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Abstract: Sediments contaminated by Hg and As from two historical mining areas have been deposited in the Nalón estuary (Asturias, northern Spain) since 1850. Total mercury (Hgtotal) concentrations in the sediments range from 0.20 $\mu\text{g}\cdot\text{g}^{-1}$ to 1.33 $\mu\text{g}\cdot\text{g}^{-1}$, most of it in the form of sulphides. Concentrations of methylmercury (303.20-865.40 $\text{pg}\cdot\text{g}^{-1}$) are up to two orders of magnitude lower than the concentration of Hgtotal. Total As concentration (Astotal) is enriched compared to the background level for the area. The relative abundance of As(V) on As(III) in the sediments ranges from 97.6% to 100%, whereas inorganic Hg accounts for more than 99% of the total Hg. The occurrence of the most toxic species, inorganic As(III) and organic methylmercury, seem to be related to redox conditions together with the amounts of sulphur which act as natural barriers which inhibit the biological and chemical speciation processes. Despite the high amounts of Hg and As present in the sediments, their transference to the water column appear to be limited thus converting sediments in an effective sink of both elements. Special attention should be paid to potential variations of the environmental conditions which might increase the element mobility and exchange between sediments and the water column.

Occurrence and speciation of arsenic and mercury in estuarine sediments affected by mining activities (Asturias, northern Spain)

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1 **Abstract**

2

3 Sediments contaminated by Hg and As from two historical mining areas have been deposited
4 in the Nalón estuary (Asturias, northern Spain) since 1850. Total mercury (Hg_{total})
5 concentrations in the sediments range from $0.20 \mu g \cdot g^{-1}$ to $1.33 \mu g \cdot g^{-1}$, ~~and only a small amount~~
6 ~~of this, is available for the methylation process because most of Hg derived from mining~~
7 ~~occurs most of it~~ in the form of sulphides. Concentrations of methylmercury ($303.20-865.40$
8 $\mu g \cdot g^{-1}$) are up to two orders of magnitude lower than the concentration of Hg_{total} . Total As
9 concentration (As_{total}) is enriched compared to the background level for the area. Speciation
10 analyses indicate that negligible quantities of organic As species are present; rather, the
11 inorganic species (As(III)) and As(V)) are dominant. As (III) concentrations range from values
12 $<0.10 \mu g \cdot g^{-1}$ to $1.356 \mu g \cdot g^{-1}$, whereas As (V) concentration falls between 16.89 and 64.96
13 $\mu g \cdot g^{-1}$. The relative abundance of As(V) on As(III) as a percentage of As_{total} ($\%As(V)$) in the
14 sediments ranges from 97.6% to 100%, whereas inorganic Hg accounts for more than 99% of
15 the total Hg. The occurrence of the most toxic species, inorganic As(III) and organic
16 methylmercury, seem to be related to redox conditions together with the amounts of sulphur
17 which act as natural barriers which inhibit the biological and chemical speciation processes.
18 Despite the high amounts of Hg and As present in the sediments, their transference to the
19 water column appear to be limited thus converting sediments in an effective sink of both
20 elements. Special attention should be paid to potential variations of the environmental
21 conditions which might increase the element mobility and exchange between sediments and
22 the water column. a maximum of 2.1% of the As_{total} is present as As (III). The clay fraction is the
23 main grain size sediment component that entraps Hg and As, and the port areas act as a sink
24 for both elements. In spite of the high total concentrations detected for As compared to Hg,
25 the speciation analysis, their grain size, and their geochemical characteristics, together with
26 evidence of bioaccumulation in the coastal food web, suggest that transference from

27 | ~~sediments to the aquatic environment is more remarkable for the Hg species than for the As~~
28 | ~~species.~~

29

30

31

32 **Keywords:** Mercury, Arsenic, sediments, estuary, speciation, mining

33 1. Introduction

34 Among aquatic environments, coastal areas are particularly fragile and are very often
35 threatened by significant direct and indirect anthropogenic pressures. Specifically, in coastal
36 marine environments, estuaries are ecosystems of global concern ~~because as~~ they exhibit high
37 biological productivity due to the special conditions produced by the mixing of fresh water and
38 seawater. Estuarine sediments also act as 'reservoirs' of contaminants and are therefore
39 ~~recognized~~ recognised as valuable indicators of the degree of contamination of these aquatic
40 environments (Liu et al., 2015; Sarkar et al., 2017). Contamination of estuaries ~~with~~ by trace
41 metals and metalloids is an important environmental issue due to their potential transfer from
42 sediments into the water column and their subsequent bioaccumulation in aquatic organisms
43 (Van el et al., 2017; Yu et al., 2017).

44

45 The Asturias region (north of Spain) is ~~characterized~~ characterised by one of the most
46 important coastal areas of the country ~~and one that which it~~ has not been high significantly
47 impacted by anthropogenic activities. Consequently, the monitoring and management of this
48 coastal ecosystem is of special concern in maintaining a good level of ecological quality.
49 ~~However,~~ several estuarine areas along the Asturias coast are very sensitive to possible
50 contamination by sources located inland. Among them, the Nalón estuary is the most
51 important transitional environment, connecting the Cantabrian Sea (the Biscay Bay) and the
52 Nalón River, which is the main hydrographical system of northern Spain. The Nalón estuary
53 contains remarkable anthropogenic contributions of trace metal(oid)s, especially arsenic (As)
54 and mercury (Hg) due to the long-term activity of two mining areas, which have been
55 identified as 'hotspots' for these elements (Loredo et al., 1999; Loredo, 2000; Fernández-
56 Martínez et al., 2005). Several studies have been conducted over the last two decades to
57 clarify the sources, processes, and dynamics of As and Hg in different environmental segments,

58 such as soils, mine tailings, and fresh and ground waters of the Nalón River basin (e.g. Loredó
59 | et al., 2010; Silva et al., 2014; Ordoñez et al., 2014). ~~R~~However, research into the impact of
60 | these elements in the Nalón River estuarine system has only recently begun. For instance, As
61 | and Hg profiles in saltmarsh sediments and in some boreholes in the main estuarine channel
62 | have been studied in detail to reconstruct the long-term contamination history of the area and
63 | to establish preliminary geochemical background values for both elements (García-Ordiales et
64 | al. 2015, 2016, 2017). Prior to this research, there have been no published reports quantifying
65 | Hg and As abundances across the entire estuarine system and determining their areal
66 | distribution as well as their sources. The only exception is the measurements performed by the
67 | Asturias Regional Port Authority on recent estuarine sediments, which ~~demonstrated~~showed
68 | significant concentrations of Hg ($0.15\text{--}1.56\ \mu\text{g}\cdot\text{g}^{-1}$) and As ($20.00\text{--}39.20\ \mu\text{g}\cdot\text{g}^{-1}$) in the period
69 | 2003–2011. However, the toxicity and mobility of As and Hg in estuarine sediments strongly
70 | depend on their specific chemical forms along with their binding with sediment particles
71 | ([Eggleton and Thomas, 2004](#); [Vidmar et al., 2017](#)). In this context, our work aims to
72 | investigate not only the total concentration distribution of these two elements but also their
73 | speciation in surface sediments, as well as the relationships between sediment particles and
74 | the specific geochemical conditions of the study area. Such information may be helpful in
75 | understanding the mechanisms influencing metal mobility from sediments and may also help
76 | ~~to~~ provide preliminary predictions of the bioavailability, if any, of these two metal(oid)s
77 | ([Pinedo-Hernández et al., 2015](#); [Beckers and Rinklebe, 2017](#)) with regard to possible effects of
78 | interventions and maintenance, such as dredging operations in the estuary for navigation
79 | purposes.

80

81 **2. Material and methods**

82 **2.1 Environmental setting**

83

84 The Nalón River estuarine system in the Asturias region ~~encompasses only a small part of the~~
85 ~~entire hydrographical basin (covers an area of 4.5 km²), which is only a small part of the entire~~
86 ~~hydrographical basin, which and~~ extends 4,777 km² inland. The estuary is over 6 km long and its
87 upper limit is established according to the salt wedge extension, which moves upstream
88 following the tidal range. The main estuarine channel has retained its natural river banks, with
89 the exception of the lower section, close to the inlet, where two small regional ports were built
90 (San Juan de la Arena ~~y and~~ San Esteban de Pravia in Fig. 1), which altered the natural
91 morphology and sedimentation dynamics of the outer part of the estuarine system (Flor-
92 Blanco et al., 2015). The main channel is more than 2 m deep and is affected by an annual
93 meso-tidal range between 1.0 and 4.2 m; in general, the tides are over 2 m ~~during for~~ more
94 than 70% of the year (Flor et al., 1998). ~~The profile of the estuary is sinuous, as meanders have~~
95 ~~developed throughout its length, which is typical for an estuary with a strong fluvial influence~~
96 ~~and transgressive sedimentary filling on the lower fluvial section. The dynamics of water~~
97 ~~circulation in the estuarine region strictly depend on the tidal regime. During neap tides, the~~
98 ~~horizontal salinity gradient is the key driving force for estuarine circulation, whereas during~~
99 ~~spring tides, almost total vertical mixing governs the estuary hydrodynamics (Flor et al., 1998).~~
100
101 ~~Currently, t~~The main activity in the estuarine area is tourism, including recreational uses
102 (fishing and yachting). ~~However, the estuary was an important industrial port for raw materials~~
103 ~~export purposes in the recent past. Upstream, in the Nalón River basin, are located s~~Several
104 urban settlements and some agricultural and mining-industrial sites ~~are located in the Nalón~~
105 ~~River basin~~. Among the mining-industrial activities, which have been active since the end of the
106 eighteenth century, the most important are related to the ~~remarkable major~~significant
107 deposits of coal, mercury, gold, and iron as well as other polymetallic ores containing copper,
108 lead, and zinc found in the area. ~~Within Among~~ the metals extraction ~~activity, industry,~~ Hg
109 mines have been especially important; ~~as~~ Asturias is the second largest Hg producer in Spain.

110 The most notable Hg deposits in Asturias are La Peña-Terronal in Mieres and La Soterraña in
111 Pola de Lena, ~~which are located in the Nalón River basin~~. The main metal ore of these deposits
112 is cinnabar [HgS], in association with low amounts of native Hg, as well as ~~important-significant~~
113 amounts of As-bearing minerals such as realgar [AsS] and pararealgar [As₄S₄], orpiment [As₂S₃],
114 and arsenic-rich pyrite (Ordoñez et al. 2013). Despite the cessation of mining activity several
115 decades ago, drainage waters flowing out from ~~the~~ inactive mines ~~where low remediation~~
116 ~~actions were implemented (Rodríguez-Pérez et al., 2014), and~~ their tailings and residual
117 deposits may still affect the quality of the fluvial waters and the sediments downstream of the
118 sources (Loredo et al., 2003; Ordoñez et al., 2013). ~~and~~ ~~The contamination has reached the~~
119 ~~estuarine environment where the historical accumulation of As and Hg in the saltmarsh and~~
120 ~~estuary channel has been correlated with~~ ~~to the historical Hg mining activity located about 40~~
121 ~~km upstream in the Nalón river drainage basin (Garcia-Ordiales et al., 2015, 2016, 2017).~~

122

123 2.2 Sampling and analysis

124

125 A total of 56 sediment samples were collected from the estuary (Fig. 1). When accessible, both
126 sides of the river banks were sampled together with the main channel area, representing the
127 whole estuarine sector of the active stream of the Nalón riverbed. Surface sediments (0-5 cm)
128 were collected by means of a plastic shovel from the river banks while they were exposed to
129 air during ebb tide conditions or by a stainless-steel Van Veen grab from the submerged parts
130 of the estuary. ~~About~~ ~~Approximately~~ 1 kg of sediments was collected from each sampling
131 point, homogenised in the field, stored in double zip-lock bags, and transported to the
132 laboratory in a portable fridge. ~~Each sample was divided into~~ ~~split in different representative~~
133 ~~subsamples, using a riffle-type sample splitter with a removable hopper.~~ Grain size and total
134 elemental content were determined in air-dried samples. For grain-size analysis, an aliquot of
135 each sample was treated with a solution of 3% (v/v) H₂O₂ for 48 h to remove most of the

136 organic matter. The sample was then wet sieved at 2 mm and analysed with a Fritsch
137 ANALYSETTE MicroTec Plus 22. Grain-size data are ~~synthesized~~synthesised using the classical
138 sand-silt-clay notation according to the Udden-Wentworth scale. Major and trace elements
139 were determined on 0.5 g freeze-dried samples, which were digested in a microwave ~~with~~
140 using a multi-acid solution (HCl–HNO₃–HF) and analysed by inductively coupled emission
141 spectroscopy (ICP-ES) and inductively coupled plasma mass spectroscopy (ICP-MS; Bureau
142 Veritas, Vancouver, Canada). The accuracy of the results was verified by comparison against
143 analysis of Standard Reference materials [PACS-2 \(marine sediment\)](#), [RTC-CRM026-050 \(sandy](#)
144 [loam soil\)](#) and [CRM042-056 \(loam soil\)](#). Percentage recoveries for all elements considered
145 ranged from 93% to 106%.

