Nd}$ measurements was estimated by repeated measurements of JNdi-1 standards (10, 20 and
274 40 ppb) over the course of a measuring session and varied between 0.18 and 0.83 ϵ_{Nd} (2σ). JNdi-1
275 solutions were measured at similar concentration and over a similar integration time as the samples.
276 The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the samples were normalized to the accepted JNdi-1 value of 0.512115
277 (Tanaka et al., 2000). Procedural blanks for Nd isotopes were less than 1% of the sample amounts
278 and were considered negligible.

279 The three laboratories (LDEO, GEOPS and GEOMAR) participated in the international
280 GEOTRACES intercalibration study for Nd isotopes and procedures followed the agreed protocols
281 (van de Flierdt et al., 2012).

282 REE concentrations have been analysed only on a subset of the samples, since most of them had been
283 entirely consumed for the ϵ_{Nd} analyses. In particular, aliquots of seawater samples were collected for
284 REE analyses of 18 samples of the Record, Meteor 84/3 and GEOTRACES 64PE370 cruises (Table
285 1). The Record and Meteor 84/3 samples were processed at GEOPS following the method by Yu et
286 al. (2017). Briefly, an ultra-pure FeCl_3 solution and a spike solution enriched in ^{141}Pr and ^{169}Tm were
287 added to each sample (~ 125 ml filtered seawater), with contents around 10-50 fold higher than REE
288 concentration in the samples. After 48h of equilibration, the pH was adjusted to ~ 8 through the
289 addition of ultraclean NH_4OH (Optima grade), leading to the formation of iron hydroxides, which in
290 turn, efficiently scavenge REEs out of the seawater samples. The REE co-precipitated fractions were
291 separated from the remaining solution through several centrifugations and MilliQ water rinsing, re-
292 dissolved in ultra-clean 3N HNO_3 and evaporated to dryness. The dried samples were re-dissolved in
293 2 ml ultra-clean 8N HNO_3 and 50 μl HF to remove any possible hydrated silica residues precipitated
294 during the Fe co-precipitation step. After drying, REEs were separated from the matrix through anion
295 exchange columns (AG1-X8 resin, mesh 100-200). The solutions were analysed using a Thermo
296 Scientific Element XR High-Resolution ICP-MS hosted at GEOPS. The added ^{141}Pr and ^{169}Tm spikes
297 allowed the calculation of the REE extraction step recovery (~ 70 -100%) and finally REE
298 concentrations by taking into account the initial Pr and Tm content in the samples. Internal REE and
299 seawater standards and BCR-1 standard solutions were analysed to monitor instrument drift.

300 The GEOTRACES 64PE370 samples were analysed at GEOMAR following Stichel et al. (2012),
301 which is in accordance with accepted GEOTRACES protocols outlined in van de Flierdt et al. (2012).

302

303 **3.3 Optimum Multiparameter Analysis**

304 An Optimum Multiparameter (OMP) analysis (Tomczak and Large, 1989; Hainbucher et al., 2013)
305 has been applied to a subsample of the dataset shown in Table S1, to estimate the water mass fractions
306 in each water sample. In particular, we used the temperature and salinity values collected during
307 cruises since 2009 (e.g. Medcor in 2009, Arcadia in 2010, Meteor 84/3 in 2011, Record in 2013,
308 MedBlack GEOTRACES 64PE370 and 64PE374 in 2013, Dubois-Dauphin et al., 2017, Garcia-
309 Solsona and Jeandel, 2020 and Garcia-Solsona et al., 2020) to avoid as much as possible the temporal
310 differences in temperature and salinity related to the climate-induced warming and salinification of
311 the Mediterranean Sea. This analysis is based on the assumption that mixing is a linear process that
312 affects temperature and salinity (as well as other seawater properties) in the same way. The analysis
313 allows to estimate the contributions of (m) water types (WTs) to each water sample, by solving a
314 system of (m+1) linear mixing equations, with one equation for each seawater property and a mass
315 conservation equation. The best mixing solution is found by minimizing the residuals for all
316 parameters and in a non-negative least squares sense.

317 In the present study, the Mediterranean has been divided into 2 sub-basins, the Eastern Mediterranean
318 and the Western Mediterranean Sea, to minimize the effect of the substantial differences in water
319 masses properties between the two basins. In each sub-basin three WTs were defined by the average
320 values of θ and S (Table S2) extracted from the decadal climatology (2006-2015) by Iona et al. (2018).
321 This approach has been chosen, given that the OMP will be applied to data collected during different
322 cruises and covering different years. For the WMED, the Atlantic Water (AW) WT was defined in
323 the Gibraltar-Alboran region (where the “pure” AW inflows), the Intermediate Water (IW) WT was
324 defined in the Sicily Channel (where the inflow of IW into the WMED occurs), while the Deep Water
325 (DW) WT was defined offshore the Gulf of Lion region (where the DW of the WMED starts
326 spreading through the basin, after it has been formed by open ocean convection and cascading of
327 dense shelf waters). For the EMED, the AW-WT has been defined in the Sicily Channel (where the
328 inflow of AW into the EMED occurs), the IW-WT has been defined in the Levantine sub-basin (where
329 the IW starts spreading through the EMED, after it has been formed by open ocean convection), and
330 the DW-WT has been defined at the exit of the Adriatic Sea (where the DW starts spreading through
331 the EMED, after it has been formed by open ocean convection and cascading of dense shelf waters).

332 The set of mixing equations to solve is $A \times X = N$, where A is the (3×3) matrix with the WT
333 properties, X is the $(3 \times n)$ matrix with the WT fractions, N is the $(3 \times n)$ matrix with the measured
334 θ and S properties, n being the number of samples. The linear equations are normalized and weighted.
335 The normalization is done using the mean and standard deviation values for the three parameters in
336 the WT matrix. Equations are weighted, considering the standard deviation of each parameter in the
337 WT matrix and its uncertainty when estimating it. Weights of 10, 10 and 50 were assigned to θ , S and
338 mass, respectively. All samples are thus considered as composed by these three WTs, with
339 percentages that vary horizontally and vertically. The approach of using the basic OMP with θ and S
340 only has certain limitations in complex basins as the Mediterranean Sea as a whole, with intense and
341 regionally varying ocean-atmosphere interactions. The fact that the samples have been collected
342 during different cruises and over a certain number of years (during which T and S are known to have
343 changed, not because of different mixing fractions, but because of climate-induced warming and
344 salinification of the Mediterranean water masses, e.g. Schroeder et al., 2017) place further limitations
345 on the use of the OMP analysis. Indeed, the inclusion of additional source water types would be
346 required to increase the degree of accuracy of mixing ratios. Beside samples in the surface mixed
347 layer, where the conservativeness assumption does not hold, samples with slight departures of the
348 total fraction percentage associated to tracers values beyond the selected end-members in the θ - S
349 space (e.g., the Levantine Surface Waters and the Cretan Intermediate Waters in the Aegean/Cretan
350 Seas) and samples with questionable mixing ratios by expert judgment due to unresolved physical
351 processes, were intentionally excluded *a priori* from the subsequent analysis.

352 The mixing fractions obtained from the OMP analysis (Table S1; Figs. S1 and S2) have been used to
353 reconstruct the conservative part of the seawater neodymium isotopic composition reflecting the large
354 scale mass distribution in the Mediterranean Sea. The ϵ_{Nd} and $[Nd]$ of the WTs (Supplementary Table
355 S2) used to calculate the conservative mixing were defined by identifying the ϵ_{Nd} and $[Nd]$ values
356 corresponding to the salinity and potential temperature definitions of the WTs. The non-conservative
357 component of ϵ_{Nd} was separated by removing the conservative component from the observations.

358 We also decided to estimate the non-conservative component of ϵ_{Nd} from the water mass fractions
359 derived from the Parametric Optimum Multiparameter (POMP) analysis of Jullion et al. (2017) based
360 on conservative (potential temperature and salinity) and quasi-conservative ($NO = 9NO_3 + O_2$ and
361 $PO = 170PO_4 + O_2$) variables, acquired during the M84/3 cruise (Tahnua et al., 2013b). Jullion et al.
362 (2017) defined 4 WTs (or source waters) for both WMED and EMED and their θ - S - PO - NO properties
363 were used as input parameters for the POMP model (Table S3). Similarly to the OMP analysis

364 performed in the present study, the conservative ϵ_{Nd} was calculated using the POMP-derived mixing
365 fractions and the ϵ_{Nd} and [Nd] of the WTs (Table S3).

366

367 **4. Results**

368

369 **4.1 Spatial distribution of measured ϵ_{Nd} values**

370

371 Results of the dissolved Nd isotopic composition and [Nd] of the seawater samples analysed in the
372 present study are reported in Table 1 and Figures 2, 3 and 4. Table 1 also shows the main physico-
373 chemical parameters (potential temperature, salinity, potential density, phosphate and nitrate
374 concentrations) at the sampling locations. The figures and Table S1 combine the ϵ_{Nd} values obtained
375 in the present study and sourced from previous publications (Dubois-Dauphin et al., 2017b; Garcia-
376 Solsona et al., 2020; Garcia-Solsona and Jeandel, 2020; Henry et al., 1994; Spivack and Wasserburg,
377 1988; Tachikawa et al., 2004; Vance et al., 2004). Note that samples from station C (1270 m), MST-
378 1 (1500 m) and MNT-1 (120 m) from Tachikawa et al. (2004) have been excluded due to
379 contamination by lithogenic material, as reported by the authors.

