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1 **Fast quantitative analysis of *n*-alkanes, PAHs and alkenones in sediments**

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19 **Keywords**

20 Selective Pressurized Liquid Extraction, Biomarker, GC-MS, *n*-alkanes, PAH, Alkenones

21

22 **Abstract**

23 The study of different organic biomarker classes is essential to elucidate global
24 Earth dynamics since different biogeochemical processes play a role in regulating
25 environmental and climatic conditions. However, multiproxy analysis generally consists
26 of labour intensive and time-consuming methodologies, which hamper the study of a
27 high number of samples. Here, we develop and validate a fast analytical method to
28 quantify different classes of organic biomarkers (PAHs, *n*-alkanes and alkenones) in
29 sediments. This new method sequentially extracts and fractionates the target compounds
30 using a pressure liquid extraction (PLE) system, which allows us to selectively obtain
31 the analytes by reducing the time of analysis, sample handling and solvent usage. We
32 show that our method provides reproducible results and high recoveries (>70%), and
33 can be applied to a wide range of sedimentary environments, such as oceanic basins,
34 continental slope and shelf, and lakes. Moreover, the method provides reproducible

35 estimates of paleoclimatic indices, such as the carbon preference index (CPI), the
36 average chain length (ACL) and the $U^{k_{37}}$ -derived sea-surface temperature (SST).
37 Therefore, this new method enables fast quantitative multiproxy analysis of oceanic,
38 coastal and lake sediments.

39

40 **1. Introduction**

41 Sedimentary organic biomarkers are commonly studied in environmental and
42 geological sciences as they provide valuable information on Earth system dynamics
43 (Jaeschke et al., 2017; Luo et al., 2019; Francescangeli et al., 2020; López-Quirós et al.,
44 2021). A range of compounds can potentially be analysed in the same unit of sediment
45 to provide complementary information as environmental or climate proxies. This
46 facilitates undertaking a paleo-multiproxy analysis, which is essential to elucidate and
47 understand natural complex processes. However, it is common to find in the literature
48 studies that are focused only in a few classes of compounds, such as *n*-alkanes,
49 alkenones or PAHs (Bolton et al., 2010; Sarma et al., 2017; Martins et al., 2021;
50 Synnott et al., 2021), rather than a wider range of available biomarker proxies. Arguably
51 this is due to the need of generating data from a large number of samples and thus
52 applying relatively simple methodologies.

53 Typically, the methodology to analyse different classes of biomarker proxies
54 requires several procedural steps to address the different polarities of the target
55 compounds (Jaeschke et al., 2017; Francescangeli et al., 2020; Bicego et al., 2021).
56 Analyses begin with sediment extraction using organic solvents. The extraction is
57 undertaken using either a Soxhlet apparatus, ultrasonic bath, microwave or PLE system.
58 The resulting extracts require a clean-up or fractionation process using column
59 chromatography packed with silica or alumina stationary phases, before instrumental
60 analysis. Detection and quantification are commonly performed by gas chromatography
61 (GC) and GC coupled to mass spectrometry (GC-MS). Consequently, conventional
62 methodologies to analyse biomarker proxies are labour intensive, time consuming, and
63 require high organic solvent usage.

64 PLE applies solvents at high pressure and temperature to efficiently extract
65 analytes from the sample matrix. Selective pressurized liquid extraction (SPLE)
66 combines extraction and clean-up in one step by incorporating adsorbents within the
67 extraction cell (Runnqvist et al., 2010; Subedi et al., 2015). Under optimised conditions,
68 the adsorbent selectively retains a fraction of matrix compounds while releasing the
69 target analytes. Therefore, SPLE can produce extracts that do not require post-extraction
70 purification procedures before instrumental analysis. SPLE has the potential to reduce
71 sample handling and solvent consumption and can significantly increase laboratory
72 productivity. There is a wealth of published SPLE methods designed to quantify
73 chemicals at trace levels (pesticides, organohalide compounds, pharmaceuticals) in
74 environmental and biological samples, and thorough reviews on PLE and SPLE
75 methodologies are available (Runnqvist et al., 2010; Subedi et al., 2015; Alvarez-Rivera
76 et al., 2020). In this study, we describe the development and validation of an SPLE
77 method to simultaneously quantify different biomarker classes in marine and lacustrine
78 sediments. We have focused our study on PAHs, *n*-alkanes and alkenones that have
79 different polarities and yield complementary information as proxies. As part of the
80 method validation, we evaluated its robustness to changes in the sedimentary matrix by
81 repeatedly analysing a set of sediments from different depositional environments (open
82 ocean, coastal and lacustrine).

83

84 **2. Materials and samples**

85 *2.1. Solvents, reagents and standards*

86 Methanol (MeOH), dichloromethane (DCM), *n*-hexane (Hex), acetone (Ac) and
87 toluene were of GC analysis grade and purchased from Merck KGaA. Silica gel 60 for

88 flash chromatography (0.04–0.06 mm, 230–400 mesh ASTM) was obtained from
89 Scharlau, anhydrous Na₂SO₄ (99.5%) from VWR, and diatomaceous earth for ASE
90 from Thermo Scientific. Prior to extraction, silica gel and anhydrous Na₂SO₄ were
91 maintained during 24 hours at 105 °C and cooled in desiccator.

92 N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl (TMS)
93 used to derivatize polar compounds (*n*-alcohols and sterols) was obtained from Thermo
94 Scientific. Standards of PAHs (D12-perylene and D10-pyrene) were obtained from
95 Supelco and Isotec, respectively. *n*-Alkane standards (hexatriacontane and eicosane)
96 were purchased from Aldrich, and a ketone standard (2-nonadecanone) from Fluka.
97 Standards of *n*-alcohol (1-heneicosanol) and sterol (5 α -androstanol-3 β -ol) were
98 obtained from TCI and Sigma, respectively.