146

147 Total carbon (C_{tot}), nitrogen (N_{tot}), and sulphur (S_{tot}) content were measured by an Elemental
148 Vario EL Cube CNHS. Organic carbon (C_{org}) in sediments was determined through progressive
149 acidification with HCl (0.1–1.0 M) at a combustion temperature of 920 °C according to the
150 method ~~set out by~~^{of} Hedges and Stern (1984). Acetanilide was used as the standard
151 compound for calibration. The detection limit for C_{org} and C_{tot} was 0.1%. The precision for C_{tot},
152 C_{org}, and N_{tot} detection was 3%.

153

154 ~~Twenty sediment samples were selected For for~~ the Hg and As speciation analysis; ~~twenty~~
155 ~~sediment samples were selected~~ (Fig. 1). These samples were chosen based on the results
156 obtained from the total concentration analyses and following the hydrodynamic criteria, which
157 were intended to cover the different sectors of the estuary and discover possible significant
158 differences among them. For As species, 0.1 g of sediment was placed together with an
159 extracting agent (1 M H₃PO₄ + 0.1 M ascorbic acid) in a microwave vessel. The extracts were
160 diluted (1:5) and filtered (<0.45 μm). The As species were separated ~~by~~ using a mobile phase of
161 2 M phosphate buffered saline (PBS)/0.2 M EDTA (pH = 6.0) in a separation column with a 1260

162 Infinity high-performance liquid chromatograph (HPLC) coupled to a 7700 ICP-MS (Agilent
163 Technologies). The accuracy of the results was verified by comparing the total arsenic
164 concentration with the sum of all species concentrations determined. [The recovery of As
165 speciation ranged from 95% to 106%.](#)

166
167 Organic Hg was analysed using the methodology proposed by Valega et al. (2006). As organic
168 mercury compounds other than methylmercury, such as dimethylmercury, have rarely been
169 detected in sediments (Ullrich et al., 2001; Mason, 2013), the organic mercury measured may
170 be considered ~~to be~~ methylmercury. In brief, sediment samples were first treated with an acid
171 solution (KBr/H₂SO₄/CuSO₄), followed by extraction of the organic Hg halide with toluene and
172 back-extraction with an aqueous sodium thiosulphate solution. The analyses were carried out
173 using an HPLC-ICPMS (Agilent Technologies). The accuracy of the results was verified against
174 the estuarine sediment IAEA-405 certified reference material (recovery range from 94% to
175 102%).

176 [Statistical analysis was performed using the SPSS 19.0 and Minitab V.15 for Windows software
177 and dispersion maps were produced using Surfer 9.8.669 software \(©Golden Software Inc.
178 2009\) and interpolating data by applying the Kriging algorithm.](#)

180 3. Results and discussion

181 3.1 General characteristics of sediments

182
183 Results of the grain size and geochemical analysis from each sampled area are presented ~~in~~
184 [Table 1 as supplementary material \(Table 1\)](#). From the grain-size distribution of the Nal3n
185 estuary sediments (Fig. 2), it is apparent that the sandy fraction is usually predominant, with ~~a~~
186 high variability (~~, ranging between~~ 38.4% and 80%). The ~~sandy-silty~~ fraction can be considered
187 subordinate to the ~~silty-sandy~~ fraction (range, 18.7% to 52.7%), and the clayey ~~fraction is the~~

188 ~~smallest component with the most consistent range~~ component is smaller but almost constant
189 (~~range, from~~ 1.3% to 9.9%).

190

191 The estuary is characterised by a specific energy pattern ~~resulting that results~~ from the
192 interactions ~~among of~~ wave motion, tidal currents, and river energy. The energy pattern
193 governs the transport and distribution pattern of suspended matter in the estuary. In the
194 upper section of the estuary, where the fluvial flow is dominant, the sandy component
195 increases as the muddy fraction decreases. This is attributed to the effects of the velocity of
196 water due to the ~~increased shallowness of the~~ channel ~~depth~~ (from 1 to 2.5 m) in that section
197 of the estuary. In the lower section of the estuary (up to about 5 m depth on average), the
198 construction of two jetties has changed the morphology of the area and has affected
199 sedimentation; the sandy component increases in the areas most exposed to tidal flows of the
200 channel and in the San Juan de la Arena area. This ~~fact-increase~~ may be attributed to the
201 energy of the depositional medium (Flor et al., 1998), which ~~locally suffers is affected by~~ wave
202 action and tidal currents, processes ~~which that~~ remove fine sediments (Sutherland et al., 2015)
203 from the channel and deposit them ~~nearby~~ on the estuarine banks ~~nearby~~. In contrast, in the
204 San Esteban port area, a significant increase is seen in the muddy fraction (silt ~~+and~~ clay). The
205 morphology of this area, where a breakwater protects the jetty, limits water mixing and
206 circulation in the inner part of the port basin, converting this area into a ~~sort of~~ sink for fine-
207 sized particles which remain entrapped.

208

209 Concentrations of C_{tot} (1.62–7.29%), N_{tot} (0.08–0.43%), and C_{org} (1.45–6.33%) (Fig. 3) are
210 strongly correlated to the clay percentage in the sediments ($r^2 = 0.886$, $r^2 = 0.931$, and $r^2 =$
211 0.942 , respectively, $p < 0.001$) (Fig. 1, supplementary material), as the finest fraction easily
212 adsorbs organic compounds in the bottom sediments. As a consequence, ~~t~~he highest
213 concentrations of these ~~variables-parameters~~ were detected in the inner part of the San

214 Esteban port basin and in the San Juan de la Arena port [where carbon and nitrogen preferably](#)
215 [tend to accumulate](#). Conversely, the lowest concentrations are progressively found in the
216 upper section of the estuary, where the coarse component appears to be more relevant.
217 [Similarly, also in the marine area in front of the estuary, a decrease in concentration occurs](#)
218 [since the sediment grain size is coarse due to the action of the marine currents and wave](#)
219 [motion \(Flor et al., 1998\)](#). Carbon in the particulate matter (C_{tot}) is mainly organic, C_{org} (avg.
220 $87.1 \pm 0.08\%$), from a minimum of 70% to a maximum value of 99%. The correlation between
221 C_{org} and sediment grain-size can be [partially](#) explained by the similar settling velocity (i.e.
222 hydrodynamics) of the particulate organic constituents and the fine-grained mineral particles
223 (Tyson 1995). Total nitrogen (N_{tot}) is significantly related to C_{org} ($r^2 = 0.866$, $p < 0.01$), and
224 plotting N_{tot} against C_{org} results in an intercept of 0.047, which indicates the percentage of N_{tot}
225 at 0% value of C_{org} , showing that there is a significant fraction of total N_{org} in the samples.
226 Calculated C_{org}/N_{tot} ratios, commonly quoted as C/N values together with $\delta^{13}C$ and $\delta^{15}N$, are
227 widely used as a tool for discriminating marine from terrestrial organic matter in sediments (Xu
228 et al., 2017). [Although the \$\delta^{13}C\$ and \$\delta^{15}N\$ isotopic composition of organic matter \(OM\) was not](#)
229 [determined in this study](#) ~~Then~~ [At this point](#), some assumptions can be made [merely](#) on the basis
230 of the C/N ratio (Covelli et al., 2012 and references therein). In the estuary sediments, the C/N
231 ratio ranges from 9.38% to 18.18% (avg. $13.02 \pm 2.18\%$), which suggests that the organic
232 matter in these sediments is prevalently terrigenous, according to Meyers (1997). This result is
233 in [accordance agreement](#) with the dynamics of the estuary [as](#) described by Flor et al. (1998),
234 where the supply of material from the river basin is the predominant source of sediments and
235 organic matter into the estuary.

236

237 In general, the distribution of the sulphur (S) (Fig. 3) concentration (0.27–2.18%) is closely
238 associated with the fine grain-sized sediments ($r^2 = 0.838$, $p < 0.01$) [\(Fig.1, supplementary](#)
239 [material\) since sulphur is primarily associated with iron sulphide in the Nalón estuary. Indeed,](#)

240 the main rivers of the drainage basin provide an abundant supply of iron-rich terrigenous
241 siliciclastic debris (Freslon et al., 2014). On the other hand, ~~showing a dispersion similar to~~
242 that of the clay component across the entire estuary. Also, ~~the S~~ displays a positive
243 correlations ~~between S and~~ with C_{org} ($r^2 = 0.802$, $p < 0.01$), and the average C/S ~~ratio value for~~
244 the sediments ($3.43 \pm 0.97\%$), ~~suggest that sediments were deposited under oxydisizing~~
245 conditions ~~generated at the bottom waters~~ is comparable to that proposed for “normal” marine
246 conditions ($2.8 \pm 1.5\%$) by other authors (Berner 1982; Raiswell and Berner, 1985); ~~normal~~
247 conditions correspond to the characteristics of an oxygenated environment. ~~However, low~~
248 C/S values, usually associated with anoxic or semi-anoxic depositional environments (Burone
249 et al., 2003) were detected ~~the obtained results with samples from~~ in the San Esteban port
250 basin ~~displayed the lowest C/S ratio values (2.40–2.81%), suggesting partial hypoxic or anoxic~~
251 conditions ~~would occur~~ in this area. ~~during deposition of sediments may have occurred in~~
252 this area. Overall, ~~Low C/S ratios are associated with anoxic or semi-anoxic depositional~~
253 environments, with potentially high sulphate reduction (Burone et al., 2003). ~~Among the~~
254 obtained results, samples from the San Esteban port basin displayed the lowest C/S ratio
255 values (2.40–2.81%), suggesting that remineralization processes through sulphate reduction
256 under hypoxic or even anoxic conditions in the surface sediments may have occurred in this
257 area.

258

259 **3.2 Arsenic in surface sediments: occurrence and speciation**

260

261 Total arsenic concentrations (As_{tot}) range from 20.10 to 68.10 $\mu\text{g}\cdot\text{g}^{-1}$ (avg. $27.43 \pm 9.96 \mu\text{g}\cdot\text{g}^{-1}$);
262 ~~as~~ the highest concentrations were found in the lower sector of the estuary, especially in the
263 San Esteban port basin.

264

265 Concentrations of As_{tot} are well above the local background level estimated by Garcia-Ordiales
266 et al. (2016) for the Nalón estuary ($9.00 \pm 0.94 \mu\text{g}\cdot\text{g}^{-1}$) and the range of 5–15 $\mu\text{g}\cdot\text{g}^{-1}$ determined
267 for uncontaminated nearshore marine and estuarine sediments (Moore and Ramamoorthy,
268 1984; Francesconi and Edmonds, 1997), ~~showing an important enrichment of this element in~~
269 ~~the surface sediments~~. These results are consistent with the concentrations detected in core
270 profiles from the same area (Garcia-Ordiales et al., 2015, 2016, 2017), ~~where the relatively~~
271 ~~high concentrations of As_{tot} in recent sediments were attributed to contributions from mining~~
272 ~~wastes located within the river basin~~. Due to ~~the~~ long-term extraction activity, the As_{tot}
273 background values have significantly increased, surpassing the consensus-based threshold
274 levels (MacDonald et al., 2000) such as the Threshold Effect Concentration (As_{TEC} , 9.97
275 $\mu\text{g}\cdot\text{g}^{-1}$), and the Probable Effect Concentration (As_{PEC} , 33.0 $\mu\text{g}\cdot\text{g}^{-1}$), the latter of which is
276 exceeded by 86% of the samples.