380 Two full replicates of sample Meteor 309, collected with two different Niskin bottles at 799 m water
381 depth in the Ionian Sea and analysed at GEOPS, gave identical ϵ_{Nd} values (Table 1). Inter-laboratory
382 reproducibility was tested on samples 64PE374-17 (25 m), 64PE374-17 (1500 m) and 64PE374-17
383 (2824 m), which were collected in duplicate in the Balearic Sea and analysed at GEOPS and
384 GEOMAR. Samples 64PE374-17 (25 m) and 64PE374-17 (1500 m) gave consistent ϵ_{Nd} values within
385 analytical uncertainty, whereas ϵ_{Nd} value for sample 64PE374-17 (2824 m) analysed at GEOMAR (-
386 7.78) was slightly higher than that obtained at GEOPS (-8.73). However, the two values overlap when
387 the external error (2σ SD) is considered.

388 On the θ -S- ϵ_{Nd} diagram in Figure 2 the end-member compositions of the five main water masses
389 prevailing in the WMED and EMED and their Nd isotope composition are defined: the relatively
390 fresh, warm and unradiogenic AW prevailing at the surface, and the more saline and more radiogenic
391 WIW, WMDW, LIW, and EMDW.

392 The ϵ_{Nd} values obtained in the present study range from -9.75 ± 0.33 at 60 m water depth in the Sicily
393 Channel (Medcor 20) to -5.21 ± 0.21 at 150 m water depth in the southern Aegean Sea (64PE370-28),
394 with the most and least radiogenic values generally corresponding to high and low salinity water

395 masses, respectively (Table 1). The ϵ_{Nd} – salinity relationship is even more evident when combining
396 our results with previously published values (Figures 2 and 3). All samples (except MNT-1 in the
397 northern Aegean Sea at 20 m water depth and 64PE370-10 in the Algerian basin at 25 m water depth),
398 with ϵ_{Nd} values more radiogenic than -7, are characterized by salinities higher than 38.7 (Figures 2
399 and 3). The values outside the salinity – ϵ_{Nd} mixing envelopes ($n = 31$, which represents 13% of the
400 total number; Figure 3) mostly correspond to samples collected at depths shallower than 150 m (68%),
401 with 39% of these samples occurring in the uppermost 50 m of the water column and 32% in depths
402 below 150 m.

403 Overall, the data display a clear ϵ_{Nd} – salinity correlation and a zonal gradient with ϵ_{Nd} systematically
404 increasing from the western to the eastern Mediterranean basin (average $\epsilon_{Nd} = -8.81 \pm 0.79$ and -
405 6.65 ± 1.02 for the entire water column, respectively) (Figures 3, 4 and 5). In particular, ϵ_{Nd} values
406 higher than -7 are only found in the EMED (with the exception of station 64PE370-10 in the Algerian
407 basin at 25 m) and values higher than -6 only occur in the Levantine basin east of 25°E and in the
408 Aegean Sea (Figure 3). This zonal gradient is particularly evident in the surface layer where AW
409 prevails. The surface waters in the western, central and part of the eastern Mediterranean are
410 characterized by unradiogenic ϵ_{Nd} values (between -10.8 to -7.8), whereas in the eastern Levantine
411 basin and the Aegean Sea the values are more radiogenic (between -7.3 to -4.2) (Figures 5 and 6).

412 The neodymium isotopic composition of the Mediterranean waters generally becomes more
413 radiogenic with depth and shows the highest values for intermediate waters, notably in the eastern
414 basin. The observed W-E and depth gradient reflects the general circulation pattern of the
415 Mediterranean Sea, with the fresh (salinity < 36.5) and unradiogenic (ϵ_{Nd} -11.8; Spivack and
416 Wasserburg, 1988) AW entering across the Strait of Gibraltar, mixing along the basin with more
417 saline and radiogenic surrounding surface and underlying intermediate waters and flowing and
418 meandering eastward at 50-200 m water depth as AW (Figure 6). The surface salinity increases from
419 ~ 36.5 in the Alboran Sea to ~ 39 in the eastern Levantine basin (Figures 2, 3 and 5). In the Cyprus-
420 Rhodes area the surface water sinks via intermediate convection and forms LIW that is characterized
421 by a salinity of 39.19 and a potential temperature of 16.39°C, resulting in a density of 28.9 kg/m³ and
422 ϵ_{Nd} signature of -6.40 ± 0.50 at 250 m water depth at station Meteor-294 (Table 1). LIW spreads
423 throughout the Mediterranean Sea as an alongslope current circulating counterclockwise and it is
424 involved in the formation of the Aegean Deep Water (AeDW), Adriatic Deep Water AdDW and
425 Western Mediterranean Deep Water (WMDW) (Figures 1 and 6). LIW advection is very rapid and

426 the transport time from the formation area to the Sicily Channel is on the order of 8-13 years (Gačić
427 et al., 2013; Roether et al., 1998). The ϵ_{Nd} signature of LIW varies from -4.8 ± 0.2 in the eastern
428 Levantine basin at 227 m depth (station 74 from Tachikawa et al., 2004) to -8.94 ± 0.26 in the western
429 basin at 250 m water depth (station 20 from Garcia-Solsona and Jeandel, 2020). This shows that the
430 tongue of radiogenic LIW is progressively diluted westwards but reaches the Alboran Sea and is part
431 of the Mediterranean Outflow at the Strait of Gibraltar. The ϵ_{Nd} distribution along the W-E section
432 matches very well the salinity pattern and closely follows the isohalines (Figure 5). However, in the
433 eastern Levantine basin, the water masses generally display highly radiogenic values (> -6.5) that are
434 associated with relatively low salinity (< 39) (Figures 3 and 5), hence not matching the isohalines in
435 this region. Similarly, the highly unradiogenic values between 800 and 1000 m (< -8.9) in the Alboran
436 Sea also do not follow the isohalines.

437 The W-E sections of potential temperature, salinity and ϵ_{Nd} (Figure 5) show the tongue of Adriatic
438 Deep Water (AdDW) that is advected south in the deep Ionian Sea below ~ 2500 m water depth and
439 becomes a major component of the EMDW (stations Meteor-306 and Meteor-307; stations 1 and 2
440 from Garcia-Solsona et al., 2020). These stations are located in the path of AdDW that brings colder,
441 less salty, better ventilated, and less radiogenic water into the deep eastern Mediterranean Sea.

442 Overall, the ϵ_{Nd} values for the different Mediterranean sub-basins, except the Aegean Sea, gradually
443 become more radiogenic from the surface to intermediate and deep waters (Figures 4, 5 and 6).

444 The mean ϵ_{Nd} values of the water masses flowing in the different Mediterranean sub-basins are
445 reported in Table 2. The surface water masses prevailing in the Alboran Sea above 110 m water depth
446 shows the least radiogenic values (-9.95 ± 0.71), whereas the most radiogenic values are found in the
447 surface (< 50 m) and intermediate (160-500 m) waters of the easternmost Levantine basin (-5.27 ± 0.96
448 and -5.58 ± 0.66 , respectively). The largest depth gradient of more than 2 ϵ_{Nd} units difference between
449 the surface water (60-75 m) and the intermediate (300-647 m) and deep (1020-1692 m) waters is
450 observed in the Sicily Channel (stations Medcor 20 and 37; station 3 from Garcia-Solsona et al.,
451 2020). The smallest depth gradient occurs in the southern Adriatic Sea where the difference between
452 the ϵ_{Nd} values for the surface, intermediate and deep waters is within the analytical uncertainty
453 (station Arcadia 50).

454 The property-property plots of ϵ_{Nd} vs. salinity, potential temperature and dissolved phosphate
455 concentration at water depth above 200 m, between 200 and 500 m (LIW), between 500 and 2000 m
456 and below 2000 m are shown in figure 7. The Nd isotope compositions of the water masses above

457 200 m show significant correlation only with salinity ($R^2 = 0.46$), whereas the ϵ_{Nd} values of the water
458 masses below 200 m display highly significant linear correlations with salinity, potential temperature
459 and dissolved phosphate concentration (Figure 7), which reflects mixing of water masses with distinct
460 ϵ_{Nd} values. However, despite the high correlations, the deviations from conservative mixing are large,
461 with values up to 2 ϵ_{Nd} units, which is consistent with previous studies (Lacan and Jeandel, 2005;
462 Abbott et al., 2015; Du et al., 2016). The three oceanographic parameters show a continuous change
463 along a W-E gradient, with the salinity and potential temperature increasing towards the eastern basin
464 and phosphate concentration decreasing along the gradient. This is consistent with the presence of
465 saltier, warmer and more oligotrophic waters in the EMED than in the WMED (Tanhua et al., 2013a)
466 and their mixing.

467 One seawater sample was collected at 3552 m depth at station Meteor-301 in the deep hypersaline
468 brine of the Urania basin (west of the Crete Island). This sample shows a less radiogenic Nd isotopic
469 signature ($\epsilon_{Nd} = -8.40$) than the other deep samples in the eastern basin (~ -7 ; Figure 6), likely
470 reflecting the admixture of the brine that originates from the dissolution of Messinian evaporites (e.g.
471 Cita, 2006).