99

100 2.2. Samples

101 Sediment samples used to develop and validate the analytical method are listed in
102 Table 1. Marine samples were retrieved in cruises EN651 (northern Tropical Atlantic)
103 and MERS (Catalan Sea, Western Mediterranean). Lacustrine samples were obtained
104 from Spanish lakes Lucenza (LUC) (Quiroga, Lugo) and Pedro Muñoz (PEM) (Mota
105 del Cuervo, Cuenca), and Lake Hula from Israel (HUL).

106 Deep ocean samples EN651-ST04 and EN651-ST13 were obtained in the
107 occidental and oriental basins of the northern tropical Atlantic Ocean, respectively, far
108 from the direct influence of the continents. Marine coastal sediment MERS-ST10 was
109 retrieved at 70 m from the continental shelf, close to the Spanish coast, whereas MERS-
110 ST7 corresponds to the continental slope, and was obtained near the location of ST10.
111 PEM lake is located in the southeast of the Iberian Peninsula and the relatively high

112 mean temperature (14 °C) and low mean precipitation (417 mm) of that region leads to a
113 Mediterranean vegetation (mainly sclerophyll species). In contrast, LUC lake is located
114 in the north east of the Peninsula. This region presents relatively low mean temperature
115 (9.5 °C) and high mean precipitation (1500 mm), which drives to a sub-Mediterranean
116 vegetation (i.e. a mix of deciduous and sclerophyll species) (Ninyerola et al., 2005). The
117 Hula valley is located in northern Israel. It is a 25 km long and 6–8 km wide valley at
118 approximately 70 m mean above sea level. It was occupied by a lake and marshes; the
119 relative extent of each depending on climate and local hydrology. HUL lake, occupying
120 the south of the valley was artificially dried in the 1950s. The region is characterized by
121 high mean temperature (18 °C) and low mean precipitation (653 mm).

122

123 **3. Method description**

124 The analytical method described below corresponds to the final conditions used to
125 test the analytical robustness. The conditions used for method development are
126 discussed in the Results & Discussion section.

127 Samples were freeze-dried and then homogenised with a Mixer Mill MM 400
128 (Retsch). PLE and clean-up were performed using an ASE-350 (Dionex Thermo)
129 equipped with 10 mL extraction cells and 60 mL collection vials. We used activated
130 silica as the stationary phase, and anhydrous Na₂SO₄ to remove water and filter residual
131 particles. Thus, extraction cells were filled from bottom to top with a glass fibre filter, 3
132 g of activated silica, 1 g of anhydrous Na₂SO₄, 1–3 g of sediment, and diatomaceous
133 earth to completely fill the cell (Fig. 1). On the top of cell, 100 µL of an internal
134 standard mixture was added for quantification. The composition of the internal standard
135 mixture was hexatriacontane (C₃₆, 5 ng·µL⁻¹), eicosane (C₂₀, 5 ng·µL⁻¹), 2-

136 nonadecanone ($5 \text{ ng} \cdot \mu\text{L}^{-1}$), D12 perylene ($0.2 \text{ ng} \cdot \mu\text{L}^{-1}$) and D10-pyrene ($0.2 \text{ ng} \cdot \mu\text{L}^{-1}$).
137 Blank samples were prepared similarly to sediment samples, but no sediment was
138 packed in the cell.

139 Samples were extracted at $100 \text{ }^\circ\text{C}$ with hexane:dichloromethane (Hex:DCM) 4:3
140 using solvent saver mode for 10 min at $2 \text{ mL} \cdot \text{min}^{-1}$. This step renews the solvent
141 mixture continuously during the extraction, at a controlled flow rate. This is different
142 from the commonly used batch mode that executes several cycles of fill and release of
143 solvents. This new mode can improve the capability of silica to retain compounds and
144 also the efficacy of the clean-up process. Continuous renewal of solvents may also
145 optimise extraction recovery. The resulting extracts were concentrated under a nitrogen
146 stream at $30 \text{ }^\circ\text{C}$ using TurboVap System (Biotage) and transferred to vials with DCM.
147 Extracts were derivatized with $50 \mu\text{L}$ of BSTFA and $50 \mu\text{L}$ of DCM at $70 \text{ }^\circ\text{C}$ during 1h
148 prior to instrumental analysis. Derivatized extracts were evaporated using a centrifugal
149 evaporator (miVac) coupled to a cold trap (Genevac) and redissolved in $20 \mu\text{L}$ of
150 toluene with 5% BSTFA.

151 For the quantification of *n*-alkanes and PAHs, the extracts were analysed using a
152 GC-MS system (Agilent Technologies 5975C) equipped with a DB-5ms ($30 \text{ m} \times 0.25$
153 mm , $0.25 \mu\text{m}$ stationary phase). The GC carrier gas was helium at a flow of 1.5
154 $\text{mL} \cdot \text{min}^{-1}$. The injection was performed in split-less mode (50 s) at $310 \text{ }^\circ\text{C}$. The oven
155 temperature program was as follows, 1 min at $70 \text{ }^\circ\text{C}$ followed by a gradient of 15
156 $^\circ\text{C} \cdot \text{min}^{-1}$ to $160 \text{ }^\circ\text{C}$, a second gradient to $310 \text{ }^\circ\text{C}$ at $6 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, and isothermal elution at
157 $310 \text{ }^\circ\text{C}$ during 15 min. MS acquisition was performed in single ion monitoring (SIM)
158 mode to improve sensitivity and selectivity (Table 2). Quantitation of the different
159 compound classes was obtained using the peak area ratios between the analyte and its
160 associated internal standard as detailed in Table 2.

161 The quantitation of total C₃₇ alkenones and the measurement of the alkenone
162 unsaturation ratio U^k₃₇ was performed using a GC-FID system equipped with a
163 capillary column HP-1 (60 m × 0.25 mm, 0.25 μm stationary phase) and 3 mL·min⁻¹ of
164 hydrogen as carrier gas. The temperature gradient used to separate the alkenones
165 consisted of a multistep gradient: initial temperature at 80 °C during 1 min, gradient to
166 120 °C at 30 °Cmin⁻¹ and a second ramp to 320 °C at 6 °Cmin⁻¹, followed by an isocratic
167 elution at 320 °C during 21 min. Sample injection was performed at 320 °C with 50 s of
168 split-less. Quantification of alkenones was performed using hexatriacontane as internal
169 standard.