277

278 The concentration of As_{tot} in the sediments was closely related to the amount of the
279 corresponding clay fraction ($r^2 = 0.831$, $p < 0.01$) and S ($r^2 = 0.825$, $p < 0.01$) ~~and C_{org} ($r^2 = 0.757$,~~
280 ~~$p < 0.01$)~~ contents (Fig. 2, supplementary material), suggesting that particle size and sulphide
281 ~~control the As retention in the solid phase and as a consequence its dispersion throughout in~~
282 ~~the estuary. The lower sector of the estuary, where a major proportion of fine particles and S~~
283 ~~contents occur, showed demonstrated the highest concentrations of As in the sediments (Fig.~~
284 ~~4), and this is especially remarkable in the San Esteban port basin that which acts as a sink for~~
285 ~~fine-sized particles.~~

286

287

288 Speciation analysis of As showed that the occurrence of the organic species
289 (monomethylarsonate and dimethylarsinate) was negligible; the inorganic arsenic species are
290 dominant in the sediments (Fig. 3, supplementary material). Moreover, within the inorganic As

291 species, arsenate was the main species-one found in the sediments due to the oxidizing
292 oxidising conditions in the aquatic environment based on the C/S values. The C_c concentration
293 of As(V) falls in the range of 16.89–64.96 $\mu\text{g}\cdot\text{g}^{-1}$ (avg. $31.39 \pm 12.85 \mu\text{g}\cdot\text{g}^{-1}$), ~~whereas its~~
294 relative abundance in comparison to the As_{tot} concentration (%As(V)) in the sediments ranges
295 from 97.6% to 100%. ~~This As(V) abundance provides relationships with N_{tot} ($r^2 = 0.813$, $p <$
296 0.01), C_{org} (0.783 , $p < 0.01$), and clay contents ($r^2 = 0.782$, $p < 0.01$) similar to those observed for~~
297 As_{tot}; ~~it also shows an analogous dispersion of their concentrations in the estuary. Whereas The~~
298 As(III) concentrations range from <DL to $1.356 \mu\text{g}\cdot\text{g}^{-1}$ (avg. $0.78 \pm 0.36 \mu\text{g}\cdot\text{g}^{-1}$). In the samples
299 from lin the upper-middle sector of the estuary, which is under the direct influence of the
300 fluvial inputs, this As (III) species was/were not detected possibly as a consequence of the
301 redox conditions in the sediments (avg. C/S 3.90 ± 1.40) which may have potentially produced
302 As(III) although below the detection limit. On the contrary, in the lower sector, where marine
303 conditions occur, the majority of the samples showed detectable amounts of As(III). The
304 arsenite component was significantly and positively correlated to As_{tot} ($r^2 = 0.784$, $p < 0.05$),
305 whereas a negatively relationship correlated to with the C/S ratio value ($r^2 = -0.742$, $p < 0.05$)
306 was detected (Fig. 5a). This negative correlation suggests that the redox conditions of the
307 sediments are/is the key factor of the presence seems to govern the amounts of arsenite
308 entrapped in the sedimentary matrix, where As(III) reached its maximum in those samples
309 wherein the C/S ratio is indicative of important anoxic or semi-anoxic conditions. The
310 relationship between redox conditions and the amounts of the As(III) species in sediments has
311 already been extensively studied by different various authors (e.g. Rochette et al. 1998, Foster,
312 2003; Mudhoo et al., 2011; Shaheen et al., 2016). The same authors demonstrated that
313 reducing conditions can increase As(III) concentrations by converting As(V) into As(III).
314 Conversely, the relative abundance of As(III) with respect to the As_{tot} concentration in the
315 samples, where detectable, range from 1.0% to 2.1% and depends on the C/S ratio ($r^2 = -0.813$,
316 $p < 0.05$) with a major proportion in the samples located at the San Esteban port basin.

317 However, the low proportion of As(III) with respect to the As_{tot} concentration (from 1.0% to
318 2.1%), despite the redox conditions (Frohne et al., 2011), suggests that the reduction of As (V)
319 to As(III) is inhibited, thus decreasing the potential release of the most mobile and toxic As (III)
320 (Pierce and Moore, 1982). In the Nalón estuary, seawaters show more than 100 mg L⁻¹ of total
321 SO₄²⁻ at Eh levels greater than 100mV and it is expected that large amounts of this SO₄²⁻
322 absorbed by the sediment potentially stabilize As by forming complex ligands (Sparks, 1999;
323 LeMonte et al., 2017). The preferential or concurrent SO₄²⁻ reduction process may preserve
324 occluded As (V) and resulting in an inhibition of As(V) reduction (Burton et al., 2013), which is a
325 possible explanation for the low proportion and amounts of As(III) detected in the sediments.

326
327
328 As it is well known that the As species entrapped in sediments may eventually be transferred
329 to biota (Watts et al. 2013), it can be useful to evaluate the speciation analysis by comparing
330 our results with previous research on trace elements and biota from nearby coastal areas
331 (Besada et al., 2014). In those sectors of the coast affected by the Nalón River supply, the As
332 concentration in tissues from filter feeder organisms varied from 10 to 12 µg·g⁻¹, showing that
333 the average concentration is similar to the average value (10.2 µg·g⁻¹) for the whole coast of
334 northern Spain. Consequently, in spite of the total As concentrations in the sediments, this
335 metalloid does not seem to present a significant bioaccumulation threat to organisms. This
336 evidence is in agreement with the detected As speciation in the sediments, where As(V) was
337 the dominant species. As(V) is less toxic and less mobile than As(III), because As(V) may be
338 adsorbed more strongly to sediment particles (Pierce and Moore, 1982). Since adsorption is
339 one of the most important immobilization processes for As (Matera et al., 2003), our results
340 suggest that the sequestration of arsenic in the form of As(V) in the sediment seems to reduce
341 its transference to the aquatic food chain, limiting its bioaccumulation in the biota.

342

343 3.3 Mercury in surface sediments: occurrence and speciation

344

345 The total mercury concentrations (Hg_{tot}) fall in the range of 0.10–1.33 $\mu\text{g}\cdot\text{g}^{-1}$ (avg. 0.41 ± 0.21
346 $\mu\text{g}\cdot\text{g}^{-1}$). Like As_{tot} , concentrations of Hg_{tot} exceed the estimated concentration of $0.2 \mu\text{g}\cdot\text{g}^{-1}$ for
347 uncontaminated marine sediments (Salomons and Forstner, 1984) and the background level
348 estimated for local estuarine sediments ($0.012 \pm 0.001 \mu\text{g}\cdot\text{g}^{-1}$, Garcia-Ordiales et al., 2016). In
349 addition, the Hg_{tot} concentrations were all above the Threshold Effect Concentration value
350 ($0.18 \mu\text{g}\cdot\text{g}^{-1}$), but only 3% of the samples exceed the Probable Effect Concentration value (1.1
351 $\mu\text{g}\cdot\text{g}^{-1}$).

352

353 -The distribution of the metal concentration in the surface estuarine (Fig. 5) sediments (Fig. 6)
354 is quite similar to that observed for As_{tot} (Fig. 4) and the highest values for Hg_{tot} are also found
355 in the port basin of San Esteban de Pravia. The two elemental concentrations are strongly
356 correlated ($r^2 = 0.884$, $p < 0.01$) (Fig. 2, supplementary material). This relationship has already
357 been reported by Silva et al. (2014) for the sediments of the Nalón river drainage basin and by
358 Garcia-Ordiales et al. (2017) for the saltmarsh sediments of its estuary. This strong correlation
359 supports a mutual origin associated with the sources identified in the mining districts and the
360 ~~subcon~~sequent common mechanism of dispersion along the river basin estuary. ~~I~~However, the
361 correlations observed between Hg_{tot} ~~and the other geochemical parameters with grain sizes,~~
362 C_{org} and S concentrations suggest ~~the~~ adsorption mechanisms ~~effor Hg are~~ different from those
363 hypothesised for As_{tot} . Concentrations of Hg_{tot} were closely related to the amount of C_{org} ($r^2 =$
364 0.896 , $p < 0.01$), clay ($r^2 = 0.843$, $p < 0.01$), and S ($r^2 = 0.782$, $p < 0.01$) (Fig. 2, supplementary
365 ~~material~~). ~~These results demonstrated that the organic fractions were likely the most~~
366 significant factor controlling the distribution concentrations of Hg in sediments together with
367 the grain size, but also the presence of sulphide species cannot be disre~~egard~~ as reflect the
368 high correlation between Hg_{tot} and S. These correlations have already been observed in other

369 ~~global~~ coastal environments ~~of the world that have been~~ impacted by Hg mining activities (e.g.
370 Covelli et al., 2001; Conaway et al., 2003) and also in the Asturias Hg mining areas (Silva et al.,
371 2014). In this geochemical context, Hg sulphide is the most common species near the source
372 but downstream Hg could be mainly found in the form of Hg²⁺. This species could be trapped in
373 the sediment by a variety of processes such as complexing or chelation with organic ligands,
374 sorption onto colloids or Fe-Mn oxides and/or incorporation into the crystal lattice of mineral
375 grains (Biester et al., 2000; Covelli et al., 2001; Silva, 2014) as is highlighted from the observed
376 correlations.

377
378 ~~They are also in agreement with previous results obtained from the Asturias Hg mining areas~~
379 ~~(Silva, 2014). Indeed, downstream from the mine sites, the cinnabar (HgS) component~~
380 ~~dominates in the total amount of Hg found in the fluvial sediments, but as the distance from~~
381 ~~the mining sources increases, the component of Hg bound to organic matter becomes more~~
382 ~~important.~~

383 ~~As for As_{tot}, concentrations of Hg_{tot} exceed the estimated concentration of 0.2 µg·g⁻¹ for~~
384 ~~uncontaminated marine sediments (Salomons and Forstner, 1984). In addition, the local~~
385 ~~background level estimated for the estuarine sediments is 0.012 ± 0.001 µg·g⁻¹ according to~~
386 ~~García-Ordiales et al. (2016). In addition, the Hg_{tot} concentrations were detected above the TEC~~
387 ~~value (0.18 µg·g⁻¹), but only 3% of the samples exceed the PEC value (1.1 µg·g⁻¹). The~~
388 ~~concentration values of MeHg in the sediments (Fig. 65) range from 303.20 to 865.40 pg·g⁻¹,~~
389 ~~and show significant positive relationships with Hg_{tot} (r² = 0.886, p < 0.01), and C_{org} (r² = 0.700,~~
390 ~~p < 0.01), clay (r² = 0.630, p < 0.01), and S (r² = 0.548, p < 0.01). Although pore waters were~~
391 ~~not extracted from sediments to analyse hydrogen sulphide (H₂S), the estimated C/S ratio as~~
392 ~~oxic or anoxic sediments conditions, together with the strong characteristic odour emitted by~~
393 ~~some samples during field work, possibly due to the production of hydrogen sulphide (H₂S),~~
394 ~~suggest the occurrence of anoxic conditions where remineralization of the organic matter via~~

395 ~~sulphate reduction is presumably involved, as stated above for As.~~ The importance of the
396 microbial activity of sulphate-reducing bacteria in mercury methylation processes has been
397 demonstrated (e.g. Gilmour et al., 1992), and the most important parameters controlling
398 methylation rate are mercury ~~and~~, sulphate concentrations and the amount of organic matter
399 (e.g. Benoit et al., 1999), ~~coincident in accordance~~ with the significant correlations
400 ~~previously~~ ~~ready~~ mentioned. The ~~mapped~~ spatial dispersion of MeHg in the estuary ~~ine~~
401 ~~sediments~~ (Fig. 56) ~~demonstrated~~ ~~showed~~ that the highest levels of MeHg occurred in the San
402 Esteban de Pravia port area, whereas the lowest values were detected in the upper part of the
403 estuary. An examination of the relative abundance of MeHg versus Hg_{tot} ~~in the sediments~~
404 allows additional insights regarding the occurrence of MeHg among the different sectors of the
405 estuary. The MeHg component ~~in the Nalón estuarine sediments (< 0.10% MeHg)~~ was similar
406 to that ~~one from of~~ other estuaries impacted by Hg mining activities (Table 21), which does not
407 generally exceed 0.5% (Conaway et al., 2003; Hines et al., 2006). In contrast, the ~~%-percentage~~
408 ~~of MeHg detected in the estuary~~ was very low compared to other estuaries where the primary
409 sources of Hg in the aquatic environment are urban, industrial, agricultural, or aerial
410 depositions, for which the MeHg component may account for values near 100% (Haris et al.,
411 2017). ~~The relationship between in situ Hg speciation and methylation is not easy to represent~~
412 ~~since as each sediment type shows a different methylation potential (Bloom et al., 2003). In~~
413 ~~the estuary, the percentage of MeHg showed that only low amounts of the Hg_{tot} are~~
414 ~~methylated, suggesting first the probable occurrence of Hg species such as cinnabar, not~~
415 ~~readily available for methylation and second, a low biological activity which is in agreement~~
416 ~~with the negligible concentrations of organic As species. In Asturias (Esbri et al., 2010), similar~~
417 ~~to other Hg mining districts (e.g. Biester et al., 2000; Domagalski, 2001; Garcia Ordiales et al.,~~
418 ~~2015), emissions from the mine sites are primarily dominated by solid mercury sulphides (HgS)~~
419 ~~as cinnabar or metacinnabar compounds, which are not readily available to the methylation~~
420 ~~processes. Thus, only low amounts of the Hg_{tot} introduced from mine liabilities is really~~

421 available for methylation process and, consequently, the concentrations of MeHg are limited.
422 This is apparent based on the ~~percentage values of MeHg~~ ~~percentage values~~, as they are quite
423 similar to ~~the those detected values from for~~ samples ~~collected~~ both outside and inside the
424 San Esteban port area in spite of the differences observed in the Hg_{tot} contents. The
425 ~~relationships among the percentage of %MeHg and the main factors affecting methylation~~
426 ~~(Benoit et al., 1999), only appear significant positively correlates with for~~ C_{org} ($r^2 = 0.825$, $p <$
427 0.01), ~~and negatively correlates with and~~ S ($r^2 = -0.651$, $p < 0.01$) ~~although in an opposite~~
428 ~~manner way~~ (Fig. 5a and 5b). Organic matter is well known ~~to for~~ playing a key role for the
429 metabolism of methylating bacteria at the water-sediment interface (e.g. Ullrich et al., 2001;
430 Hines et al., 2017 and references herein). Conversely, the negative correlation of MeHg/Hg
431 ~~with sulphur suggests not only a greater availability of Hg for methylation when present in~~
432 ~~forms not associated with sulphur but also that this element acts as a limiting factor of~~
433 ~~methylation where sediments are highly anoxic (Fig. 5b). It is indeed possible that high rates of~~
434 ~~SO_4 reduction in sediment near the surface, especially in summer, produce sufficient sulphide~~
435 ~~to lower the availability of Hg for methylation (Hines et al., 2006).~~