472 The Nd concentrations of the seawater samples analysed in the present study range from 18.96 and
473 33.73 pmol/kg (Table 1 and S4), which are consistent with values reported in the literature for the
474 Mediterranean Sea (Henry et al., 1994; Spivack and Wasserburg, 1998; Censi et al., 2004; Tachikawa
475 et al., 2004; Vance et al., 2004; Garcia-Solana and Jeandel, 2020; Garcia-Solsona et al., 2020). In
476 particular, the [Nd] values obtained from the station Record 10 in the Sicily Channel are very similar
477 to those reported by Garcia-Solsona et al. (2020) for station 3, with a maximum difference of 1.5
478 pmol/kg at ~ 70 m water depth (Table S1). In addition, the relatively high [Nd] values obtained from
479 sample Meteor-294 at 254 m in the Levantine basin (33.73 pmol/kg) and Meteor-288 at 27 m in the
480 Aegean Sea (32.00 pmol/kg) are similar, within error, to those reported in Tachikawa et al. (2004)
481 for the stations 74 at 202-252 m (33.6 pmol/kg) and MST-1 at 10 m (34.7 pmol/kg).

482 The shale (PAAS)-normalized REE patterns of all the samples are typical of seawater, showing a
483 distinct negative Ce anomaly and an enrichment of heavy REE (HREE) over light REE (LREE)
484 (Figure S3), which is indicative of preferential LREE scavenging by marine particles (e.g. Elderfield,
485 1988). All samples display a very similar pattern shape, however samples Meteor-288 (25 m) and
486 Meteor-294 (254 m) have higher LREE and HREE concentrations, and Meteor-309 (5 m) and Record
487 28 (25 m) show higher LREE concentrations compared to the other samples. The four samples are

488 also characterized by a less pronounced cerium anomaly, with values between 0.49 and 0.52, which
489 is likely indicative of lithogenic input.

490

491 **4.2 OMP- and POMP-derived ϵ_{Nd} values**

492 Figures S1 and S2 show the overall results of the OMP analysis, with the vertical sections of the
493 mixing fractions of the three WTs in each sub-region. The mixing analysis was characterized by small
494 mass residuals (<3%) in the intermediate and deep layer. Fractions of AW as high as 60-70% were
495 calculated for the western and eastern Mediterranean basins at shallower depths. The AW signal is
496 progressively diluted going from the west to the east in both basins, in agreement with the eastward
497 propagation of the Atlantic-sourced water mass from the Strait of Gibraltar to the Levantine basin.
498 Intermediate water values up to 100% and 70-90% were calculated for depths of 254 m in the
499 Levantine basin (Meteor-294) and 200-500 m in the Ionian Sea (Station 2 from Garcia-Solsona et al.,
500 2020), respectively (Figure S2). In the WMED, IW values up to 90% were obtained at 200-700 m in
501 the south and central Tyrrhenian Sea (stations 4, 5, 7, 8 and 9 from Garcia-Solsona et al., 2020;
502 64PE374-13). The DW fractions in the Balearic and Algerian basin below ca. 1000 m and in the
503 Tyrrhenian Sea below ca. 2000 m are higher than 90%. DW values as high as 80% were calculated
504 in the Gulf of Lion below 500 m (Station 20 from Garcia-Solsona and Jeandel, 2020), which is the
505 site where the DW end-member has been defined for the WMED. Finally, DW fractions higher than
506 70% were calculated for the EMED at depths below 500-700 m and higher than 95% in the Ionian
507 Sea at depths below 2500 m.

508 Overall, the OMP-derived fractions for AW, IW and DW correspond to the large-scale circulation
509 pattern of the western and eastern Mediterranean Sea (Figure 1), although there are some
510 inconsistencies, such as the high DW fraction values (> 50%) at relatively shallow depths (100-300
511 m), that are likely the result of the OMP limitations in complex basins such as the Mediterranean Sea
512 and the fact that samples have been collected during different cruises and over a number of years.
513 The inclusion of additional source water type end-members would likely increase the degree of
514 accuracy of mixing ratios.

515 Figures 8 and 9 show the measured vs. OMP-derived (predicted) ϵ_{Nd} values for the WMED and
516 EMED, respectively. The mean difference is very close to zero for both basins and residual values
517 show a Gaussian type distribution, with the largest differences being 1.5-2 ϵ_{Nd} (inset in figures 8 and
518 9). About 75% and 55% of the OMP-derived ϵ_{Nd} values of the WMED and EMED fall inside the

519 band formed by the 1:1 slope ± 0.5 epsilon units. The size of the band is based on the maximum 2σ
520 external reproducibility of the $^{143}\text{Nd}/^{144}\text{Nd}$ measurements at GEOPS. However, if we consider the
521 highest 2σ uncertainty from GEOMAR (i.e. $0.83 \epsilon_{\text{Nd}}$), the percentage of values increases to 88% and
522 77% for WMED and EMED, respectively. Both basins show positive and negative anomalies (Figures
523 8 and 9). In particular, 7 samples from the Balearic Sea (64PE374-17; Stations 20 and 22 from Garcia-
524 Solsona and Jeandel, 2020), 1 from the Alboran Sea (Station BR-I from Dubois-Dauphin et al.
525 2017b), 4 from the Ionian Sea (Meteor-309) and the Aegean Sea (64PE370-28 and 64PE370-31) and
526 1 sample from the Levantine basin (Meteor-294) have a more radiogenic ϵ_{Nd} signature than expected
527 from the OMP analysis. Conversely, 6 samples from the Tyrrhenian Sea (Stations 7 and 8 from
528 Garcia-Solsona et al., 2020; 64PE374-13 and 64PE374-15), 2 from the Alboran Sea (Stations BR-I
529 and OMS from Dubois-Dauphin et al. 2017b), 2 from the Balearic Sea (Station 22 from Garcia-
530 Solsona and Jeandel, 2020; 64PE374-17), 2 from the Sicily Channel (Medcor 37), 5 from the Ionian
531 Sea (Stations 1 and 2 from Garcia-Solsona et al., 2020) and 1 sample from the Adriatic Sea (64PE374-
532 8) have lower ϵ_{Nd} values than predicted (Figures 8 and 9).

533 Figure 5 shows the comparison between the measured and the POMP-derived ϵ_{Nd} values along a W-
534 E transect from the Strait of Gibraltar to the Levantine Basin. Overall, the two longitudinal sections
535 show comparable values for the different sub-basins, which suggests a strong control of the water
536 mass mixing over the large-scale Mediterranean seawater Nd isotopic composition. The differences
537 between measured and calculated values are mostly within 1 ϵ_{Nd} unit, with the notable exception of
538 the easternmost Levantine Basin and the Alboran Sea, where differences up to 2 units are observed,
539 suggesting local and regional deviations from conservative behaviour. The radiogenic signature of
540 the LIW flowing to the western Mediterranean is clearly visible also in the POMP-derived section,
541 and it seems to propagate more westward in the Alboran Sea compared to the measured values.

542

543 **5. Discussion**

544

545 The present study reports a comprehensive compilation of the dissolved Nd isotopic composition of
546 Mediterranean seawater, based on which a detailed assessment of the factors controlling its
547 distribution is now possible for the entire Mediterranean basin.

548 The ϵ_{Nd} signature closely correlate with both conservative (i.e. salinity and potential temperature) and
549 non-conservative (i.e. nutrients) tracers of water masses at depths > 200 m in the Mediterranean Sea,
550 as already reported for other ocean basins (e.g. Goldstein and Hemming, 2003; Hu et al., 2016;

551 Piotrowski et al., 2008; Dubois-Dauphin et al., 2017b; Tachikawa et al., 2017). This is indicative of
552 water mass mixing along a longitudinal gradient between saltier, warmer and oligotrophic
553 intermediate-deep waters originating from the eastern basin with relatively colder, less saline and
554 nutrient-rich intermediate-deep waters from the western basin, which are characterized by distinct
555 ϵ_{Nd} values. The correlation between ϵ_{Nd} and the water mass properties is significantly weaker for
556 seawater samples shallower than 200 m. In fact, 68% of the values outside the salinity- ϵ_{Nd} mixing
557 lines (Figure 3) correspond to samples collected at depths shallower than 150 m suggesting that
558 salinity in the surface waters of the Mediterranean Sea is not a conservative indicator of water masses,
559 as previously observed by Tachikawa et al., (2004), due to the strong influence of evaporation
560 processes on this oceanographic parameter.

561 Our results, combined with previously published ϵ_{Nd} values, show that the Mediterranean water
562 masses are clearly distinguishable by their Nd isotope signatures.

563 **5.1 Comparison between measured and OMP- and POMP-derived ϵ_{Nd} values**

564 The comparison between measured and OMP and POMP-derived ϵ_{Nd} values allows evaluating to
565 what extent the ϵ_{Nd} reflects conservative water mass mixing in the Mediterranean Sea and quantifying
566 the variability related to non-conservative Nd addition locally and regionally. In general, the
567 measured values are consistent with pure water mass mixing (Figures 5, 8 and 9), which indeed exerts
568 the key control over the general Nd isotope composition in the Mediterranean basin, although
569 deviations exist in almost all sub-basins. Considering also the water mass mixing envelopes in figure
570 3, the regions showing the largest deviations from conservative mixing are the Alboran Sea, the
571 Tyrrhenian Sea, the Ionian Sea, the eastern Levantine Basin and the Aegean Sea. The 1-2 epsilon unit
572 difference between predicted and measured values in the Tyrrhenian and Ionian Sea at shallow and
573 bottom waters is consistent with results of the OMP analysis by Garcia-Solsona et al. (2020).

574 Intermediate and bottom waters in the Alboran Sea deviate from the conservative behaviour and are
575 characterized by less radiogenic ϵ_{Nd} signature than expected from the OMP and POMP analysis
576 (Figure 5 and 8). On the other hand, intermediate and deep water masses (shallower than 1500-2000
577 m) in the eastern Levantine Basin generally exhibit a radiogenic Nd isotope excess (i.e. negative
578 difference between predicted and measured ϵ_{Nd}), which cannot be explained by physical seawater
579 transport. Therefore, additional local and regional processes other than conservative water mass
580 mixing are necessarily involved in modifying the ϵ_{Nd} signature of those water masses. These
581 processes are discussed in chapters 5.3, 5.4 and 5.5.