170

171 **4. Results and Discussion**

172 *4.1. Method Development and Optimisation*

173 SPLE method development aims at finding the optimum extraction conditions to
174 achieve quantitative analyte recovery while minimizing matrix interferences in the final
175 extract. In this study, we used long-chain *n*-alcohols and sterols as representative of
176 polar interferences in the sedimentary matrix. The recovery of non-polar analytes (*n*-
177 alkanes, PAHs, alkenones) and the elimination of polar interferences was investigated
178 by spiking sediment samples with the following standards: *n*-alkanes (C₂₀, C₃₂, C₃₄, and
179 C₃₆), PAHs (D10-pyrene, D12-perylene and retene), ketone (2-nonadecanone), *n*-
180 alcohol (1-heneicosanol), and sterol (5 α -androstan-3- β -ol). Accordingly, the criteria to
181 optimise extraction conditions were both maximum analyte recovery (*n*-alkanes,
182 ketones, and PAHs) and minimum recovery of interfering polar compounds. We have
183 used *n*-alcohols and sterols as tracers for polar compounds in the final extract, assuming
184 that the removal of these lipids of medium polarity will ensure an adequate removal of

185 other polar interfering compounds. Recoveries of the analytes of interest were measured
186 in duplicate to assess the method reproducibility obtained using different solvent
187 mixtures.

188 Optimisation of SPLE conditions in the ASE350 solvent saver mode includes the
189 following parameters: solvent composition, temperature, solvent flow and extraction
190 time. Several studies have investigated the retention capacity of different hydrophilic
191 adsorbents (alumina, Florisil™ and silica gel) and concluded that silica gel has the
192 greatest retention capacity (Lundstedt et al., 2006; Osman and Saim, 2012; Subedi et al.,
193 2015). Hence, we assumed that silica gel is the optimum adsorbent to selectively extract
194 compounds of interest and we focused on the optimisation of the remaining parameters.

195

196 *4.1.1. Selection of SPLE solvent mixture composition*

197 Several solvent combinations were tested to maximize analyte recoveries and
198 minimize recoveries of polar compounds: a) Hex:DCM, b) Hex:Ac, and C)
199 DCM:MeOH. For each combination, several mixtures with variable proportions of the
200 polar solvent component (DCM, Ac, and MeOH) were studied. The remaining
201 experimental parameters were maintained constant (extraction temperature of 100 °C,
202 extraction in solvent saver mode at 1 mL·min⁻¹ during 10 min). Extraction tests were
203 performed with both spiked blanks and marine sediment MERS-ST7. Extraction cells
204 were replenished with diatomaceous sand to minimize dead volume when needed.

205 Recoveries of spiked blank samples provided information on the retention
206 capacity of silica gel in the absence of a sedimentary matrix. As detailed in Figs. 2a-c,
207 both *n*-alkanes and PAHs are not retained by silica gel when using Hex:DCM and
208 Hex:Ac mixtures. Ketones require low volumes of DCM (29 %) or Ac (17 %) to elute

209 from the silica gel adsorbent. However, DCM:MeOH solvent mixtures provided
210 inadequate and highly irreproducible results, (Figure 2). Severe reproducibility
211 problems were observed at MeOH contents higher than 20 %, where recovery of *n*-
212 alkanes, ketones and PAHs varied randomly between 0 and 100 %. In contrast, polar
213 interfering compounds (Fig. 3a-b) display a different distribution pattern, with higher
214 recoveries with DCM:MeOH and Hex:Ac solvent mixtures. Hex:DCM mixtures
215 provided erratic (*n*-alcohols) or low (sterols) recoveries. Accordingly, silica gel can
216 partially retain aliphatic *n*-alcohols and sterols when using Hex:DCM as elution solvent
217 mixtures.

218 Recoveries of spiked samples containing both sediment and silica gel provided
219 similar patterns as spiked blank samples (Figs. 2d-f and 3c-d). Thus, recoveries higher
220 than 80% for our target compounds were obtained when using Hex:DCM and Hex:Ac
221 solvent mixtures. Again, the use of polar DCM:MeOH solvent mixtures resulted in
222 generally irreproducible and low recoveries of *n*-alkanes, PAHs and ketones. In
223 contrast, polar compounds were quantitatively recovered with Hex:Ac and DCM:MeOH
224 solvent mixtures. Quantitation in samples obtained with a high proportion of MeOH
225 (>30 %) was complicated due to the co-extraction of abundant sedimentary
226 components. Sediment extracts obtained with DCM/MeOH contained abundant
227 components that affected the GC-MS analysis, resulting in irreproducible and unreliable
228 calculated recoveries (Figure 2). An exception to the general pattern was D12-perylene,
229 which could not be recovered from the sedimentary matrix by any of the tested solvents
230 (dashed lines in Fig. 2). Low recoveries of D12-perylene were systematically observed
231 in all tested sediments (data not shown) and could not be related to losses during sample
232 processing (see Fig. 2b). Accordingly, low recoveries are probably caused by an
233 unusually strong affinity of this compound to the sedimentary matrix.

234 Overall, most Hex:DCM and Hex:Ac solvent mixtures provide good and
235 reproducible recoveries (80-110 %) of our target compounds. However, the retention
236 capability of silica gel is not enough to retain interferences (*n*-alcohols and sterols),
237 when using polar Ac as a modifier (Fig. 3). Therefore, the optimum balance between
238 recoveries of the compounds of interest and retention of interfering polar compounds
239 was established at Hex:DCM 4:3. These results also indicate that moderately polar
240 components of the sedimentary matrix, such as *n*-alcohols and sterols may be
241 selectively recovered in a second extraction using Hex:Ac mixtures.