436
437
438

439 The speciation analysis shows that the less toxic and less mobile inorganic Hg is the dominant
440 form of mercury in the estuarine sediments. However, despite the apparent limited availability
441 of MeHg (<0.1%), which is diametrically opposed to the availability of As, the local biota
442 showed significant bioaccumulation of this element in the coastal areas close to the Nalón
443 estuary (Besada et al., 2014). These results suggest that Hg is relatively more mobile and
444 bioavailable than As in the Nalón estuary and the nearby coasts. In spite of the low
445 concentrations detected in the sediments, the ease of mobility of MeHg from sediments to the
446 water column and/or to biota increases the risk of transference. Hall et al. (1997)

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447 ~~demonstrated that even at low concentrations, as detected in the estuary, MeHg~~
448 ~~bioaccumulates in organisms. Thus, the mere presence of low amounts of MeHg in the~~
449 ~~estuarine sediments of the Nalón River does not remove the possibility of a potential risk to~~
450 ~~aquatic organisms.~~

451

452 **4. Conclusions**

453

454 The correlation between the total As and Hg concentration in sediments revealed the
455 important ~~parallel~~ contributions derived from mine sites to the estuary. It is apparent that ~~thea~~
456 spatial distribution of the two elements is strictly correlated to decreasing grain size.
457 Consequently, the high levels of As and Hg are mainly restricted to the port areas where
458 artificial barriers have allowed the accumulation of fine sediments. The high presence of
459 sulphides and the redox conditions seem to govern the speciation cycles of As and Hg in the
460 sediments reducing the formation of the most toxic species of As(III)and MeHg. The resistant
461 sulphur complex ligands acts as ~~an~~ inhibitor for the biological and chemical speciation
462 processes, reducing the apparent environmental threat. Possible changes in environmental
463 conditions, such as extreme hydrological events or eutrophication, could alter the current
464 status, thus limiting or enhancing the availability of metal(loid)s in the aquatic environment. In
465 addition, anthropogenic activities, such as dredging operations could affect ~~the~~ remobilization
466 of metal(loid)s from bottom sediments through resuspension, which could represent a
467 potential secondary pollution source not only within the estuary environment but also in the
468 nearby Cantabrian sea coastal environments as a result of tidal flux exchange. Future research
469 in the Nalón estuarine environment should focus on exploring the effects of possible
470 resuspension of bottom sediments contaminated by Hg and As as well as estimating their
471 mobility and exchanges between sediments and the water column at selected estuarine sites.

472 The European Marine Strategy Framework to protect the marine environment calls for
473 improvement of our knowledge of the amount of pollutants delivered to the sea. In this
474 context, this study provides a snapshot of the environmental quality of the Asturias estuary
475 area of the Nalón river as a result of Hg mining contributions from the main hydrological
476 system of northern Spain. The results indicate that Hg and As concentrations in recently
477 sampled estuary sediments exceed the background levels of the area and the environmental
478 quality standards for coastal sediments. Therefore, the mine areas remain primary suppliers of
479 significant amounts of both elements to the estuary and the coastal environments. This work
480 has explored the variability of several parameters related to bottom sediments. It is apparent
481 that total As and Hg concentrations in estuary sediments show a spatial distribution strictly
482 correlated to decreasing grain size. Consequently, the high levels of As and Hg are restricted
483 mainly to the port areas where artificial barriers have allowed the accumulation of fine
484 sediments.

485
486 The most toxic species of As(III) and MeHg are related to the total As and Hg concentrations in
487 sediments. However, whereas As speciation seems to depend on the redox conditions of the
488 sediments, Hg speciation appears to follow the amounts of autochthonous organic matter
489 binding on fine particles of sediments, suggesting different mechanisms of speciation for each
490 element. Although both elements pose an apparent environmental threat, the speciation
491 analysis, the relationships between Hg and As species and grain size, and other geochemical
492 components, together with the comparisons of bioaccumulation of both elements by biota,
493 suggest that in the current environmental conditions, transference from sediments to the
494 environment is more effective for Hg species than for As species.

495
496 Possible changes in environmental conditions, such as extreme hydrological events or
497 eutrophication, could alter the current status, thus limiting or enhancing the availability of

498 metal(loid)s in the aquatic environment. In addition, anthropogenic activities, such as dredging
499 operations, could affect remobilization of metal(loid)s from bottom sediments through
500 resuspension, which could represent a potential secondary pollution source not only within
501 the estuary environment but also in the nearby Cantabrian sea coastal environments as a
502 result of tidal flux exchange. Future research in the Nalón estuarine environment should focus
503 on exploring the effects of possible resuspension of bottom sediments contaminated by Hg
504 and As as well as estimating their mobility and exchanges between sediments and the water
505 column at selected estuarine sites.

506

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508

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515

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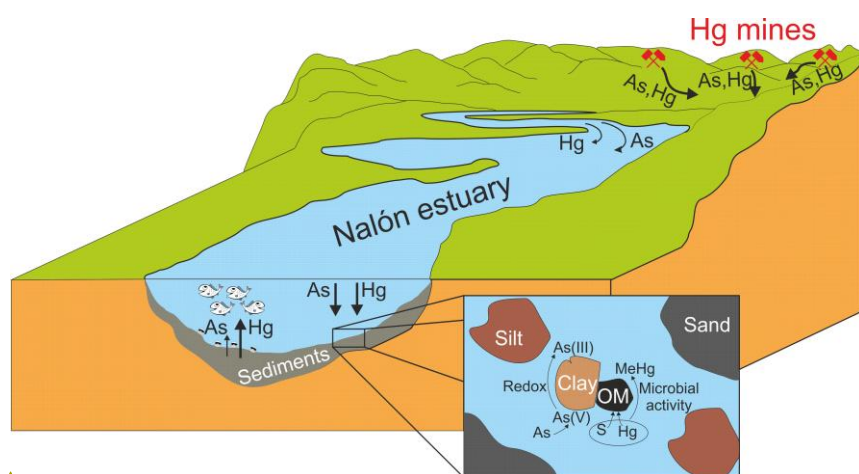
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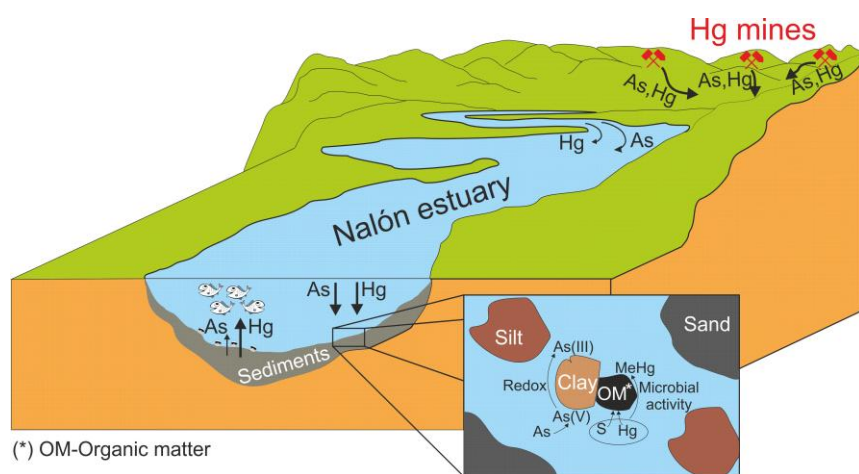
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Graphical abstract



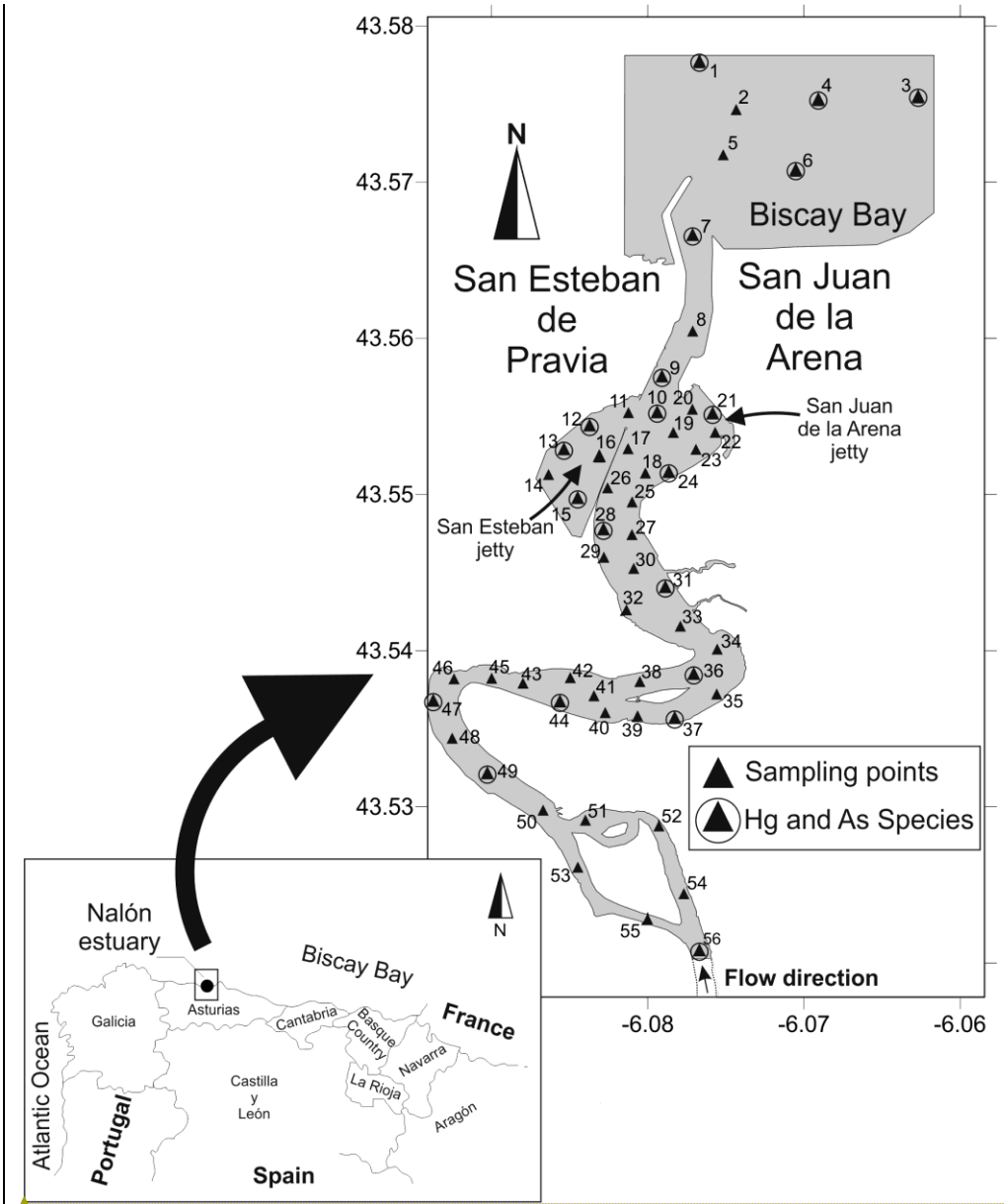
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(*) OM-Organic matter