582 **5.2 Comparison between measured and modelled ϵ_{Nd} values**

583 The new extended ϵ_{Nd} dataset obtained in this study was also compared to the modelled data obtained
584 by Ayache et al. (2016) (Figures 10 and 11). These authors already carried out such comparison in
585 their publication but the dataset of observed ϵ_{Nd} values was limited at that time. The Nd isotopic
586 compositions of the different seawater masses in the Mediterranean Sea were simulated using the
587 high-resolution ($1/12^\circ$) regional oceanic model NEMO-MED12 and taking into account only the
588 boundary exchange process as Nd source while excluding dust and river inputs. The boundary
589 exchange was parameterized by a relaxing equation between the ocean and the continental margin,
590 which considers the ϵ_{Nd} of the seawater and ϵ_{Nd} of the material deposited along the continental margin
591 down to ~ 540 m. The Nd isotopic signature of the margins in the model corresponds to the ϵ_{Nd} values
592 of the surface sediments collected on the shelf or the slope, or the erodible material deposited along
593 the coasts (Supplementary material from Ayache et al., 2016).

594 The modelled ϵ_{Nd} distribution at 25 m water depth displays a clear W-E gradient, with values
595 becoming more radiogenic from the western (~ -9) to the eastern (~ -5) Mediterranean basin, which
596 is consistent with the overall gradient observed in the measured ϵ_{Nd} data (Figures 6 and 10). However,
597 most of the measured values at shallow depths (< 62 m) are $\sim 2-4$ epsilon units less radiogenic than
598 those obtained from the model simulation. The model-data difference for the surface waters is more
599 pronounced in the eastern Mediterranean basin, in particular in the Ionian Sea, Aegean Sea and south
600 of Crete, where modelled surface (25 m) ϵ_{Nd} values are up to 4.5 epsilon units more radiogenic than
601 *in situ* measurements (Figure 10). Significant differences (up to 4.5 epsilon units) are also observed
602 in the Sicily Channel at intermediate depth (Figure 11). Similarly, modelled ϵ_{Nd} values for the LIW
603 are overestimated (i.e. too radiogenic) in the Alboran Sea by 4 epsilon units (Figure 11). The model-
604 data misfit is also observed at deeper depths in the western Mediterranean basin, particularly in the
605 Alboran Sea, Tyrrhenian Sea and Sicily Channel, corresponding to the WMDW, EMDW and TDW,
606 whereas differences close to zero or slightly negative (i.e. measured data are more radiogenic than
607 modelled values) are observed in the central part of the eastern basin at depths below ~ 1000 m and
608 in the eastern Levantine basin along the entire water column (Figure 11).

609 Overall, this indicates that most of the ϵ_{Nd} signature simulated by the regional model of Ayache et al.
610 (2016) at depths shallower than ~ 1000 m are too radiogenic compared to the observations, as also
611 previously acknowledged by the same authors. Ayache et al. (2016) explained the model-data
612 disagreement by the fact that their model only took into account the exchange between the continental

613 margins and seawater as a Nd source, excluding the atmospheric dust and the dissolved river input.
614 A similar mismatch between modelled and measured ϵ_{Nd} data was also observed by Vadsaria et al.
615 (2019), which used a model configuration very similar to Ayache et al. (2016).

616 The large model-data difference in the Alboran Sea (Figure 11) was explained with a low simulated
617 net water input from the Atlantic compared to the observed range, which reduces the advection of
618 unradiogenic surface Atlantic waters ($\epsilon_{Nd} = -11.8$; Spivack and Wasserburg, 1988) in the
619 Mediterranean Sea (Ayache et al., 2016). Following this reasoning, it is possible that the effect of a
620 reduced net water flux likely propagates to the other parts of the Mediterranean Sea and the modelled
621 too radiogenic signature of the surface waters in the eastern basin is partially the result of the reduced
622 advection of unradiogenic waters of Atlantic origin.

623 Ayache et al. (2016) and Vadsaria et al. (2019) noted that the seawater ϵ_{Nd} simulation slightly
624 improved when also including the dust deposition and concluded that the highly radiogenic signatures
625 simulated by the model might be corrected by taking into account all Nd sources and sinks. However,
626 dust inputs only result in significant ϵ_{Nd} deviations in the surface layer of the water column
627 (Tachikawa et al., 1999; Goldstein and Hemming, 2003; Sticher et al., 2015). Consequently the
628 model-data differences for intermediate and deep waters in the Mediterranean Sea, especially in the
629 western basin and in the Sicily Channel (Figure 11), are difficult to explain, even considering a dust
630 contribution in the model. A working hypothesis is that these model-data misfits could be the result
631 of a detrital lithogenic ϵ_{Nd} signature acquired through interaction with sediments at depth (e.g. > 540
632 m), which was not considered in the model by Ayache et al. (2016). The arbitrary choice of restricting
633 BE to the margins shallower than ~ 540 m could in fact be a strong limitation of the model that should
634 be fixed. Moreover, it is also known that the sedimentary ϵ_{Nd} flux is not necessarily equal to the
635 sediment ϵ_{Nd} , as certain reactive sediment phases are likely more important contributors to sediment
636 influence (Wilson et al., 2013; Abbott et al., 2016; Blaser et al., 2016; Du et al., 2016). The sediment
637 flux ϵ_{Nd} map in the model may thus be wrong. Therefore, at present, it is difficult to say whether the
638 model-data misfits are real or reflect inaccurate representation of boundary exchange in the model,
639 which ultimately limits the interpretation of the observed discrepancies.

640 **5.3 Evaluation of African dust input on dissolved ϵ_{Nd} in the eastern and western** 641 **Mediterranean basins**

642 The relative contribution of partial dissolution of Saharan dust to the Mediterranean Sea differs for
643 the different sub-basins and depends on the ϵ_{Nd} composition of potential African source areas for dust

644 production, as identified by Scheuven et al. (2013). These authors compiled a large number of Nd
645 and Sr isotope data from marine sediments, aerosols and soils from the Mediterranean Sea and from
646 6 major preferential source areas of dust generation (PSAs) in northern Africa. These areas represent
647 the world's largest source of mineral dust, accounting for ~ 70% of the global dust budget (Laurent
648 et al., 2008) and are the dominant sediment suppliers to the Mediterranean Sea (Weldeab et al., 2002).
649 The geochemical data by Scheuven et al. (2013) have been recently revised by Blanchet (2019) and
650 made available at <https://doi.org/10.5880/GFZ.4.3.2019.001>. The ϵ_{Nd} values of the soil samples in
651 the eastern part of northern Africa (Egypt) are relatively high (-10.5 to -3.9) and become less
652 radiogenic in the central and western part of northern Africa (Libya: -15.3; Morocco: -13.6) (Figure
653 6; Scheuven et al., 2013), reflecting the geology of the source rocks. This broad E-W geochemical
654 trend has been also identified by Jewell et al. (2021) through the analysis of Sr and Nd isotopes of
655 sediments from dried lakes and river beds in Chad, Morocco, Sudan and Mauritania (Figure 6). The
656 ϵ_{Nd} values of the aerosol samples collected in the Mediterranean Sea vary from -12.1 to -8.2 in the
657 Levantine basin (Frost et al., 1986) and from -14.6 to -10.9 in the Liguro-Balearic and Tyrrhenian
658 basin (Colin, 1993; Grousset et al., 1988). This W-E isotopic gradient towards more radiogenic values
659 in north-eastern Africa is consistent with the longitudinal gradient of the surface waters. Neodymium
660 is released congruently from dust, which is reflected in surface ocean isotopic compositions being
661 very close to those of the dust (Rickli et al., 2010). However, the quantitative contribution of the dust
662 in the Mediterranean Nd cycle is not well constrained but it is generally considered not very
663 significant also given its low fractional solubility and REE mobilization (Greaves et al., 1994;
664 Tachikawa et al., 2004). Our new ϵ_{Nd} values for the surface waters in the WMED and EMED differ
665 significantly from the unradiogenic isotope composition of Saharan dust, confirming the previous
666 findings (Tachikawa et al., 2004). Moreover, the recent study by Garcia-Solsona et al. (2020)
667 concluded that dust inputs cannot explain the negative correlation of light rare earth elements (LREE)
668 concentrations with distance to the closest continental shelf for the Tyrrhenian surface samples, which
669 is instead the result of dissolved LREE released from the continental margin sediments. Therefore,
670 our new ϵ_{Nd} values, combined with previously published data, suggest that the relative importance of
671 dust in modifying the ϵ_{Nd} signature of surface waters in the Mediterranean Sea is very minor.