242

243 *4.1.2. Optimisation of SPLE solvent flow rate, temperature and time*

244 We performed a set of 16 experiments designed to identify the optimum
245 temperature, time, and solvent flow rate to quantitatively extract the compounds of
246 interest and minimize the presence of polar compounds in the extract (Table 3). For all
247 tests, we extracted the sediments twice. The first fraction was obtained with Hex:DCM
248 4:3 to elute non-polar compounds, and the second fraction was obtained with Hex:Ac
249 1:1 to extract polar compounds. The separation of the 5 compounds classes (*n*-alkanes,
250 PAHs, ketones, *n*-alcohols and sterols) among the two fractions is expressed by the
251 concentration ratio (CR) between the first fraction and the total recovery ($CR =$
252 $Fr1/(Fr1+Fr2) \times 100$) and is shown in Table 3. Hence, CR close to 100 is associated
253 with high recoveries in the first fraction, whereas CR close to 0 indicates high
254 recoveries in the second fraction. Ideally, compounds of interest should be recovered in
255 the first fraction and show high CR values, while interfering polar compounds should be
256 eluted in the second fraction and present low CR values.

257 Our results show that high temperature (>150 °C) provides high CR (>75 %) for
258 all compound classes (Table 3), indicating that both polar and non-polar compounds are
259 eluted in the first fraction. In contrast, lower temperatures generally present high CR for
260 the target compounds (>75 %) and low CR for interferences (<25 %). Our data also
261 show that increasing time and solvent flow rate enhance CR of the analytes. Hence, we
262 selected 100 °C, 10 min and 2 mL·min⁻¹ as the optimum conditions for temperature,
263 time and solvent flow, respectively. These conditions allow us to quantitatively recover
264 all target compounds in the first fraction and minimize the presence of polar
265 interferences.

266

267 *4.2. Method Validation*

268 The analytical procedure was developed to identify quantitative changes in the
269 sedimentary biomarker composition, which helps to elucidate past environmental
270 changes. In order to measure the capability to detect concentration changes, we
271 measured the analytical reproducibility and robustness to quantitate C₂₁-C₃₃ *n*-alkanes,
272 PAHs, and C₃₇ alkenones. We also studied the reproducibility of some indices
273 commonly used to investigate past sedimentary conditions, such as the alkenone U^k₃₇
274 and *n*-alkane CPI and ACL indices. To this end, we performed six analytical runs in
275 different days, distributed within a time period of 3 months to account for temporal
276 changes in the laboratory setup. Moreover, the analytical robustness to changes in the
277 sample matrix was assessed by comparing reproducibility and internal standard
278 recoveries in samples of different sedimentary environments (lacustrine, coastal marine,
279 and pelagic ocean, see Table 1). The results of the method validation have been
280 summarized in Table 4 and Figs. 4 and 5.

281 Coefficient of variation (CV) of C₂₁-C₃₃ *n*-alkanes ranged between 3.4–12.5 %,
282 with higher values in lacustrine sediments (10.6–12.5 %) compared to marine and
283 oceanic sediments (3.4–6.5%). Similar analytical uncertainty was obtained irrespective
284 of total C₂₁-C₃₃ *n*-alkanes concentration, which ranges from 1.04 to 22.3 μg·g⁻¹.
285 Remarkably, pelagic sediment samples presented similar concentration values (1.07–
286 2.73 μg·g⁻¹) compared to coastal (1.04–1.23 μg·g⁻¹) and lacustrine sediment samples
287 (PEM lake, 1.84 μg·g⁻¹). Good reproducibility was also obtained for the lacustrine
288 sample LUC in spite of the exceptionally high *n*-alkane content (22.3 μg·g⁻¹). The
289 analytical method also provided reproducible CPI and ACL indexes. Estimated CPI
290 values ranged between 5.3–7.0 with standard deviations within 0.11–0.68. These values
291 are representative of *n*-alkanes distributions associated with higher plants (Fig. 4). All
292 samples provided similar ACL indices (29.6–30.3), within an analytical uncertainty of
293 0.03–0.21.

294 Obtained PAH concentrations were 3 orders of magnitude lower than *n*-alkanes
295 (0.86–126 ng·g⁻¹, Table 4). In addition, all sediments showed marked differences in
296 both PAH concentration and the distribution of individual compounds (Fig. 4). Despite
297 these large differences in composition, the analytical uncertainty remained within
298 acceptable limits (CV = 8.8–21%) for all samples.

299 In spite of being relatively abundant in marine sediments (39–800 ng·g⁻¹), the
300 analytical uncertainty in the quantitation of total C₃₇ alkenones was higher than for *n*-
301 alkanes and PAHs (CV = 16.2–21.2 %). This could be related to small differences in the
302 recovery of the internal standard (C₃₆ *n*-alkane) and the alkenones during the extraction
303 process. However, the alkenone-derived U^k₃₇ index provided reproducible SST
304 estimates within 0.5 °C uncertainty, in concordance with previous studies (Villanueva
305 and Grimalt, 1997). The high uncertainty observed in coastal sample ST10, collected at

306 70 m water depth, is related to the presence of interfering compounds in the GC-FID
307 profile. Although alkenones are present in most marine sediments, they are not always
308 detected in lacustrine sediments (Zink et al., 2001). Therefore, the absence of alkenones
309 in PEM and LUC samples likely reflects the absence of alkenone-producing organisms
310 in the related lacustrine environments.