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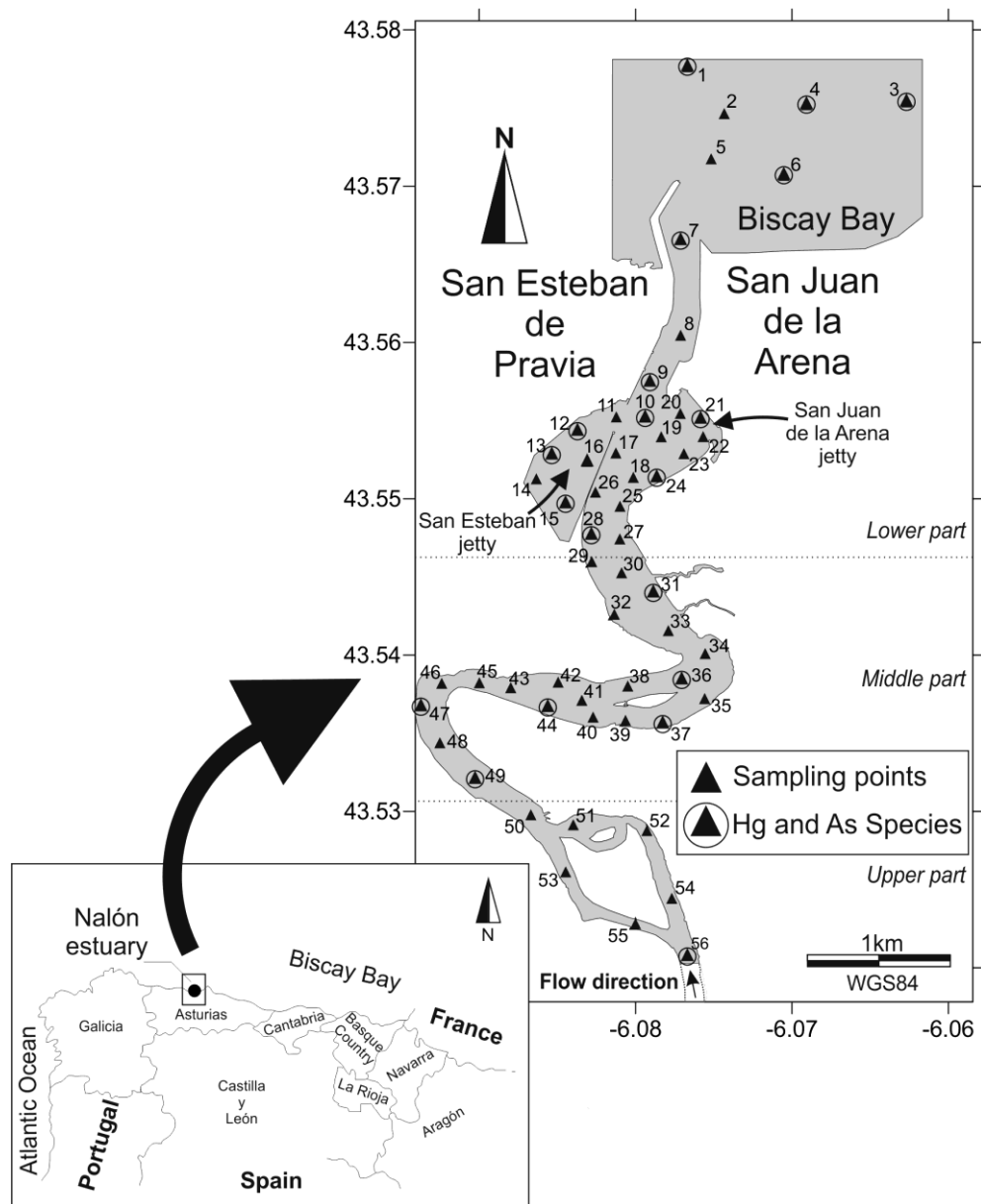


Figure 1. [The study area](#) [Index map](#) of the Nalón River estuary [and along with location of the sediment sampling points](#)

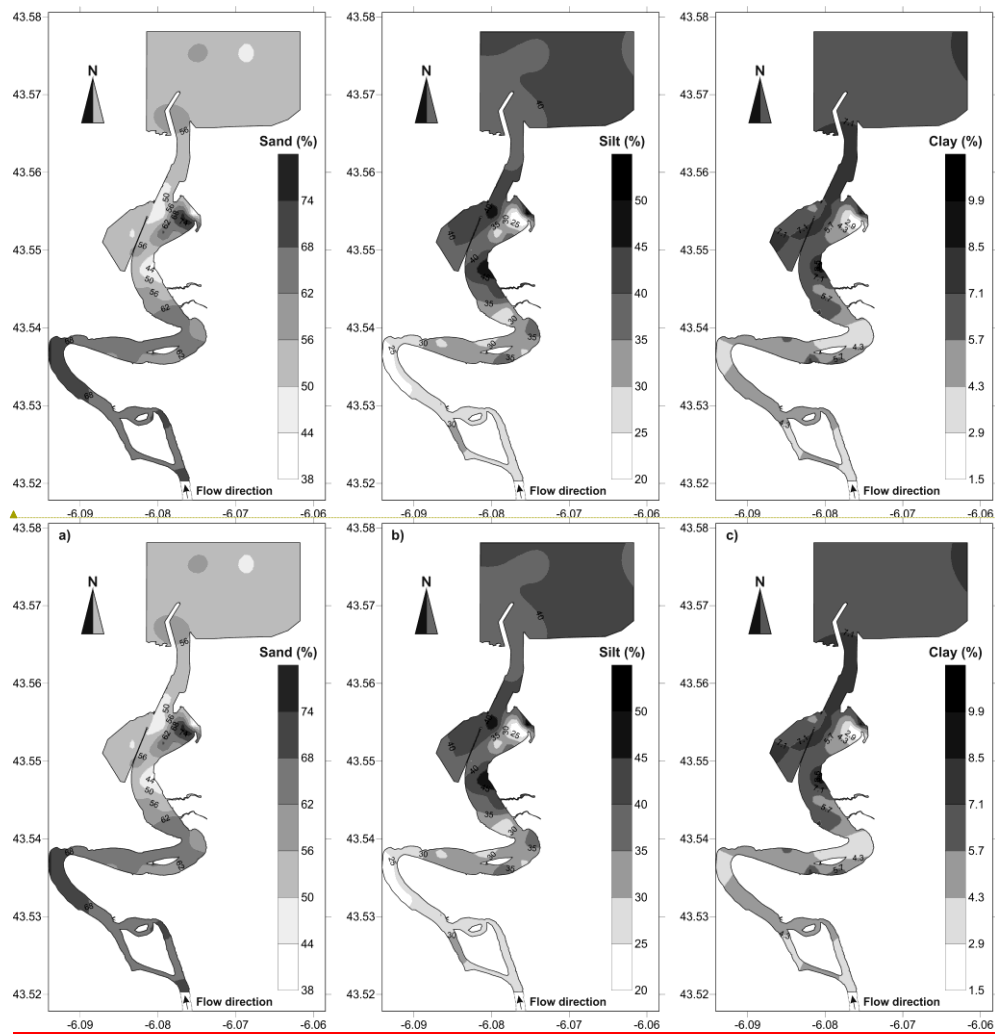


Figure 2. Spatial distribution of the sand (a), silt (b) and clay (c) fractions in the surface sediments of the Nalón estuary.

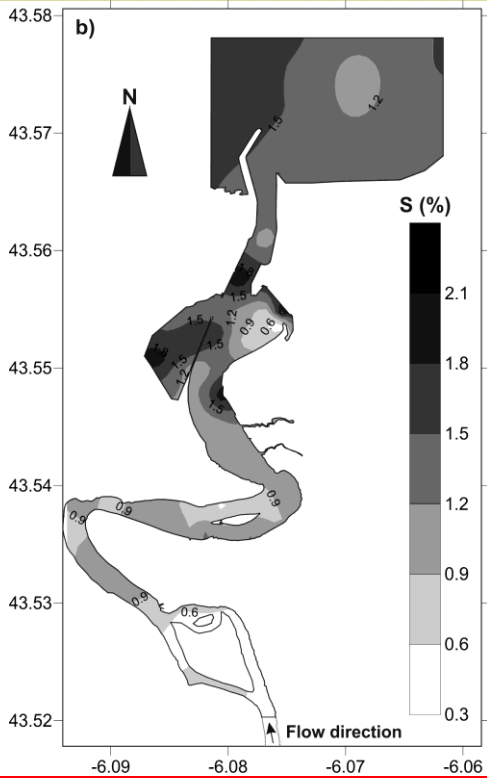
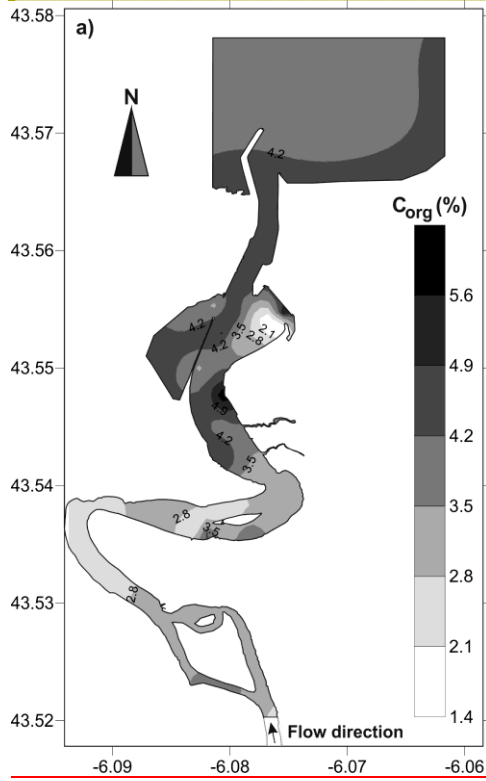
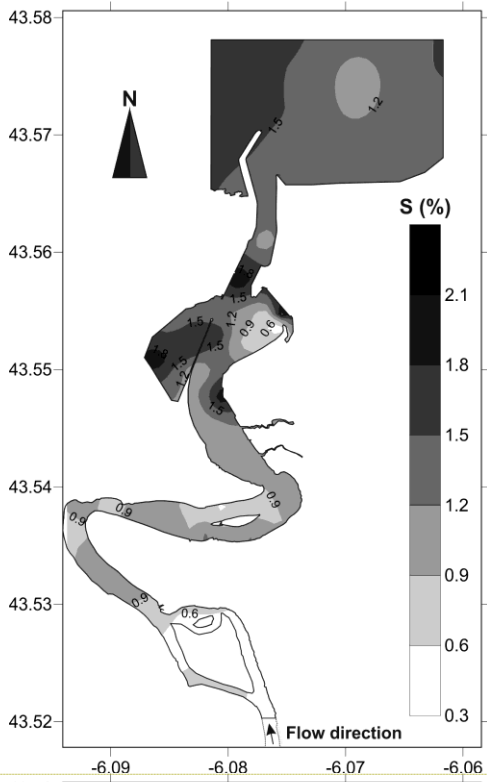
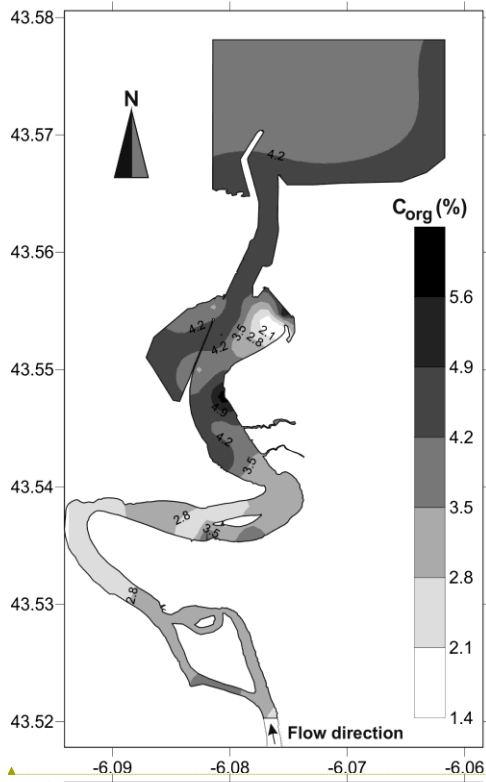


Figure 3. Spatial distribution of C_{org} (a) and S_{tot} (b) concentrations (%) in the surface sediments of the [Nalón](#) estuary.