672 **5.4 ϵ_{Nd} of surface water masses**

673 The distribution of the ϵ_{Nd} signatures in the surface layer follows the mean surface circulation patterns
674 obtained from the reanalysis flow field (Figure 6; Pinardi et al., 2015). The Atlantic Water enters the
675 Strait of Gibraltar with an isotopic signature of -11.8 (Spivack and Wasserburg, 1988) and circulates

676 within the Mediterranean Sea meandering around small and large gyres and cyclonic and anticyclonic
677 eddies. The AW propagates north-eastward and eastward along the Balearic Islands and the Sardinia
678 Channel following the Western Mid-Mediterranean Current and the Southerly Sardinia Current
679 (Pinardi et al., 2015). In the Sardinia Channel the AW splits into two branches, one flowing into the
680 Tyrrhenian Sea and the other entering the Sicily Channel as the Algerian Current. The AW moves
681 eastward along the Cretan passage via the Mid-Mediterranean jet and the Southern Levantine Current
682 until it finally reaches the eastern Levantine basin (Pinardi et al., 2015). AW also enters the Aegean
683 Sea between Crete and Rhodes via the Asia Minor Current and the Adriatic Sea across the Strait of
684 Otranto. The pattern of surface ϵ_{Nd} values displayed in figure 6 closely follows the large-scale basin
685 circulation. The Nd isotopic values become systematically more radiogenic along the W-E and S-N
686 gradients, from the Alboran Sea (-9.95 ± 0.71) to the Balearic and Tyrrhenian Sea (-9.22 ± 0.17 and
687 -9.07 ± 0.45), Sicily Channel (-9.40 ± 0.36), Adriatic Sea (-7.80) and the eastern Levantine basin ($-$
688 5.27 ± 0.96) (Table 2), consistent with the main surface currents and a general cyclonic flowpath with
689 several eddies and meanders. According to our OMP analysis (Figure S2) and results from the
690 multiparameter mixing model by Garcia-Solsona et al. (2020) that considers temperature, salinity and
691 oxygen, the fraction of AW along the Sicily Channel is as high as 70-100% in the uppermost waters,
692 which explains the highly unradiogenic values across the passage between WMED and EMED (e.g.
693 -9.75 ± 0.33 for Station Medcor 20 at 60 m depth and -9.52 ± 0.25 for station 3 at 75 m from Garcia-
694 Solsona et al., 2020). The ϵ_{Nd} difference between the surface water flowing through the Cretan
695 passage (-9.30 ± 0.20) and the eastern Levantine basin (-5.27 ± 0.96) is very large (~ 4 epsilon units)
696 and is the result of a sharp contrast between the unradiogenic AW and a highly radiogenic water mass.
697 The most likely source of this radiogenic signature is the Nile river that supplies highly radiogenic
698 dissolved and particulate Nd to the easternmost Levantine basin (~ -1.2 to -3.25 ; Goldstein et al.,
699 1984; Tachikawa et al., 2004). Partially dissolved Nile river particles rather than river water likely
700 contribute most of the radiogenic Nd to the eastern Mediterranean (Tachikawa et al., 2004). On the
701 global scale, it has been calculated that the dissolution of less than 3% of the riverine particulate load
702 in the water column can account for the “missing” Nd source in the ocean (Jeandel and Oelkers,
703 2015).

704 The north-eastward surface current in the eastern Levantine basin carries and distributes the Nile
705 sediment load along the Egyptian-Israeli margin. Weldeab et al. (2002) analysed the lithogenic
706 surface sediments of the eastern Mediterranean Sea and showed a pronounced E-W gradient in ϵ_{Nd} ,
707 with the easternmost sediment samples off the Israeli coast characterized by the highest values ($\sim -$
708 2.5). Weldeab et al. (2002) also observed a significant decrease in the Nile sediment contribution

709 towards the west. Therefore, it is very likely that the most radiogenic surface seawater samples
710 observed in the Mediterranean Sea north of Egypt acquired their signature from partial dissolution of
711 Nile river particles. This also agrees with previous studies (Piepgras and Wasserburg, 1987; Jones et
712 al., 2008; Siddall et al., 2008; Arsouze et al., 2009) that suggest that the surface water ϵ_{Nd} signature
713 mainly reflects the river input and only to a minor extent atmospheric dust. Low-density hypopycnal
714 plumes originating from the Nile mouth may have played a significant role in enhancing the
715 dispersion of the Nile river particles in the surface layer and hence releasing Nd in the water column
716 during flooding periods (Ducassou et al., 2008), especially prior the completion of the Aswan High
717 Dam in 1964. Considering that the seawater samples in the easternmost Levantine basin were
718 collected in the early 2000s and the residence time of seawater in the eastern Mediterranean Sea is on
719 the order of 60 years, we consider that their Nd isotopic composition at least partly reflects pre-Aswan
720 Dam conditions, when Nile discharge was extensive ($\sim 6 \times 10^{10} \text{ m}^3/\text{yr}$; Béthoux and Gentili, 1996).
721 A recent study has demonstrated the impact of riverine sediment discharge on the Nd isotopic
722 composition of surface and intermediate waters in the Bay of Bengal, supporting a rapid exchange of
723 Nd between riverine particles originating from hypopycnal plumes and seawater (Singh et al., 2012;
724 Yu et al., 2017).

725 The observed surface ϵ_{Nd} values in the easternmost Levantine basin may also be the result of the
726 exchange between the shelf sediments (ϵ_{Nd} up to +6 along the Israeli margin; Ayache et al., 2006)
727 and seawater. In particular, post depositional Nd release driven by sediment diagenesis could play a
728 key role in the Nd cycle (Abbott et al., 2016). However, the locally confined radiogenic values close
729 to the Nile river delta supports the Nile particle load as the main Nd source for the surface waters.
730 The mixing between AW flowing eastwards with local detrital signals from the Nile river particles at
731 shallow depths ultimately results in an average ϵ_{Nd} signature of -5.27 ± 0.96 in the surface waters of
732 the eastern Levantine Basin.

733 **5.5 ϵ_{Nd} of intermediate and deep water masses**

734
735 The surface water of the Levantine basin contributes to the formation of the LIW in the Cyprus-
736 Rhodes area and conveys its highly radiogenic signature derived from the Nile river and its suspend
737 particles to the intermediate depths along the entire Mediterranean basin. The Nd isotopic signature
738 of the LIW then becomes progressively less radiogenic along its westward flowpath (Fig. 6). The
739 high Nd concentration (33.73 pmol/kg) and relatively high Ce/Ce* value (0.50) at station Meteor-294
740 (254 m) are comparable to the surface water samples and indicate an imprint of lithogenic supply
741 (e.g. Solsona et al., 2020). This could be the result of partial dissolution of sinking particles or the

742 advection of lithogenic supplies (BE) to the intermediate water depths south of Cyprus, or a
743 combination of the two processes.

744 The comparison between measured and OMP- and POMP-derived ϵ_{Nd} values in the eastern Levantine
745 Basin reveals a radiogenic Nd isotope excess, in particular for depths shallower than ~ 1500 - 2000 m
746 (Figure 5, 6 and 9), with differences between predicted and measured ϵ_{Nd} values ranging from 0.6 to
747 1.4 epsilon units. The positive non-conservative ϵ_{Nd} signature at intermediate-deep depths most likely
748 reflects the interaction with the reactive components of the Nile sourced detrital sediments, which
749 contain highly radiogenic volcanic fractions ($\epsilon_{Nd} > -4$; Padoan et al., 2011) derived from the
750 weathering of Ethiopian Tertiary basaltic rocks. The eastern Levantine Basin thus offers a high ϵ_{Nd}
751 sedimentary source that contributes (e.g. via benthic fluxes of pore water Nd; Abbott et al., 2016) to
752 the non-conservative ϵ_{Nd} signature of the intermediate-deep waters ($< \sim 1500$ - 2000 m) in this region.
753 This non-conservative radiogenic component is then advected laterally and vertically along the
754 Mediterranean Sea, most likely through sinking particles. However, the measured values from bottom
755 water samples for stations 74 at 2257 m (Tachikawa et al., 2004) and GeoB 7709-1 at 1080 m (Vance
756 et al., 2004) in the easternmost Levantine basin, which represent the EMDW, have an isotopic
757 composition that is up to 4 epsilon units lower than the lithogenic surface sediment below (Figure
758 12), as also observed by Tachikawa et al. (2004). This likely indicates that either the interaction with
759 the sediment is not strong enough to substantially modify (overprint) the water ϵ_{Nd} signature in this
760 region at deeper depths, or BE is still a significant process even in the deep eastern Mediterranean
761 Sea but the residence time of the bottom waters in contact with the highly radiogenic sediments is
762 short enough to prevent a full sediment-water isotopic equilibration (i.e. short benthic exposure time
763 relative to circulation timescales).

764 The EMDW is formed primarily by the AdDW ($\epsilon_{Nd} \sim -7$) and flows eastward (Figure 1) without
765 changing its Nd isotopic composition significantly (Figure 6), even though it is in contact with highly
766 radiogenic sediments in the easternmost Levantine basin that might modify its signature. The non-
767 conservative component for waters deeper than ~ 1500 - 2000 m in this region is minor, with the
768 difference between measured and POMP-derived ϵ_{Nd} values being lower than 0.5 epsilon units
769 (Figure 5). Overall, this indicates that water mass mixing plays a major role in controlling the Nd
770 isotopic composition of the bottom water in the Levantine basin (Figure 6), with minor sedimentary
771 modification along the circulation pathway.

772 The strong negative non-conservative ϵ_{Nd} fraction in the Alboran Sea in intermediate and deep waters,
773 with differences between predicted and measured ϵ_{Nd} values of up to 1.5-2 epsilon units (Figure 5
774 and 8), requires a sediment source with ϵ_{Nd} more negative than seawater ϵ_{Nd} . The isotopic signature
775 of the marine surface sediments in the Alboran Sea is among the least radiogenic in the entire
776 Mediterranean Sea (Blanchet, 2019), with ϵ_{Nd} values of ~ -11 . This suggests that deviations of
777 observed seawater ϵ_{Nd} from the conservative behaviour in this region might result from the interaction
778 with a less radiogenic sediment source. This could also be the case for other specific sites in the
779 Tyrrhenian Sea, showing negative non-conservative ϵ_{Nd} (Figure 8). The observed relationship
780 between intermediate-deep water ϵ_{Nd} values and the detrital lithogenic signatures reflects the good
781 correlation between non-conservative ϵ_{Nd} and coretop detrital sediment ϵ_{Nd} at global scale (Du et al.,
782 2020), suggesting a major role of the sediment flux also in the Mediterranean Sea, especially in the
783 eastern Levantine Basin and Alboran Sea.