311 Internal standards (IS) are used to correct for sample losses during the analytical
312 procedure. In addition, the analysis of IS recoveries can provide information on the
313 procedural efficiency and therefore, can identify potential systematic deviations in the
314 quantitative measurements (Runnqvist et al., 2010; Subedi et al., 2015). Averaged IS
315 recoveries for marine sediment samples ranged between 70 and 120 %, indicating
316 limited losses during sample processing (Fig. 5). Changes in analyte recoveries were
317 adequately compensated by IS, resulting in global analytical uncertainties below 22 %
318 for all compound classes. However, lower IS recoveries (20–65 %) were obtained in
319 lake sediments with high total organic carbon concentrations (HUL 2.3% and LUC
320 18%, Fig. 5). These low recoveries were concurrent with the abundance of polar
321 interfering compounds (sterols, *n*-alcohols, fatty acids and esters) in the final extract, as
322 detected by GC-MS (data not shown). In particular, HUL sample corresponds to
323 shallow lake sediments that have not been subject to extensive post-depositional
324 diagenesis. In addition, the extractable lipid composition of LUC sediment contained
325 very high amounts of fatty acids and esters that masked *n*-alkane and PAH signals (data
326 not shown). These results prompt the conclusion that silica gel was unable to retain and
327 fractionate the extracted polar constituents, producing extracts that were unfit for
328 quantitative analysis. Therefore, the analytical setup may produce reproducible, but
329 inaccurate results when applied to shallow lake sediments with high organic carbon
330 content (>2 %). Reliable analysis of these organic-rich lake samples requires method

331 modification that involves extensive clean-up processes to achieve successful
332 interference removal and higher extraction recovery of the analytes.

333 The recovery of D12-perylene was systematically low for all tests performed with
334 sediment samples, irrespective of the extraction conditions (solvent composition,
335 extraction temperature and extraction time). The fact that blank samples produced good
336 D12-perylene recoveries (Fig. 2b) indicates that perylene losses are not related to
337 irreversible adsorption to silica nor losses during sample handling. Published analytical
338 procedures that use PLE to extract PAH from sediments do not report recoveries of
339 D12-perylene nor quantitative perylene (Martinez et al., 2004; Liguori et al., 2006; Choi
340 et al., 2014; Gauchotte-Lindsay et al., 2014; Net et al., 2014; Magill et al., 2015). In
341 contrast, good recoveries of D12-perylene have been reported for fish and soil samples
342 (Lundstedt et al., 2006; Lund et al., 2009). Accordingly, low perylene recoveries are
343 probably related to strong affinity between this compound and unknown components of
344 the sedimentary matrix.

345

346 **5. Conclusions**

347 A number of studies have described significant differences in the concentration values
348 among extraction methodologies (Saim et al., 1997; Hawthorne et al., 2000; Flotron et al., 2003;
349 Wang et al., 2007; Lau et al., 2010; Xia et al., 2021). In particular, PLE and Soxhlet systems
350 tend to produce relatively higher concentration values than ultrasonic-assisted (UAE) or
351 supercritical fluid assisted (SFE) methods (Saim et al., 1997; Calvo et al., 2003; Wang et al.,
352 2007; Lau et al., 2010), suggesting a higher extraction recovery. SFE selectively extracts apolar
353 compounds and therefore produces cleaner extracts with a relatively lower recovery (Hawthorne
354 et al., 2000). Differences in extraction recoveries and/or matrix effects complicate the direct
355 comparison of quantitative values obtained using different procedures. Accordingly, we have

356 not performed a direct comparison of the quantitative data produced by the SPLE method and
357 other technologies. However, using spiked standards, we have demonstrated that the SPLE
358 procedure quantitatively recovers extractable *n*-alkanes, PAHs, and aliphatic ketones. The
359 estimated recoveries for all tested internal standards (70–120 %) are similar to reported values
360 (50–120 %) using different methodologies (Berset et al., 1999; Hawthorne et al., 2000; Flotron
361 et al., 2003; Martinez et al., 2004; Haskins et al., 2011; Choi et al., 2014; Xia et al., 2021). Also,
362 the analytical reproducibility of the SPLE method (CV between 2 and 21 %) is also comparable
363 to other methodologies based on different extraction technologies, that report CV values
364 between 3 and 35 % (Saim et al., 1997; Berset et al., 1999; Hawthorne et al., 2000; Calvo et al.,
365 2003; Flotron et al., 2003; Martinez et al., 2004; Lundstedt et al., 2006; Li et al., 2007; Wang et
366 al., 2007; Lau et al., 2010; Choi et al., 2014; Magill et al., 2015; Subedi et al., 2015).

367 Sediment extracts produced by SPLE are free of interfering compounds and are adequate
368 for high throughput routine quantitation of *n*-alkanes, PAHs and alkenones. The resulting
369 extracts may contain other compounds, such as long-chain *n*-alcohols, and therefore extract
370 derivatization with BSFTA is recommended prior to GC-MS analysis. However, selectivity of
371 GC-MS detection in SIM mode adequately removes many potential interferences. According to
372 our experience, other generally abundant components of the extractable lipidic fraction, such as
373 fatty acids and sterols, are quantitatively retained in the silica gel during the extraction
374 procedure. However, the processing method may not be adequate for samples with very high
375 TOC content (>2 %). Recoveries in organic-rich sediments dropped to 30–70 %, indicating a
376 reduced performance in samples with high TOC. These samples typically contain high
377 concentrations of polar interfering extractable compounds (fatty acids, esters, alcohols, etc.) that
378 can overload the silica gel adsorption capacity. These situations typically result in decreased IS
379 recoveries, indicating incomplete sample extraction and/or purification (i.e. samples LUC and
380 HUL). Nevertheless, this can be overcome by reducing the mass of extracted sediment or by
381 implementing additional post-extraction purification protocols. Therefore, potential biases in the
382 analytical accuracy can be detected by implementing systematic controls on the internal

383 standard recovery. Alternatively, systematic detection of polar compounds, such as fatty acids,
384 in the final extract provides another means to identify defective sample clean-up processes. Both
385 indicators can be used to control the quality of the extraction process on a sample-to-sample
386 basis.