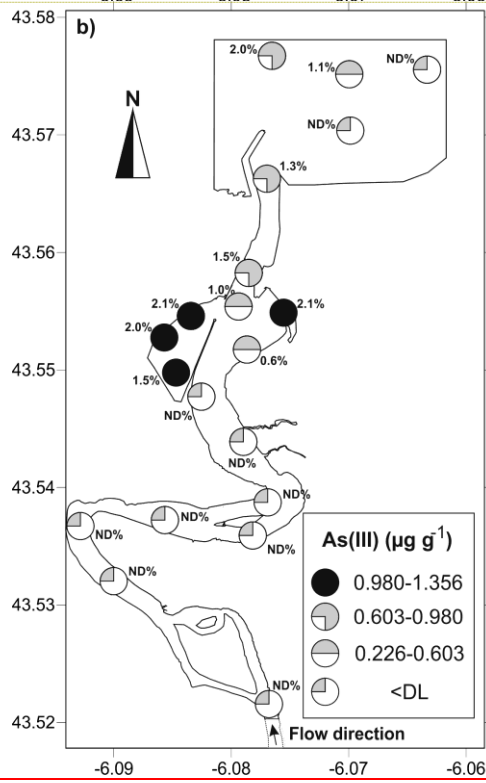
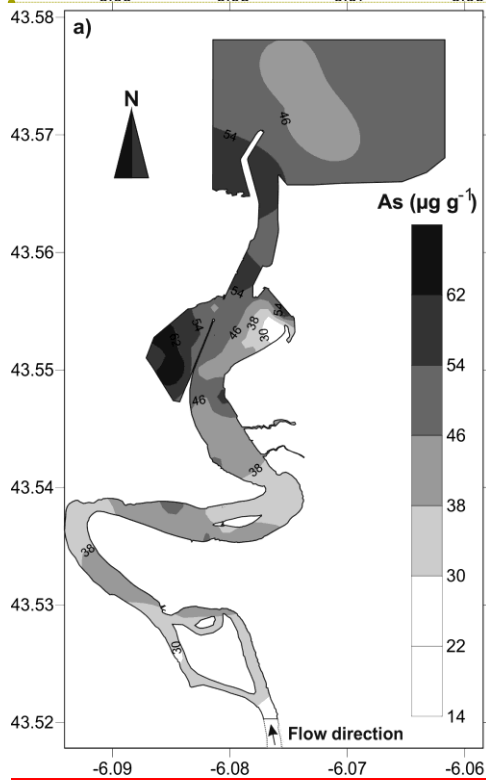
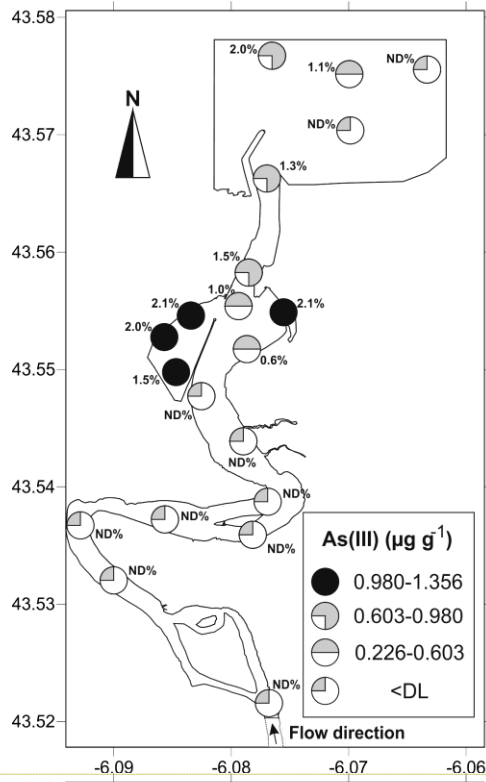
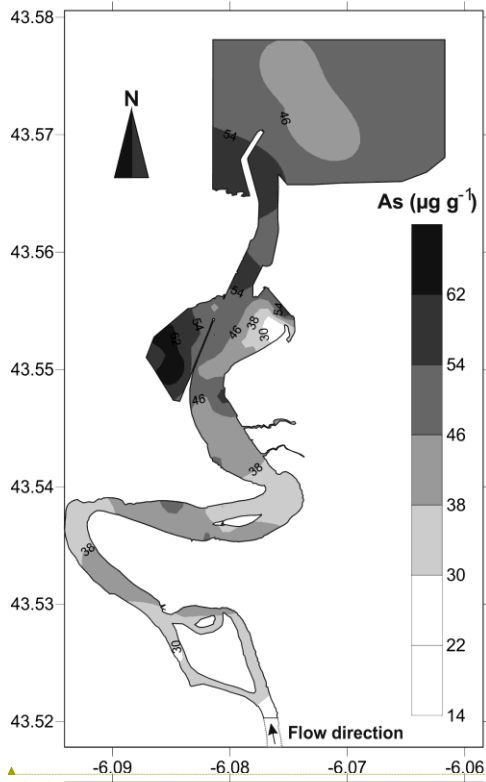
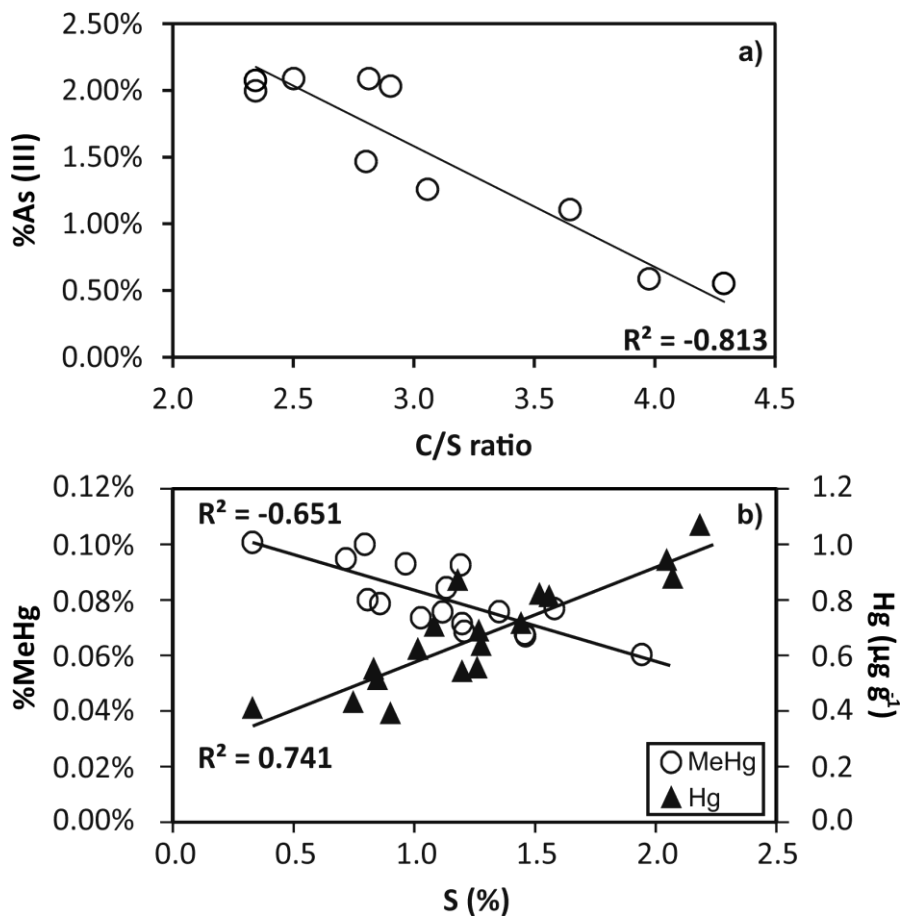


Figure 44. Spatial distribution of As_{tot} (a) and $As(III)$ (b) concentrations ($\mu g g^{-1}$) in the surface sediments of the Nalón estuary. Percentage values represent the abundance of $As(III)$ with respect to the ~~the~~ concentration of As_{tot} concentrations.



-Figure 5. Scatterplots of %As(III) as a function of C/S ratio and of Hg ($\mu\text{g g}^{-1}$) and %MeHg as a function of S concentrations (%) in the surface sediments of the Nalón estuary.

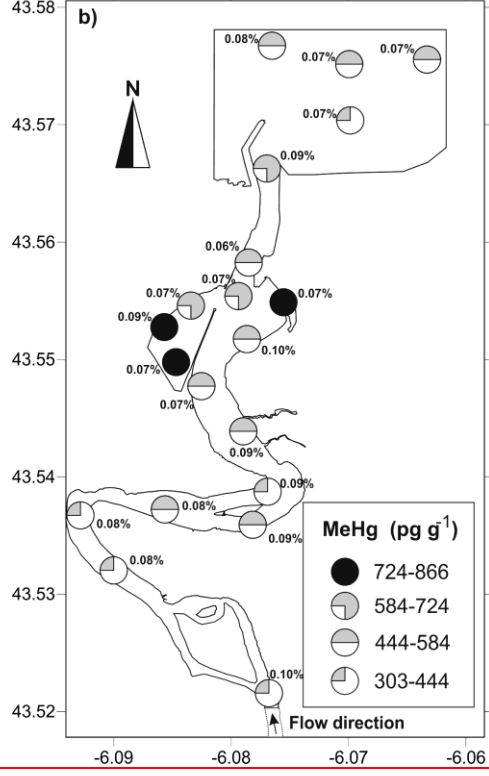
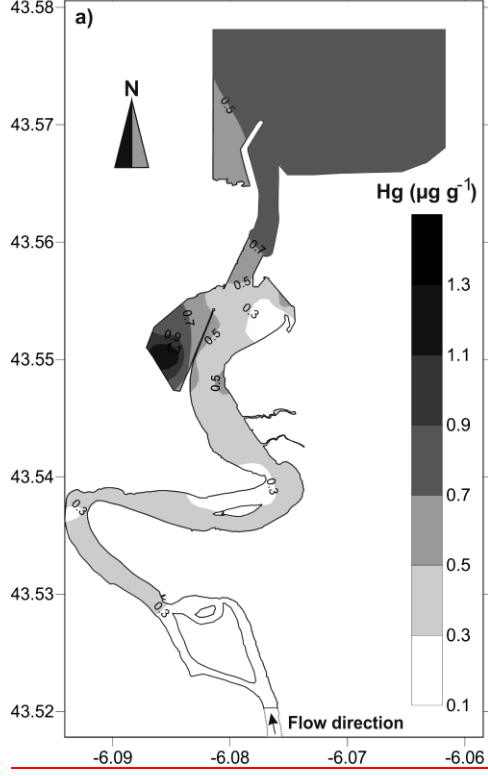
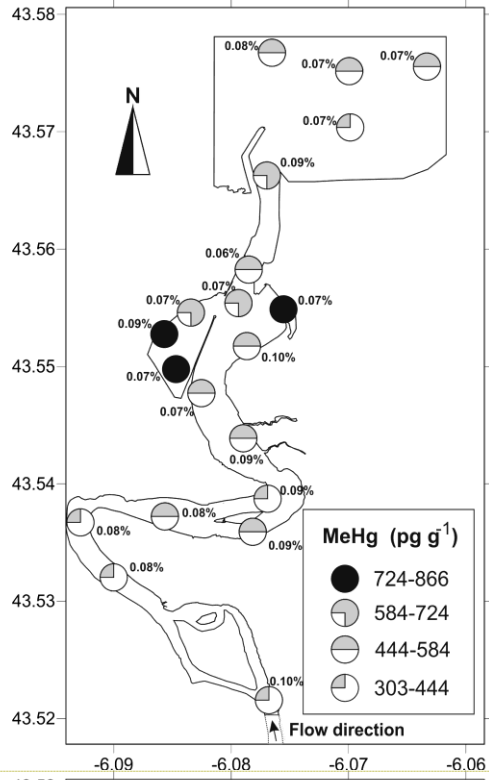
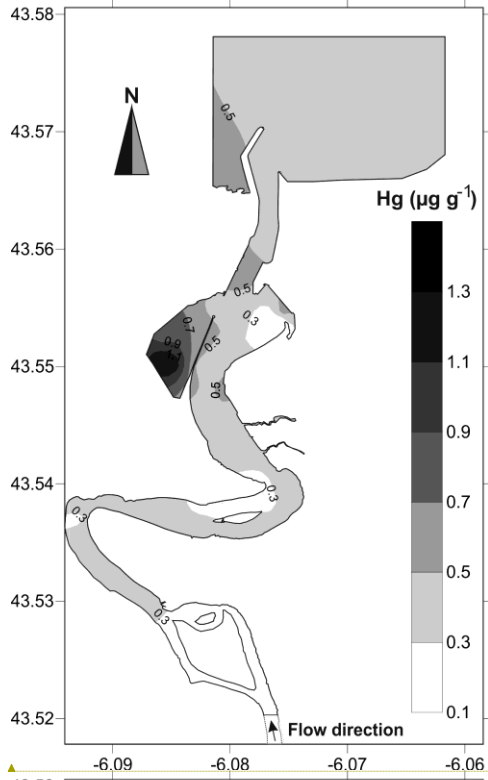


Figure 56. Spatial distribution of Hg_{tot} (a, in $\mu g g^{-1}$) and MeHg (b, in $pg g^{-1}$) concentrations in the surface sediments of the Nalón estuary. Percentage values represent the abundance of the MeHg component with respect to the total concentration of Hg (Hg_{tot}).

1 *Table 1. Results of selected parameters determined in the sediments of the Nalón estuary.*2 *Note: <DL-Below detection limit*