784 However, most of the Mediterranean regions show less pronounced non-conservative behaviour
785 (Figures 5, 8 and 9), which is consistent with rapid advection and mixing of eastern radiogenic and
786 western unradiogenic water masses as the dominant processes controlling the Nd cycle and dissolved
787 Nd isotope distribution in the present-day Mediterranean Sea, which is characterized by a highly
788 efficient intermediate and deep-water ventilation.

789

790 **6. Conclusions**

791

792 This study presents the dissolved ϵ_{Nd} compositions of 80 new seawater samples that were recovered
793 from 24 stations between 10 and 4087 m water depth covering the entire Mediterranean basin. The
794 new dataset adds to the previous results and represents one third of the total number of samples
795 ($n = 240$) obtained so far in the Mediterranean Sea for ϵ_{Nd} . Our new data support the strong W-E
796 gradient, with the western basin mainly characterized by less radiogenic signature (< -7) and the
797 eastern basin showing a highly radiogenic signature (> -7). In particular, values higher than -6 occur
798 only in the Levantine basin east of 25°E and in the Aegean Sea. This longitudinal gradient is
799 particularly evident in the surface layer that is dominated by AW. The radiogenic signature of the
800 eastern basin is propagated westward at intermediate depth with Levantine Intermediate Water and is
801 progressively diluted during advection from its source region in the eastern Levantine basin ($-$
802 5.58 ± 0.66) by the mixing with less radiogenic surface and bottom water along its flowpath towards

803 the Alboran Sea (-9.33 ± 0.69). Our data also show a highly significant ϵ_{Nd} – salinity correlation and a
804 clear distinction between the different surface, intermediate and deep water masses of the
805 Mediterranean Sea based on their ϵ_{Nd} signature. We used an Optimum Multiparameter (OMP)
806 analysis and results from the Parametric Optimum Multiparameter (POMP) analysis of Jullion et al.
807 (2017) to evaluate the conservative ϵ_{Nd} behaviour in the Mediterranean Sea and quantify the
808 variability related to local and regional non-conservative Nd addition. Based on the comparison
809 between observed and OMP- and POMP-derived ϵ_{Nd} values, we can conclude that most of the
810 measured values are consistent with pure water mass mixing (Figures 5, 8 and 9), which indeed exerts
811 a key overall control over the Nd isotope distribution in the Mediterranean basin. However, data-
812 model ϵ_{Nd} misfits exist in almost all sub-basins, especially in the eastern Levantine Basin and Alboran
813 Sea, which can be explained by the influence of highly radiogenic Nile sourced volcanic sediment
814 fractions and unradiogenic detrital sediments, respectively. Therefore, we can conclude that partially
815 dissolved Nile river particles and the sediment flux contributed by the boundary exchange process
816 play a major role in specific regions of the Mediterranean Sea. The non-conservative contributions
817 originating from sediment sources are then propagated by water mass circulation (with distinct
818 preformed ϵ_{Nd}) along the Mediterranean Sea as conservative components. The results of the present
819 study indicate that ϵ_{Nd} effectively traces the mixing between the different water masses in this semi-
820 enclosed basin and is a suitable water mass tracer.

821 Measured ϵ_{Nd} values differ significantly (up to +4.8 epsilon units) from model outputs (Ayache et al.,
822 2016), notably for surface waters in the eastern Mediterranean Sea and intermediate and deep waters
823 in the western Mediterranean basin. The model-data disagreement is likely the result of a combination
824 of different factors, such as low simulated net water input and advection from the Atlantic, the lacking
825 inclusion of all external Nd inputs and sinks in the model simulation and the poor implementation of
826 the BE term in the model. In particular, the model BE implementation does not seem to be able to
827 capture boundary exchange or sediment influence in reality (Du et al. 2020). The use of a fully
828 prognostic coupled dynamical/biogeochemical model with an explicit representation of all Nd
829 sources and sinks, as suggested by Ayache et al. (2016), coupled with a better implementation of BE
830 and comparison with this new extended ϵ_{Nd} dataset, could help improving model simulations and
831 better quantifying the relative proportions of external Nd sources, which will allow us to improve our
832 understanding of the relevant processes affecting the Nd cycle in the Mediterranean Sea.

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1138 Figure captions

1139 **Fig. 1.** Map of the Mediterranean Sea showing the locations of the new stations of this study (white
1140 dots) and those of previously published Nd isotope profiles (black dots), with geographic names
1141 reported in the main text. The schematic circulation pattern of the Levantine Intermediate Water (grey
1142 arrows) and deep water (dotted black arrows) is modified from Pinarti and Masetti (2000) and
1143 Schroeder et al. (2012).

1144 **Fig. 2.** S- θ - ϵ_{Nd} plot for all stations discussed in the paper (coloured dots). Grey dots represent full T-
1145 S profiles for the Meteor 84/3 and MedBlack GEOTRACES 64PE370 and 64PE374 cruises. Stars
1146 correspond to the salinity and potential temperature values of the most important water masses in the
1147 Mediterranean Sea, based on water properties reported in Manca et al. (2004). AW = Atlantic Water;
1148 LIW = Levantine Intermediate Water; WIW = Winter Intermediate Water; EMDW = Eastern
1149 Mediterranean Deep Water; WMDW = Western Mediterranean Deep Water. The ϵ_{Nd} signature for
1150 AW, LIW, WIW, EMDW and WMDW represent spatially averaged ϵ_{Nd} values from the Gulf of
1151 Cadiz, Eastern Levantine Basin, Balearic Sea, Ionian Sea and Balearic Sea, respectively (Table 2).

1152 **Fig. 3.** ϵ_{Nd} -S-longitude plot showing all the values available for the Mediterranean Sea (this study
1153 and previously published results) and calculated 2 end-member mixing lines. Mixing envelopes were
1154 calculated based on 1σ SD of the average ϵ_{Nd} signature for each end-member (Table 2). Grey stars
1155 represent surface, intermediate and deep water mass end-members (AW, LIW, EMDW, WMDW).

1156 **Fig. 4.** ϵ_{Nd} depth profiles for the Aegean Sea, Adriatic Sea, Western and Eastern Mediterranean
1157 basins. Shaded areas indicate the depth range of the main water masses in the Mediterranean Sea
1158 (AW = Atlantic Water; LIW = Levantine Intermediate Water; WMDW = Western Mediterranean
1159 Deep Water; EMDW = Eastern Mediterranean Deep Water; AdDW = Adriatic Deep Water; MLD =
1160 Mixed Layer Depth; TMW = Transitional Mediterranean Water; CDW = Cretan Deep Water). MLD,
1161 TMW and CDW are observed in the South Aegean (Vervatis et al., 2011).

1162 **Fig. 5.** Sections of potential temperature, salinity, measured and POMP-derived ϵ_{Nd} values along a
1163 longitudinal transect from the Strait of Gibraltar to the eastern Levantine Basin. The water mass

1164 fractions used to calculate the POMP-derived ϵ_{Nd} values were obtained from the Parametric Optimum
1165 Multiparameter analysis of Jullion et al. (2017) based on conservative (potential temperature and
1166 salinity) and quasi-conservative ($NO = 9NO_3 + O_2$ and $PO = 170PO_4 + O_2$) variables, acquired during
1167 the M84/3 cruise (Tanhua et al., 2013b). The red and yellow lines in the map represent the W-E
1168 transects for the measured and calculated ϵ_{Nd} values, respectively. Sampled depths are indicated by
1169 grey and black dots. White lines superimposed on the ϵ_{Nd} values represent salinity contours.

1170 **Fig. 6.** Maps of the ϵ_{Nd} signature for the Mediterranean Sea. A) Surface water (< 100 m); B)
1171 Intermediate water (200 – 500 m); C) Intermediate-deep waters (500 – 2000 m); D) Deep waters (>
1172 2000 m). The schematic circulation pattern marked by grey arrows is modified by Pinardi and Masetti
1173 (2000), Pinardi et al. (2015) and Schroeder et al. (2012). The ϵ_{Nd} data for the rivers are from Goldstein
1174 et al. (1984), Frost et al. (1986), Henry et al. (1994) and Tachikawa et al. (2004). White dots represent
1175 average values for surface sediments from the eastern Levantine Basin (-2.5; Weldeab et al., 2002)
1176 and Nile River particles (-1.2; Tachikawa et al., 2004). The ϵ_{Nd} data of the soil samples in northern
1177 Africa are from Scheuven et al. (2013) and Blanchet (2019). The ϵ_{Nd} composition of the three North
1178 African preferential dust source areas (Western, Central and Eastern PSA) is from Jewell et al. (2021).
1179 Coloured rectangles with ϵ_{Nd} values denote the isotopic composition of the aerosol samples analysed
1180 by Colin (1993), Frost et al. (1986) and Grousset et al. (1988). The dotted line off-shore the Nile
1181 mouth shows the potential extent of the hypopycnal plume from the Nile, based on Ducassou et al.
1182 (2008).