387 Overall, analytical reproducibility and recovery of the proposed SPLE method is similar
388 to other analytical technologies, such as Soxhlet, MAE (microwave-assisted extraction), UAE
389 and SFE. The main advantage of the proposed SPLE method is that sample handling has been
390 significantly reduced by combining extraction and clean-up processes using a SPLE system.
391 This represented a significant reduction in solvent consumption and human manipulation, with
392 the consequent reduction in cost and environmental impact. The use of automatable SPLE
393 systems also has improved the analytical reliability and diminished accidental sample losses
394 during handling. Therefore, time required for sample processing is significantly reduced and,
395 according to our experience, a trained user can routinely process and quantify 40–50 samples
396 per week. The main drawback of the SPLE method is that commercial SPLE systems are
397 expensive and require regular maintenance that make them unaffordable unless the analysis of a
398 high number of samples is projected. This is the case of studies directed to elucidate the
399 evolution of past environments. This methodology has been optimized to meet the requirements
400 of high throughput, robustness, and small sample size associated with the stratigraphic analysis
401 of sediment cores for paleoclimatic reconstructions. We have also demonstrated that the
402 methodology provides reproducible data of paleoenvironmental indexes, such as SST, CPI and
403 ACL.

404

405 **CRediT author statement**

406 **M. Raja:** Writing – Original Draft, Supervision **J. Villanueva:** Writing – Original
407 Draft, Review & Editing, Methodology, Supervision **C. Moreu:** Investigation **M.**
408 **Giaime:** Investigation **A. Rosell-Melé:** Funding acquisition

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553

554 **FIGURE CAPTIONS:**

555 **Figure 1.** Pressurized Liquid Extraction (PLE) packed cell.

556 **Figure 2.** Recoveries of biomarkers in spiked blank (a,b,c) and sediment (d,e,f) samples
557 as a function of the extraction solvent composition. The x-axis indicates the percent of
558 modifier used in each test: DCM (blue), acetone (green), and methanol (purple). Results
559 obtained for D12-Perylene were different from the other PAH standards and are
560 represented by dotted lines. Experiments were performed in duplicate (see dots).

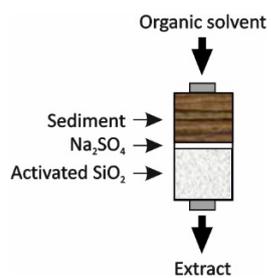
561 **Figure 3.** Recoveries of interfering polar compounds in spiked blank (a,b) and sediment
562 (c,d) samples.

563 **Figure 4.** Concentration of n-alkanes (a-c), PAHs (d-f) and alkenones (g-h) in oceanic
564 (EN651_ST04 and EN651_ST13), coastal, (ST7 and ST10), and lake (PEM and LUC)
565 sediments. The error bar indicate the standard deviation calculated from six replicates

566 **Figure 5.** Recoveries averages of internal standard of different biomarker compounds
567 (n=6) in oceanic (EN651_ST04 and EN651_ST13), coastal, (ST7 and ST10), and lake
568 (PEM, HUL and LUC) sediments. Black line shows the sedimentary total organic
569 carbon (TOC) content.

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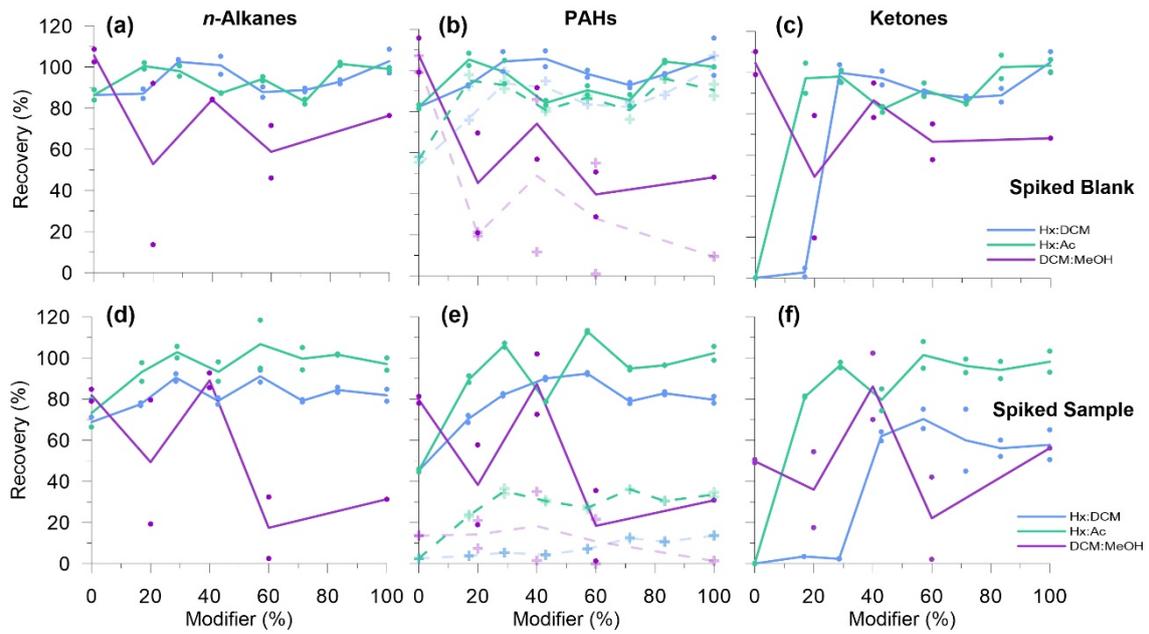