Sample	Lat	Long	Sand (%)	Silt (%)	Clay (%)	TC (%)	TOC (%)	N (%)	S (%)	As ($\mu\text{g g}^{-1}$)	As(V) ($\mu\text{g g}^{-1}$)	As(III) ($\mu\text{g g}^{-1}$)	%As(III)	Hg ($\mu\text{g g}^{-1}$)	MeHg ($\mu\text{g g}^{-1}$)	%MeHg
1	-6.076	43.578	49.40	44.40	6.20	4.76	3.94	0.29	1.68	46.10	44.20	0.90	2.0%	0.65	492.20	0.08%
2	-6.075	43.576	58.90	35.40	5.70	4.71	4.02	0.28	1.49	41.70	-	-	-	0.70	-	-
3	-6.062	43.576	54.00	38.60	7.40	6.10	4.30	0.31	1.55	50.30	48.90	<DL	ND	0.74	487.00	0.07%
4	-6.069	43.575	49.20	44.50	6.30	5.56	3.96	0.25	1.08	54.10	53.50	0.60	1.1%	0.71	509.20	0.07%
5	-6.076	43.572	53.10	40.80	6.10	4.26	3.79	0.28	1.53	46.70	-	-	-	0.57	-	-
6	-6.072	43.571	52.60	41.70	5.70	4.89	3.88	0.26	1.28	38.10	37.90	<DL	ND	0.64	426.80	0.07%
7	-6.077	43.567	57.50	35.40	7.10	4.59	4.41	0.37	1.44	59.20	58.46	0.74	1.3%	0.72	642.60	0.09%
8	-6.077	43.561	52.70	39.50	7.80	4.84	4.52	0.35	1.10	49.70	-	-	-	0.83	-	-
9	-6.079	43.558	48.50	42.30	8.20	5.71	4.89	0.42	2.07	59.20	58.30	0.91	1.5%	0.88	512.20	0.06%
10	-6.080	43.555	39.70	52.10	8.20	5.49	5.06	0.36	1.18	53.20	52.69	0.51	1.0%	0.87	647.00	0.07%
11	-6.081	43.555	54.80	40.10	5.10	3.57	3.32	0.22	1.22	43.30	-	-	-	0.63	-	-
12	-6.084	43.554	51.20	42.50	6.30	4.24	4.04	0.31	1.43	61.50	60.22	1.28	2.1%	0.82	610.80	0.07%
13	-6.086	43.552	54.20	38.80	7.00	4.87	4.41	0.39	1.52	66.80	65.44	1.36	2.0%	0.94	824.60	0.09%
14	-6.086	43.551	54.70	37.40	7.90	6.74	5.02	0.35	2.05	56.70	-	-	-	1.17	-	-
15	-6.085	43.550	53.50	40.00	6.50	4.65	4.35	0.33	1.55	68.10	67.10	1.00	1.5%	1.33	865.40	0.07%
16	-6.082	43.552	49.20	42.40	7.40	4.64	4.23	0.23	1.81	52.90	-	-	-	0.81	-	-
17	-6.081	43.553	50.20	41.70	8.10	5.67	5.13	0.43	1.75	55.40	-	-	-	0.69	-	-
18	-6.079	43.552	71.50	24.40	4.10	2.87	2.69	0.18	0.90	36.80	-	-	-	0.40	-	-
19	-6.078	43.554	71.20	25.00	3.80	2.45	2.23	0.19	0.85	34.50	-	-	-	0.29	-	-
20	-6.077	43.555	76.00	21.30	2.70	2.17	2.03	0.12	0.65	29.50	-	-	-	0.24	-	-
21	-6.076	43.555	38.40	52.70	8.90	7.29	5.47	0.39	2.18	63.50	62.18	1.32	2.1%	1.07	779.40	0.07%
22	-6.076	43.554	80.00	18.70	1.30	1.62	1.45	0.08	0.27	20.10	-	-	-	0.10	-	-
23	-6.076	43.552	69.10	27.80	2.10	2.32	1.98	0.14	0.75	26.50	-	-	-	0.23	-	-
24	-6.078	43.552	55.30	39.20	5.50	3.47	3.32	0.33	0.83	38.70	38.47	0.23	0.6%	0.55	549.80	0.10%
25	-6.081	43.549	49.90	43.00	7.10	6.00	4.47	0.31	1.48	45.80	-	-	-	0.73	-	-
26	-6.083	43.550	60.20	34.10	5.70	3.92	3.29	0.35	0.81	43.70	-	-	-	0.50	-	-
27	-6.081	43.548	39.60	50.50	9.90	6.83	6.33	0.43	2.07	62.40	-	-	-	1.03	-	-
28	-6.082	43.547	48.50	44.80	6.70	4.75	4.34	0.32	1.27	43.50	43.32	<DL	ND	0.69	481.60	0.07%
29	-6.083	43.546	54.10	39.40	6.50	6.20	4.71	0.29	1.01	44.20	-	-	-	0.79	-	-
30	-6.081	43.545	56.80	38.10	5.10	3.99	3.87	0.26	1.08	41.30	-	-	-	0.59	-	-
31	-6.079	43.544	51.20	43.50	5.30	4.83	3.86	0.26	1.02	40.80	41.10	<DL	ND	0.62	574.80	0.09%
32	-6.081	43.542	60.80	31.70	7.50	5.39	5.06	0.37	1.24	47.10	-	-	-	0.77	-	-
33	-6.078	43.542	67.30	26.80	5.90	3.55	3.42	0.31	1.05	40.50	-	-	-	0.58	-	-
34	-6.075	43.539	59.60	36.60	3.80	4.10	3.24	0.20	1.07	32.70	-	-	-	0.53	-	-
35	-6.076	43.537	66.70	28.50	4.80	3.46	2.81	0.27	0.88	37.80	-	-	-	0.29	-	-
36	-6.077	43.539	64.50	32.30	3.20	3.18	2.82	0.16	0.75	31.80	31.50	<DL	ND	0.43	407.00	0.09%
37	-6.078	43.536	55.20	38.50	6.30	4.38	4.17	0.27	1.26	45.10	44.70	<DL	ND	0.56	510.80	0.09%
38	-6.081	43.538	68.40	28.40	3.20	2.03	1.92	0.20	0.51	28.20	-	-	-	0.22	-	-
39	-6.081	43.536	61.00	33.60	5.40	3.33	2.89	0.29	1.02	38.40	-	-	-	0.48	-	-
40	-6.082	43.536	56.20	35.70	8.10	6.25	4.75	0.38	1.31	50.10	-	-	-	0.70	-	-
41	-6.083	43.536	66.20	29.80	4.00	2.18	2.06	0.22	0.88	38.20	-	-	-	0.20	-	-
42	-6.085	43.538	62.50	31.50	6.00	3.52	3.29	0.28	0.93	45.30	-	-	-	0.58	-	-
43	-6.086	43.537	66.50	28.80	4.70	4.75	3.39	0.25	1.06	39.60	-	-	-	0.59	-	-
44	-6.086	43.536	58.80	36.00	5.20	3.88	3.27	0.23	1.20	40.30	36.70	<DL	ND	0.54	452.40	0.08%
45	-6.090	43.538	66.20	29.40	4.40	3.29	2.40	0.23	0.77	37.50	-	-	-	0.35	-	-
46	-6.092	43.538	70.30	25.40	4.30	2.64	2.32	0.22	1.15	32.50	-	-	-	0.31	-	-
47	-6.093	43.535	71.20	24.60	4.20	2.60	2.57	0.21	0.90	37.70	39.60	<DL	ND	0.39	303.20	0.08%
48	-6.090	43.532	70.50	24.60	4.90	2.53	2.46	0.26	1.06	40.10	-	-	-	0.31	-	-
49	-6.086	43.530	65.10	30.20	4.70	3.82	3.06	0.28	0.85	35.20	33.70	<DL	ND	0.52	410.60	0.08%
50	-6.084	43.529	68.20	26.80	5.00	3.25	2.96	0.22	0.58	38.80	-	-	-	0.43	-	-
51	-6.079	43.529	69.30	26.20	4.50	3.71	3.02	0.23	0.52	37.30	-	-	-	0.49	-	-
52	-6.084	43.526	64.10	32.10	3.80	3.34	3.26	0.19	0.50	32.10	-	-	-	0.54	-	-
53	-6.078	43.524	66.20	29.90	3.90	3.02	2.89	0.23	0.45	32.40	-	-	-	0.45	-	-
54	-6.094	43.537	72.50	23.60	3.90	2.75	2.32	0.22	0.57	30.10	-	-	-	0.24	-	-
55	-6.080	43.523	67.20	27.80	5.00	4.84	3.86	0.30	0.87	35.20	-	-	-	0.58	-	-
56	-6.077	43.520	69.30	26.90	3.80	3.27	2.73	0.21	0.33	32.30	30.20	<DL	ND	0.41	412.40	0.10%

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6 | Table 21. Ranges of mercury and arsenic concentrations reported in literature for in other
 7 | coastal environments. (na- not available and <DL- Below detection limit).

	As ($\mu\text{g g}^{-1}$)	Hg ($\mu\text{g g}^{-1}$)	MeHg (ng g^{-1})	Primary source	Authors
Nalón estuary (Spain)	20.10-68.10	0.10-1.33	0.30-0.87	Hg mining	This study
Tagus estuary (Portugal)	1.90-1022.00	0.20-66.70	<DL-6.70	Industry	Vale et al., 2008 Canario et al., 2007
Marano and Grado Lagoon (Italy)	na	0.68-9.95	0.47-7.85	Hg mining and industry	Acquavita et al., 2012
Venice Lagoon (Italy)	8.9-68.9	0.64-3.41	0.40-1.56	Industry	Giusti and Zhang, 2002
Gulf of Trieste (Italy)	6.40-18.20	0.10-23.30	0.20-60.10	Hg mining	Acquavita et al., 2010 Covelli et al., 2001
Northern Tyrrhenian Sea (Italy)	5.43-35.38	0.03-2.20	na	Hg mining	Piazzolla et al., 2015 Scanus et al., 2016
Kastela Bay (Croatia)	15.00-33.00	17.60-74.00	6.05-16.40	Industry	Orescanin et al., 2005 Kwokal et al., 2002
Aegean Sea (Turkey)	7.00-70.00	0.05-102.00	na	Hg mining	Ozkan et al., 2017
San Francisco Bay (USA)	2.25-13.50	0.03-2.65	0.01-10.3	Hg mining	Yee et al., 2017
Tomales Bay (USA)	na	0.05-3.10	0.30-70.00	Hg mining	Johnson et al., 2009
Honda Bay, Palawan (Philippines)	na	0.03-570.00	-	Hg mining	Benoit et al., 1994

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Supplementary Material

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Occurrence and speciation of arsenic and mercury in estuarine sediments affected by mining activities (Asturias, northern Spain)

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1 **Abstract**

2

3 Sediments contaminated by Hg and As from two historical mining areas have been deposited
4 in the Nalón estuary (Asturias, northern Spain) since 1850. Total mercury (Hg_{total})
5 concentrations in the sediments range from $0.20 \mu g \cdot g^{-1}$ to $1.33 \mu g \cdot g^{-1}$, most of it in the form of
6 sulphides. Concentrations of methylmercury ($303.20-865.40 \text{ pg} \cdot g^{-1}$) are up to two orders of
7 magnitude lower than the concentration of Hg_{total} . Total As concentration (As_{total}) is enriched
8 compared to the background level for the area. The relative abundance of As(V) on As(III) in
9 the sediments ranges from 97.6% to 100%, whereas inorganic Hg accounts for more than 99%
10 of the total Hg. The occurrence of the most toxic species, inorganic As(III) and organic
11 methylmercury, seem to be related to redox conditions together with the amounts of sulphur
12 which act as natural barriers which inhibit the biological and chemical speciation processes.
13 Despite the high amounts of Hg and As present in the sediments, their transference to the
14 water column appear to be limited thus converting sediments in an effective sink of both
15 elements. Special attention should be paid to potential variations of the environmental
16 conditions which might increase the element mobility and exchange between sediments and
17 the water column.

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21 **Keywords:** Mercury, Arsenic, sediments, estuary, speciation, mining

22 **1. Introduction**

23 Among aquatic environments, coastal areas are particularly fragile and are very often
24 threatened by significant direct and indirect anthropogenic pressure. Specifically, in coastal
25 marine environments, estuaries are ecosystems of global concern as they exhibit high
26 biological productivity due to the special conditions produced by the mixing of fresh water and
27 seawater. Estuarine sediments also act as 'reservoirs' of contaminants and are therefore
28 recognised as valuable indicators of the degree of contamination of these aquatic
29 environments (Liu et al., 2015; Sarkar et al., 2017). Contamination of estuaries by trace metals
30 and metalloids is an important environmental issue due to their potential transfer from
31 sediments into the water column and their subsequent bioaccumulation in aquatic organisms
32 (Van el et al., 2017; Yu et al., 2017).

34 The Asturias region (north of Spain) is one of the most important coastal areas of the country
35 and one which has not been significantly impacted by anthropogenic activities. Consequently,
36 the monitoring and management of this coastal ecosystem is of special concern in maintaining
37 a good level of ecological quality. Several estuarine areas along the Asturias coast are very
38 sensitive to possible contamination by sources located inland. Among them, the Nalón estuary
39 is the most important transitional environment, connecting the Cantabrian Sea (the Biscay
40 Bay) and the Nalón River, which is the main hydrographical system of northern Spain. The
41 Nalón estuary contains remarkable anthropogenic contributions of trace metal(oid)s,
42 especially arsenic (As) and mercury (Hg) due to the long-term activity of two mining areas,
43 which have been identified as 'hotspots' for these elements (Loredo et al., 1999; Loredo, 2000;
44 Fernández-Martínez et al., 2005). Several studies have been conducted over the last two
45 decades to clarify the sources, processes, and dynamics of As and Hg in different
46 environmental segments, such as soils, mine tailings, and fresh and ground waters of the Nalón

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47 River basin (e.g. Loredó et al., 2010; Silva et al., 2014; Ordoñez et al., 2014). Research into the
48 impact of these elements in the Nalón River estuarine system has only recently begun. For
49 instance, As and Hg profiles in saltmarsh sediments and in some boreholes in the main
50 estuarine channel have been studied in detail to reconstruct the long-term contamination
51 history of the area and to establish preliminary geochemical background values for both
52 elements (García-Ordiales et al. 2015, 2016, 2017). Prior to this research, there have been no
53 published reports quantifying Hg and As abundances across the entire estuarine system and
54 determining their areal distribution as well as their sources. The only exception is the
55 measurements performed by the Asturias Regional Port Authority on recent estuarine
56 sediments which demonstrated significant concentrations of Hg ($0.15\text{--}1.56\ \mu\text{g}\cdot\text{g}^{-1}$) and As
57 ($20.00\text{--}39.20\ \mu\text{g}\cdot\text{g}^{-1}$) in the period 2003–2011. However, the toxicity and mobility of As and Hg
58 in estuarine sediments strongly depend on their specific chemical forms along with their
59 binding with sediment particles (Eggleton and Thomas, 2004; Vidmar et al., 2017). In this
60 context, our work aims to investigate not only the total concentration distribution of these two
61 elements but also their speciation in surface sediments, as well as the relationships between
62 sediment particles and the specific geochemical conditions of the study area. Such information
63 may be helpful in understanding the mechanisms influencing metal mobility from sediments
64 and may also help provide preliminary predictions of the bioavailability, if any, of these two
65 metal(oid)s (Pinedo-Hernández et al., 2015; Beckers and Rinklebe, 2017) with regard to
66 possible effects of intervention and maintenance, such as dredging operations in the estuary
67 for navigation purposes.