1183 **Fig. 7.** Property-property plots (ϵ_{Nd} vs. salinity, potential temperature and phosphate) for data from
1184 water depths above 227 m (A, B and C), between 227 and 500 m (D, E and F), between 500 and 2000
1185 m (G, H and I) and below 2000 m (J, K and L).

1186 **Fig. 8.** Comparison between measured and OMP-derived ϵ_{Nd} values for the western Mediterranean
1187 Sea. Deviations from conservative mixing exceed ± 0.5 epsilon units (dotted lines) from the 1:1 line.
1188 Inset shows the histogram of the differences between OMP-derived and measured ϵ_{Nd} values.

1189 **Fig. 9.** Comparison between measured and OMP-derived ϵ_{Nd} values for the eastern Mediterranean
1190 Sea. Deviations from conservative mixing exceed ± 0.5 epsilon units (dotted lines) from the 1:1 line.
1191 Inset shows the histogram of the differences between OMP-derived and measured ϵ_{Nd} values.

1192 **Fig. 10.** Comparison between modelled and observed ϵ_{Nd} values. The colouring shows the modelled
1193 surface (25 m) ϵ_{Nd} distribution (from Ayache et al. 2016). Coloured dots represent measured ϵ_{Nd}
1194 values at shallow depths (< 62 m).

1195 **Fig. 11.** E-W section of the modelled ϵ_{Nd} distribution (from Ayache et al. 2016) (same track as in Fig.
1196 5). Coloured dots in the upper panel represent measured ϵ_{Nd} values. Difference between modelled and
1197 measured values is displayed in the lower panel.

1198 **Fig. 12.** Section of the ϵ_{Nd} distribution in the eastern Levantine basin. White numbers represent the
1199 Nd isotopic composition of lithogenic surface sediments from Weldeab et al. (2002). Inset shows the
1200 map of the eastern Levantine Basin with isolines of the Nd isotopic composition of lithogenic surface
1201 sediments (Weldeab et al., 2002).

1202 **Fig. S1.** Sections showing the AW, IW and DW fractions for the western Mediterranean Sea, derived
 1203 from the OMP analysis. Inset shows the transect from the Strait of Gibraltar to the Sicily Channel
 1204 used to generate the seawater sections. Yellow stars represent the sites of the water type end-members
 1205 for the OMP analysis. Potential temperature, salinity, ϵ_{Nd} and Nd concentration of the AW, IW and
 1206 DW end-members used for the OMP analysis are different for the two basins (see section 3.3 and
 1207 Table S2).

1208 **Fig. S2.** Sections showing the AW, IW and DW fractions for the eastern Mediterranean Sea, derived
 1209 from the OMP analysis. Inset shows the transect from the Sicily Channel to the Levantine Basin used
 1210 to generate the seawater sections. Yellow stars represent the sites of the water type end-members for
 1211 the OMP analysis. Potential temperature, salinity, ϵ_{Nd} and Nd concentration of the AW, IW and DW
 1212 end-members used for the OMP analysis are different for the two basins (see section 3.3 and Table
 1213 S2).

1214 **Fig. S3.** REE patterns for the Mediterranean seawater samples analysed in this study. REE values are
 1215 normalized to the Post Archean Australian Shale (PAAS, Taylor and MacLennan, 1985) and plotted
 1216 on a log scale.

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1218

Cruise	Station	Lat [°N]	Long [°E]	Depth	θ	Salinity	σ_t	Phosphate	Nitrate	$^{143}Nd/^{144}Nd$ (bias corrected)	Internal error (2 σ SE)	ϵ_{Nd}	External error (2 σ SD)	Nd	
				(m)	(°C)	(kg/m ³)	(μ mol/kg)	(μ mol/kg)	(pmol/kg)						
Medcor	37	35.813	14.082	140	15.99	38.22	28.23	0.14	0.96	0.512154	0.000012	-9.44	0.33		
	37			300	14.17	38.79	29.08	0.09	3.31	0.512249	0.000012	-7.58	0.33		
	37			800	13.74	38.75	29.15	0.32	4.33	0.512291	0.000011	-6.78	0.33		
	37			1020	13.71	38.75	29.15	0.19	5.53	0.512278	0.000016	-7.02	0.33		
	20	35.504	14.078	60	17.97	37.87	27.48	0.10	0.11	0.512138	0.000011	-9.75	0.33		
	20			647	13.82	38.75	29.16	0.14	3.92	0.512252	0.000013	-7.54	0.33		
Arcadia	50	41.296	17.254	40	13.62	38.46	28.94	0.02	1.56	0.512238	0.000012	-7.80	0.33		
	50			170	13.38	38.58	29.09	0.04	2.55	0.512252	0.000011	-7.52	0.33		
	50			473	13.54	38.69	29.14	0.16	4.56	0.512263	0.000013	-7.31	0.33		
	50			718	13.44	38.70	29.17	0.13	4.43	0.512263	0.000012	-7.31	0.33		
Record	10	36.500	13.212	65	16.48	37.51	27.57	0.09	0.10					23.26	
	10			200	14.67	38.83	29.00	0.13	1.73						23.79
	10			800	13.88	38.79	29.15	0.41	4.65						20.68
	10			1200	13.84	38.78	29.15	0.18	5.42						23.37
	10			1710	13.80	38.78	29.15	0.19	5.02						19.96
	28	38.702	8.912	25	19.04	38.06	27.35	0.01	0.16	0.512138	0.000022	-9.75	0.50	30.06	
	28			451	13.80	38.68	29.08	0.34	6.5	0.512228	0.000023	-8.00	0.50	22.37	
Meteor 84/3	287	37.667	25.600	25	16.42	39.21	28.89	0.01	0.13	0.512300	0.000013	-6.60	0.50		
	287			506	14.65	39.10	29.22	0.07	1.4	0.512320	0.000016	-6.20	0.50		
	287			807	14.39	39.09	29.27	0.06	1.09	0.512305	0.000014	-6.50	0.50		
	288	35.649	26.227	27	16.85	39.23	28.80	0.00	0.17	0.512320	0.000018	-6.20	0.50	32.00	
	288			1015	14.31	39.02	29.23	0.12	3.52	0.512330	0.000018	-6.00	0.50	18.96	
	294	33.700	31.002	26	18.11	39.03	28.34	0.01	0.07	0.512264	0.000015	-7.30	0.50		
	294			254	16.35	39.19	28.89	0.02	1.17	0.512310	0.000013	-6.40	0.50	33.73	
	294			1776	13.62	38.78	29.19	0.21	4.9	0.512338	0.000016	-5.85	0.50		