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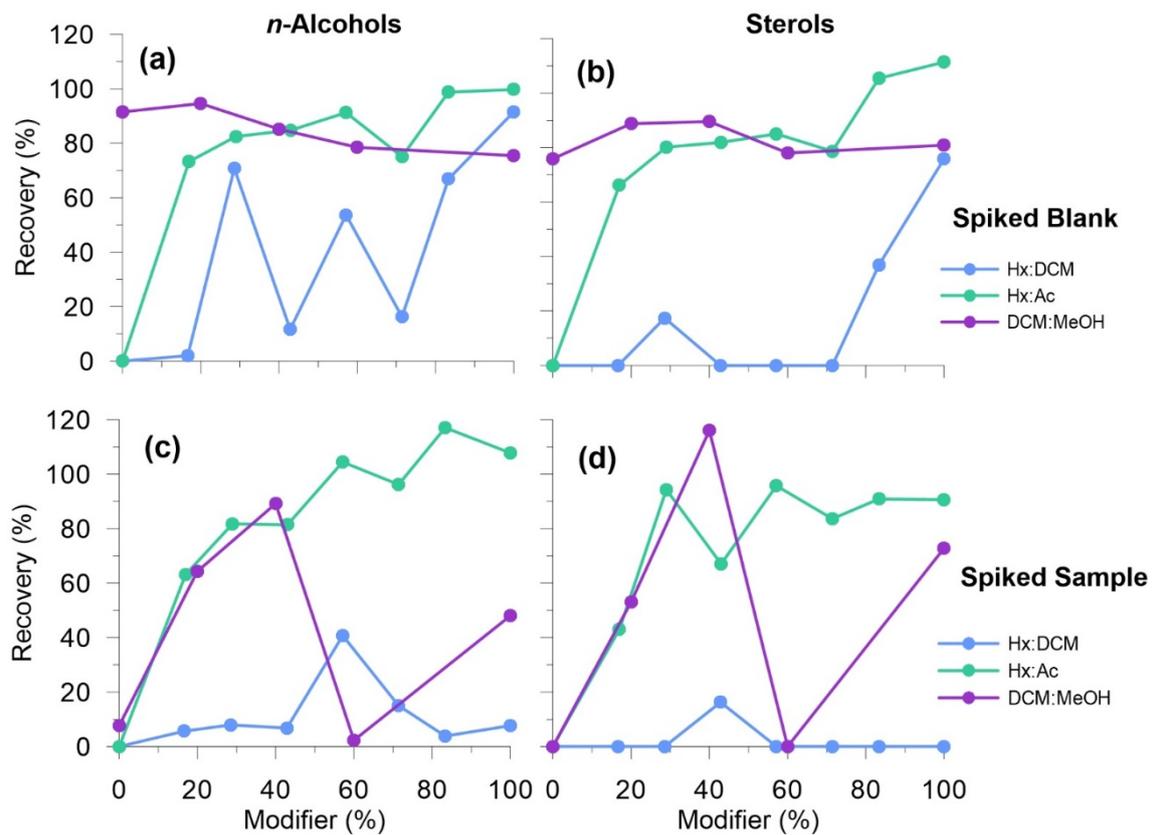
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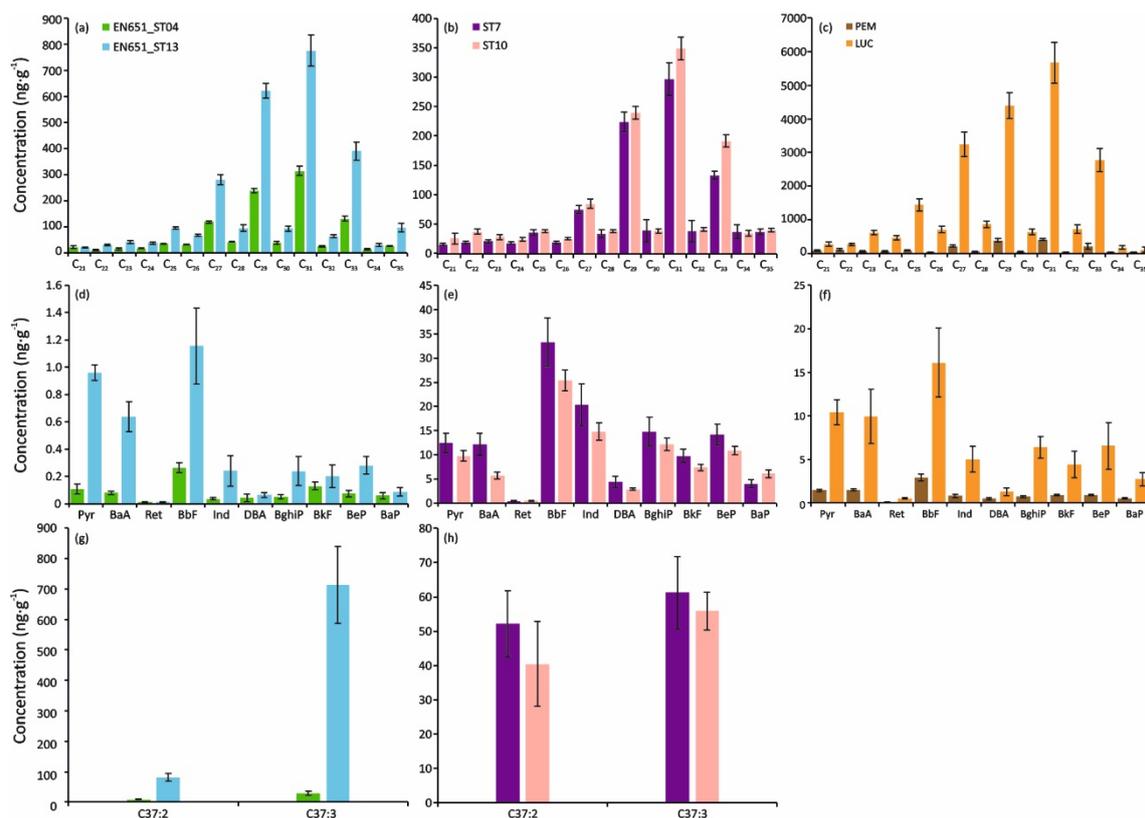
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584 **Figure 3.** Recoveries of interfering polar compounds in spiked blank (a,b) and sediment
 585 (c,d) samples.