	301	35.233	21.483	3552	15.36	152.00	119.80	1.29	0	0.512207	0.000014	-8.40	0.50	23.02
	305	35.600	17.240	4087	13.40	38.73	29.20	0.18	4.36	0.512269	0.000019	-7.20	0.50	22.05
	306	36.500	19.000	255	14.93	39.00	29.08	0.14	3.87	0.512284	0.000013	-6.90	0.50	
	306			3478	13.41	38.73	29.20	0.19	4.44	0.512259	0.000012	-7.40	0.50	
	307	38.000	19.300	3335	13.42	38.73	29.20	0.15	4.5	0.512284	0.000016	-6.90	0.50	
	309*	39.500	18.801	799	13.54	38.74	29.18	0.18	4.84	0.512317	0.000014	-6.26	0.50	22.88
	309*			799	13.54	38.74	29.18	0.18	4.84	0.512317	0.000011	-6.26	0.50	
	317	39.220	11.751	26	15.36	37.52	27.84	0.01	0.07	0.512141	0.000013	-9.70	0.50	
	317			811	13.64	38.67	29.11	0.31	6.56	0.512233	0.000015	-7.90	0.50	21.76
	317			3268	12.96	38.49	29.11	0.37	7.94	0.512192	0.000013	-8.70	0.50	
	338	35.951	-5.749	304	13.10	38.49	29.08	0.44	9.79	0.512177	0.000018	-9.00	0.50	
GEOTRACES- Med	64PE370-10	37.575	4.774	11	16.98	36.90	26.98	0.02	0.14	0.512152	0.000005	-9.48	0.18	24.61
	64PE370-10			25	16.81	36.91	27.03	0.10	2.47	0.512346	0.000008	-5.70	0.21	
	64PE370-10			40	15.99	37.00	27.30	0.17	4.04	0.512211	0.000020	-8.34	0.46	
	64PE370-10			80	14.37	37.69	28.19	0.16	4.17	0.512164	0.000009	-9.25	0.34	20.83
	64PE370-10			200	13.22	38.35	28.95	0.46	10.16	0.512195	0.000021	-8.65	0.46	
	64PE370-10			400	13.28	38.54	29.08	0.47	9.84	0.512189	0.000019	-8.77	0.46	
	64PE370-10			1000	12.95	38.48	29.11	0.43	9.02	0.512180	0.000022	-8.93	0.46	
	64PE370-10			1500	12.89	38.47	29.11	0.41	8.84	0.512233	0.000022	-7.90	0.46	
	64PE370-28	35.296	26.641	50	17.61	39.07	28.50	0.01	0.05	0.512321	0.000025	-6.19	0.49	
	64PE370-28			100	16.89	39.08	28.68	0.01	0.53	0.512365	0.000022	-5.33	0.46	
	64PE370-28			150	16.50	39.10	28.79	0.01	0.85	0.512371	0.000005	-5.21	0.21	
	64PE370-28			400	14.97	39.06	29.12	0.06	2.40	0.512344	0.000006	-5.73	0.21	
	64PE370-28			800	13.87	38.83	29.19	0.19	5.09	0.512352	0.000005	-5.57	0.21	
	64PE370-28			1000	14.00	38.88	29.20	0.17	4.69	0.512366	0.000017	-5.30	0.46	
	64PE370-28	1200	14.09	38.92	29.21	0.15	4.40	0.512343	0.000021	-5.75	0.46			
	64PE370-31	39.048	25.210	10	20.48	39.08	27.75	0.03	0.02	0.512320	0.000005	-6.20	0.21	
	64PE370-31			60	16.12	39.06	28.85	0.03	0.02	0.512350	0.000007	-5.61	0.18	24.81
	64PE370-31			120	15.43	39.00	28.97	0.03	0.93	0.512355	0.000014	-5.52	0.46	
	64PE370-31			200	15.07	38.99	29.04	0.04	1.25	0.512340	0.000007	-5.82	0.18	22.87
	64PE370-31			276	14.40	38.98	29.18	0.09	2.40	0.512361	0.000017	-5.41	0.46	
	64PE370-31	294	14.22	38.98	29.22	0.11	2.73	0.512305	0.000019	-6.49	0.46			
	64PE374-1	35.637	24.920	25	23.60	39.16	26.92	0.02	0.03	0.512280	0.000015	-6.99	0.50	
	64PE374-8	40.961	18.536	235	13.97	38.82	29.15	0.07	3.15	0.512239	0.000008	-7.78	0.50	
	64PE374-8			874	13.04	38.71	29.27	0.12	3.78	0.512263	0.000018	-7.31	0.50	
	64PE374-9	40.154	18.817	739	13.48	38.76	29.21	0.07	3.10	0.512250	0.000012	-7.57	0.50	
	64PE374-12	39.007	14.502	3464	13.00	38.50	29.11	0.37	8.25	0.512202	0.000009	-8.50	0.50	
	64PE374-13	39.878	13.010	20	21.13	37.90	26.67	0.02	0.02	0.512179	0.000019	-8.95	0.50	
	64PE374-13			400	14.12	38.76	29.07	0.24	6.01	0.512250	0.000014	-7.58	0.50	
	64PE374-13			499	14.03	38.76	29.09	0.26	6.22	0.512236	0.000011	-7.84	0.50	
	64PE374-13			1000	13.54	38.65	29.11	0.31	7.11	0.512260	0.000021	-7.38	0.50	
	64PE374-13			3576	12.98	38.50	29.11	0.39	8.36	0.512158	0.000015	-9.36	0.50	
	64PE374-15	42.051	10.568	25	17.87	38.11	27.70	0.03	0.01	0.512187	0.000011	-8.80	0.50	
64PE374-15	299			13.98	38.67	29.04	0.27	6.26	0.512207	0.000017	-8.41	0.50		
64PE374-15	1244			13.30	38.58	29.11	0.36	7.73	0.512210	0.000008	-8.35	0.50		
64PE374-17**	40.070	5.947	25	20.44	37.11	26.26	0.02	0.01	0.512172	0.000011	-9.08	0.50		
64PE374-17**			25	20.44	37.11	26.26	0.02	0.01	0.512153	0.000006	-9.46	0.21		

64PE374-17	55	15.74	37.22	27.52	0.03	0.02	<i>0.512170</i>	<i>0.000033</i>	-9.13	0.66	
64PE374-17	85	14.59	38.13	28.48	0.03	0.02	<i>0.512167</i>	<i>0.000007</i>	-9.19	0.21	
64PE374-17	175	13.28	38.34	28.93	0.27	6.94	<i>0.512209</i>	<i>0.000023</i>	-8.38	0.46	
64PE374-17	199	13.34	38.41	28.97	0.31	7.58	0.512218	0.000016	-8.19	0.50	
64PE374-17	500	13.27	38.56	29.10	0.41	8.93	<i>0.512218</i>	<i>0.000013</i>	-8.19	0.46	
64PE374-17	1000	12.96	38.49	29.11	0.41	8.78	<i>0.512243</i>	<i>0.000020</i>	-7.70	0.46	
64PE374-17**	1500	12.86	38.47	29.12	0.41	8.71	0.512198	0.000011	-8.58	0.50	
64PE374-17**	1500	12.86	38.47	29.12	0.41	8.71	<i>0.512209</i>	<i>0.000008</i>	-8.37	0.21	
64PE374-17	2000	12.90	38.48	29.12	0.39	8.47	<i>0.512190</i>	<i>0.000006</i>	-8.73	0.12	
64PE374-17	2500	12.90	38.49	29.12	0.39	8.46	<i>0.512245</i>	<i>0.000042</i>	-7.67	0.83	
64PE374-17	2785	12.90	38.49	29.12	0.39	8.43	<i>0.512193</i>	<i>0.000020</i>	-8.69	0.46	
64PE374-17**	2824	12.91	38.49	29.12	0.39	8.42	0.512190	0.000016	-8.73	0.50	
64PE374-17**	2824	12.91	38.49	29.12	0.39	8.42	<i>0.512239</i>	<i>0.000021</i>	-7.78	0.46	

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1221 **Table 1.** Hydrographic data, Nd isotopic composition, ϵ_{Nd} values and Nd concentration of the
1222 seawater samples analysed in the present study. The uncertainties are given at the two-sigma (2σ)
1223 level for the internal and external error. The external reproducibility of $^{143}Nd/^{144}Nd$ measurements
1224 was estimated by repeated measurements of the international standards JNdi-1 and La Jolla. * Intra-
1225 laboratory replicate samples (GEOPS); ** Inter-laboratory replicate samples (GEOPS and
1226 GEOMAR). Samples in italics were analysed at GEOMAR.

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1228

Basin	Sub-basin	Water mass	Depth (m)	$\epsilon_{Nd} \pm 1SD$	N. of samples	Reference
Western	Alboran Sea	AW	0-110	-9.95 ± 0.71	13	2, 3, 4
		LIW	200-400	-9.33 ± 0.69	8	3, 4
		WMDW	800-1270	-9.23 ± 0.25	4	3
	Balearic Sea	AW	25-85	-9.22 ± 0.17	4	1, 7
		WIW	100-250	-8.56 ± 0.44	6	1, 7
		LIW	250-501	-8.31 ± 0.52	6	1, 7
		WMDW	1000-2825	-8.61 ± 0.49	17	1, 7
	Tyrrhenian Sea	AW	20-140	-9.07 ± 0.45	15	1, 8
		LIW	240-580	-7.81 ± 0.35	13	1, 8
		TDW	811-1500	-8.26 ± 0.66	9	1, 8
WMDW		2264-3576	-8.65 ± 0.34	7	1, 8	
Eastern	Sicily Channel	AW	60-140	-9.40 ± 0.36	4	1, 8
		LIW	300-647	-7.46 ± 0.31	4	1, 5, 8
		EMDW	1020-1692	-7.03 ± 0.01	2	1, 8
	Ionian Sea	AW	25-130	-8.21 ± 0.58	4	8
		LIW	200-300	-6.88 ± 0.38	5	1, 8
		AdDW	799-874	-6.97 ± 0.48	4	1, 8
		EMDW	2718-4086	-6.87 ± 0.24	4	1, 8
South Adriatic Sea	AW	40	-7.80	1	1	

	LIW	235-473	-7.55	±0.33	2	1
	AdDW	718-874	-7.40	±0.15	3	1
South Crete	AW	11-62	-9.30	±0.00	2	3
	LIW	200-430	-7.43	±0.44	4	3
	EMDW	1313-2228	-7.34	±0.40	5	3
Eastern Levantine Basin	AW	1-50	-5.27	±0.96	7	6, 1
	LIW	160-500	-5.58	±0.66	6	1, 3, 6
	EMDW	800-2257	-6.39	±0.80	7	1, 3, 6
Aegean Sea	Surface water	10-75	-6.63	±0.74	10	1, 3
	Intermediate water	200-700	-5.89	±0.50	6	1, 3
	Deep water	1000-1500	-7.13	±2.61	6	1, 3

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1230 **Table 2.** Spatially averaged ϵ_{Nd} signature of the main water masses in the different Mediterranean
1231 sub-basins. Reference: 1 = this study; 2 = Spivack and Wasserburg (1988); 3 = Tachikawa et al.
1232 (2004); 4 = Dubois-Dauphin et al. (2017b); 5 = Henry et al. (1994); 6 = Vance et al. (2004); 7 =
1233 Garcia-Solsona and Jeandel (2020); 8 = Garcia-Solsona et al. (2020).

1234 **Table S1.** Hydrographic data, Nd isotopic composition, ϵ_{Nd} values and Nd concentration of the
1235 seawater samples analysed in the present study and literature data. The uncertainties are given at the
1236 two-sigma (2σ) level for the internal and external error. The table reports also the water mass fractions
1237 calculated through the OMP analysis.

1238 **Table S2.** Potential temperature, salinity, ϵ_{Nd} and Nd concentration of the source water type end-
1239 members used as input parameters for the OMP analysis in the WMED and EMED and the calculation
1240 of predicted ϵ_{Nd} values.

1241 **Table S3.** Potential temperature, salinity, NO, PO, ϵ_{Nd} and Nd concentration of the source water type
1242 end-members used as input parameters for the POMP analysis in the WMED and EMED (Jullion et
1243 al., 2017) and to calculate the predicted ϵ_{Nd} values.

1244 **Table S4.** Dissolved Rare Earth Elements concentrations (in pmol/kg of seawater) and Ce anomalies
1245 (Ce/Ce^*) of the samples analysed in the present study.

1246