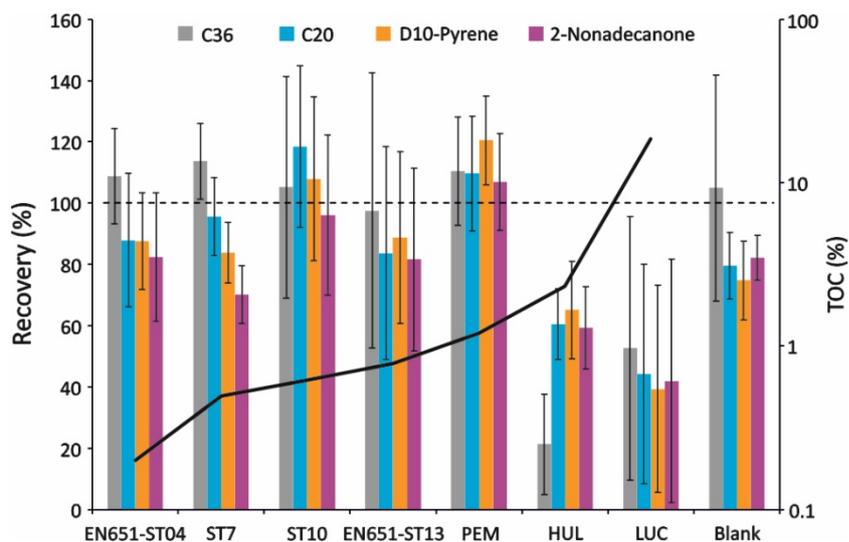
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592

593 **Figure 5.** Recoveries averages of internal standard of different biomarker compounds
 594 (n=6) in oceanic (EN651_ST04 and EN651_ST13), coastal, (ST7 and ST10), and lake
 595 (PEM, HUL and LUC) sediments. Black line shows the sedimentary total organic
 596 carbon (TOC) content.

Table 1. Location of samples and type of sediment.

Sample	Type of sediment	Latitude	Longitude	Water depth (m)
EN651-ST04	Oceanic	5.00	-35.79	3993
EN651-ST13	Oceanic	10.36	-20.99	5130
MERS-ST7	Coastal	40.07	1.53	1476
MERS-ST10	Coastal	40.30	0.80	70
PEM	Lake	39.39	-2.88	-
LUC	Lake	42.59	-7.11	-
HUL	Lake	33.08	35.61	-

Table 2. MS parameters used in biomarkers quantification.

Biomarker class	Compound	Internal Standard (IS)	$m \cdot z^{-1}$ (IS $m \cdot z^{-1}$)
<i>n</i> -Alkanes	C ₂₁ - C ₃₅	C ₃₆	99.0 (99.0)
PAHs	Perylene (Per)	D12-Perylene	252.0 (264.0)
	Benzo[a]pyrene (BaP)	D10-Pyrene	252.0 (212.0)
	Benzo[e]pyrene (BeP)		
	Benzo[b]fluorantrene (BbF)		
	Benzo[k]fluoroanthracene (BkF)		
	Pyrene (Pyr)	D10-Pyrene	202.0 (212.0)
	Fluoranthracene (Flu)	D10-Pyrene	276.0 (212.0)
	Indenopyrene (Ind)		
	Benzo[g,h,i]perylene (BghiP)		
	Dibenzoanthracene (DBA)		
Retene (Ret)			
Benz[a]anthracene (BaA)	D10-Pyrene	228.0 (212.0)	

Table 3. Optimisation of SPLE conditions and concentration ratios (CR).

Test #	Temp. (°C)	Time (min)	Solvent Flow (mL·min ⁻¹)	CR <i>n</i> -Alkanes	CR PAHs	CR Ketones	CR <i>n</i> -Alcohols	CR Sterols
1	75	5	1	56	49	36	14	0
2	75	5	2	88	85	67	30	1
3	75	10	1	83	77	48	15	0
4	75	10	2	92	96	93	60	1
5	100	5	1	45	43	14	4	0
6	100	5	2	93	91	56	23	0
7	100	10	1	90	90	59	20	0
8	100	10	2	94	95	92	57	1
9	150	5	1	71	66	20	6	0
10	150	5	2	96	99	85	74	4
11	150	10	1	89	88	55	49	8
12	150	10	2	93	100	97	92	85
13	200	5	1	97	99	89	84	65
14	200	5	2	95	95	79	76	48
15	200	10	1	94	100	93	90	95
16	200	10	2	97	100	99	95	100

Table 4. Summary of data obtained during method validation. Concentration values are expressed in ng·g⁻¹ and sea-surface temperatures in °C.

	Oceanic sediment (EN651_ST04)				Coastal sediment (ST7)				Lacustrine sediment (PEM)			
	<i>n</i> -Alkanes	PAHs	Alkenones	s.d.	<i>n</i> -Alkanes	PAHs	Alkenones	s.d.	<i>n</i> -Alkanes	PAHs	Alkenones	s.d.
Sum	1.07 ×10 ³	0.86	39	-	1.04 ×10 ³	126	114	-	1.84 ×10 ³	10.1	<LOD	-
CV (%)	3.4	9.7	21.3	-	3.9	17.1	17.3	-	12.5	9.7	n.d.	-
Uk'37	-	-	0.768	0.022	-	-	0.540	0.019	-	-	n.d.	n.d.
SST	-	-	16.7	0.5	-	-	11.5	0.4	-	-	n.d.	n.d.
CPI	5.7	-	-	0.34	5.8	-	-	0.45	7.0	-	-	0.68
ACL	29.9	-	-	0.05	30.1	-	-	0.03	29.6	-	-	0.21
	Oceanic sediment (EN651_ST13)				Coastal sediment (ST10)				Lacustrine sediment (LUC)			
	<i>n</i> -Alkanes	PAHs	Alkenones	s.d.	<i>n</i> -Alkanes	PAHs	Alkenones	s.d.	<i>n</i> -Alkanes	PAHs	Alkenones	s.d.
Sum	2.73 ×10 ³	3.88	796	-	1.23 ×10 ³	95.5	96.4	-	22.3 ×10 ³	63.3	<LOD	-
CV (%)	6.5	21.1	17.2	-	4.3	8.8	16.2	-	10.6	20.4	n.d.	-
Uk'37	-	-	0.897	0.009	-	-	0.587	0.064	-	-	n.d.	n.d.
SST	-	-	19.6	0.2	-	-	12,6	1.5	-	-	n.d.	n.d.
CPI	6.2	-	-	0.30	5.3	-	-	0.11	5.5	-	-	0.32
ACL	30.0	-	-	0.04	30.3	-	-	0.03	29.6	-	-	0.03