68 69 **2. Material and methods**

70 **2.1 Environmental setting**

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72 The Nalón River estuarine system in the Asturias region encompasses only a small part of the
73 entire hydrographical basin (4.5 km²) and extends 4,777 km² inland. The estuary is over 6 km
74 long and its upper limit is established according to the salt wedge extension which moves
75 upstream following the tidal range. The main estuarine channel has retained its natural river
76 banks with the exception of the lower section close to the inlet, where two small regional
77 ports were built (San Juan de la Arena and San Esteban de Pravia in Fig. 1), which altered the
78 natural morphology and sedimentation dynamics of the outer part of the estuarine system
79 (Flor-Blanco et al., 2015). The main channel is more than 2 m deep and is affected by an annual
80 meso-tidal range between 1.0 and 4.2 m; in general the tides are over 2 m for more than 70%
81 of the year (Flor et al., 1998).

82
83 The main activity in the estuarine area is tourism, including recreational uses (fishing and
84 yachting). Several urban settlements and some agricultural and mining-industrial sites are
85 located in the Nalón River basin. Among the mining-industrial activities, which have been
86 active since the end of the eighteenth century, the most important are related to the
87 significant deposits of coal, mercury, gold, and iron as well as other polymetallic ores
88 containing copper, lead, and zinc found in the area. Among the metal extraction industry, Hg
89 mines have been especially important; Asturias is the second largest Hg producer in Spain. The
90 most notable Hg deposits in Asturias are La Peña-Terronal in Mieres and La Soterraña in Pola
91 de Lena. The main metal ore of these deposits is cinnabar [HgS], in association with low
92 amounts of native Hg, as well as significant amounts of As-bearing minerals such as realgar
93 [AsS] and pararealgar [As₄S₄], orpiment [As₂S₃], and arsenic-rich pyrite (Ordoñez et al. 2013).
94 Despite the cessation of mining activity several decades ago, drainage waters flowing out from
95 inactive mines where low remediation actions were implemented (Rodríguez-Pérez et al.,
96 2014), their tailings and residual deposits may still affect the quality of the fluvial waters and
97 the sediments downstream of the sources (Loredo et al., 2003; Ordoñez et al., 2013). The

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98 contamination has reached the estuarine environment where the historical accumulation of As
99 and Hg in the saltmarsh and estuary channel has been correlated to the historical Hg mining
100 activity located about 40 km upstream in the Nalón river drainage basin (Garcia-Ordiales et al.,
101 2015, 2016, 2017).

102

103 **2.2 Sampling and analysis**

104

105 A total of 56 sediment samples were collected from the estuary (Fig. 1). When accessible, both
106 sides of the river banks were sampled together with the main channel area, representing the
107 whole estuarine sector of the active stream of the Nalón riverbed. Surface sediments (0-5 cm)
108 were collected by means of a plastic shovel from the river banks while they were exposed to
109 air during ebb tide conditions or by a stainless-steel Van Veen grab from the submerged parts
110 of the estuary. Approximately 1 kg of sediment was collected from each sampling point,
111 homogenised in the field, stored in double zip-lock bags, and transported to the laboratory in a
112 portable fridge. Each sample was divided into different representative subsamples, using a
113 riffle-type sample splitter with a removable hopper. Grain size and total elemental content
114 were determined in air-dried samples. For grain-size analysis, an aliquot of each sample was
115 treated with a solution of 3% (v/v) H₂O₂ for 48 h to remove most of the organic matter. The
116 sample was then wet sieved at 2 mm and analysed with a Fritsch ANALYSETTE MicroTec Plus
117 22. Grain-size data are synthesised using the classical sand-silt-clay notation according to the
118 Udden-Wentworth scale. Major and trace elements were determined on 0.5 g freeze-dried
119 samples, which were digested in a microwave using a multi-acid solution (HCl–HNO₃–HF) and
120 analysed by inductively coupled emission spectroscopy (ICP-ES) and inductively coupled
121 plasma mass spectroscopy (ICP-MS; Bureau Veritas, Vancouver, Canada). The accuracy of the
122 results was verified by comparison against analysis of Standard Reference materials PACS-2

123 (marine sediment), RTC-CRM026-050 (sandy loam soil) and CRM042-056 (loam soil).

124 Percentage recoveries for all elements considered ranged from 93% to 106%.

125

126 Total carbon (C_{tot}), nitrogen (N_{tot}), and sulphur (S_{tot}) content were measured by an Elemental

127 Vario EL Cube CNHS. Organic carbon (C_{org}) in sediments was determined through progressive

128 acidification with HCl (0.1–1.0 M) at a combustion temperature of 920 °C according to the

129 method set out by Hedges and Stern (1984). Acetanilide was used as the standard compound

130 for calibration. The detection limit for C_{org} and C_{tot} was 0.1%. The precision for C_{tot} , C_{org} , and N_{tot}

131 detection was 3%.

132

133 Twenty sediment samples were selected for the Hg and As speciation analysis (Fig. 1). These

134 samples were chosen based on the results obtained from the total concentration analyses and

135 following the hydrodynamic criteria, which were intended to cover the different sectors of the

136 estuary and discover possible significant differences among them. For As species, 0.1 g of

137 sediment was placed together with an extracting agent (1 M H_3PO_4 + 0.1 M ascorbic acid) in a

138 microwave vessel. The extracts were diluted (1:5) and filtered (<0.45 μm). The As species were

139 separated using a mobile phase of 2 M phosphate buffered saline (PBS)/0.2 M EDTA (pH = 6.0)

140 in a separation column with a 1260 Infinity high-performance liquid chromatograph (HPLC)

141 coupled to a 7700 ICP-MS (Agilent Technologies). The accuracy of the results was verified by

142 comparing the total arsenic concentration with the sum of all species concentrations

143 determined. The recovery of As speciation ranged from 95% to 106%.

144

145 Organic Hg was analysed using the methodology proposed by Valega et al. (2006). As organic

146 mercury compounds other than methylmercury, such as dimethylmercury, have rarely been

147 detected in sediments (Ullrich et al., 2001; Mason, 2013), the organic mercury measured may

148 be considered methylmercury. In brief, sediment samples were first treated with an acid

149 solution (KBr/H₂SO₄/CuSO₄), followed by extraction of the organic Hg halide with toluene and
150 back-extraction with an aqueous sodium thiosulphate solution. The analyses were carried out
151 using an HPLC-ICPMS (Agilent Technologies). The accuracy of the results was verified against
152 the estuarine sediment IAEA-405 certified reference material (recovery range from 94% to
153 102%).

154 Statistical analysis was performed using the SPSS 19.0 and Minitab V.15 for Windows software
155 and dispersion maps were produced using Surfer 9.8.669 software (©Golden Software Inc.
156 2009) and interpolating data by applying the Kriging algorithm.

157

158 **3. Results and discussion**

159 **3.1 General characteristics of sediments**

160

161 Results of the grain size and geochemical analysis from each sampled area are presented as
162 supplementary material (Table 1). From the grain-size distribution of the Nalón estuary
163 sediments (Fig. 2), it is apparent that the sandy fraction is usually predominant, with a high
164 variability (38.4% and 80%). The silty fraction can be considered subordinate to the sandy
165 fraction (range, 18.7% to 52.7%), and the clayey fraction is the smallest component with the
166 most consistent range (from 1.3% to 9.9%).

167

168 The estuary is characterised by a specific energy pattern resulting from the interactions of
169 wave motion, tidal currents, and river energy. The energy pattern governs the transport and
170 distribution pattern of suspended matter in the estuary. In the upper section of the estuary
171 where the fluvial flow is dominant, the sandy component increases as the muddy fraction
172 decreases. This is attributed to the effects of the velocity of water due to the shallowness of
173 the channel (from 1 to 2.5 m) in that section of the estuary. In the lower section of the estuary
174 (up to about 5 m depth on average), the construction of two jetties has changed the

175 morphology of the area and has affected sedimentation; the sandy component increases in the
176 areas most exposed to tidal flows of the channel and in the San Juan de la Arena area. This
177 increase may be attributed to the energy of the depositional medium (Flor et al., 1998), which
178 is affected by wave action and tidal currents, processes which remove fine sediments
179 (Sutherland et al., 2015) from the channel and deposit them on the estuarine banks nearby. In
180 contrast, in the San Esteban port area, a significant increase is seen in the muddy fraction (silt
181 and clay). The morphology of this area, where a breakwater protects the jetty, limits water
182 mixing and circulation in the inner part of the port basin, converting this area into a sink for
183 fine-sized particles which remain entrapped.

184
185 Concentrations of C_{tot} (1.62–7.29%), N_{tot} (0.08–0.43%), and C_{org} (1.45–6.33%) (Fig. 3) are
186 strongly correlated to the clay percentage in the sediments ($r^2 = 0.886$, $r^2 = 0.931$, and $r^2 =$
187 0.942 , respectively, $p < 0.001$)(Fig. 1, supplementary material), as the finest fraction easily
188 adsorbs organic compounds in the bottom sediments. As a consequence, the highest
189 concentrations of these parameters were detected in the inner part of the San Esteban port
190 basin and in the San Juan de la Arena port where carbon and nitrogen preferably tend to
191 accumulate. Conversely, the lowest concentrations are progressively found in the upper
192 section of the estuary where the coarse component appears to be more relevant. Similarly, in
193 the marine area in front of the estuary, a decrease in concentration occurs since the sediment
194 grain size is coarse due to the action of the marine currents and wave motion (Flor et al.,
195 1998). Carbon in the particulate matter (C_{tot}) is mainly organic, C_{org} (avg. $87.1 \pm 0.08\%$), from a
196 minimum of 70% to a maximum value of 99%. The correlation between C_{org} and sediment
197 grain-size can be partially explained by the similar settling velocity (i.e. hydrodynamics) of the
198 particulate organic constituents and the fine-grained mineral particles (Tyson 1995). Total
199 nitrogen (N_{tot}) is significantly related to C_{org} ($r^2 = 0.866$, $p < 0.01$), and plotting N_{tot} against C_{org}
200 results in an intercept of 0.047, which indicates the percentage of N_{tot} at 0% value of C_{org} ,

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201 showing that there is a significant fraction of total N_{org} in the samples. Calculated C_{org}/N_{tot}
202 ratios, commonly quoted as C/N values together with $\delta^{13}C$ and $\delta^{15}N$, are widely used as a tool
203 for discriminating marine from terrestrial organic matter in sediments (Xu et al., 2017). At this
204 point, some assumptions can be made merely on the basis of the C/N ratio (Covelli et al., 2012
205 and references therein). In the estuary sediments, the C/N ratio ranges from 9.38% to 18.18%
206 (avg. $13.02 \pm 2.18\%$), which suggests that the organic matter in these sediments is prevalently
207 terrigenous, according to Meyers (1997). This result is in agreement with the dynamics of the
208 estuary as described by Flor et al. (1998), where the supply of material from the river basin is
209 the predominant source of sediments and organic matter into the estuary.

210
211 In general, the distribution of the sulphur (S) (Fig. 3) concentration (0.27–2.18%) is closely
212 associated with the fine grain-sized sediments ($r^2 = 0.838$, $p < 0.01$) (Fig.1 , supplementary
213 material) since sulphur is primarily associated with iron sulphide in the Nalón estuary. Indeed,
214 the main rivers of the drainage basin provide an abundant supply of iron-rich terrigenous
215 siliciclastic debris (Freslon et al., 2014). On the other hand, the positive correlation between S
216 and C_{org} ($r^2 = 0.802$, $p < 0.01$) and the average C/S value (3.43 ± 0.97), suggest that sediments
217 were deposited under oxydising conditions at the bottom (Berner 1982; Raiswell and Berner,
218 1985). Low C/S values, usually associated with anoxic or semi-anoxic depositional
219 environments (Burone et al., 2003) were detected in the San Esteban port basin (2.40–2.81),
220 suggesting partial hypoxic or anoxic conditions would occur in this area.

221

222 **3.2 Arsenic in surface sediments: occurrence and speciation**

223

224 Concentrations of As_{tot} are well above the local background level estimated by Garcia-Ordiales
225 et al. (2016) for the Nalón estuary ($9.00 \pm 0.94 \mu g \cdot g^{-1}$) and the range of 5–15 $\mu g \cdot g^{-1}$ determined
226 for uncontaminated nearshore marine and estuarine sediments (Moore and Ramamoorthy,

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227 1984; Francesconi and Edmonds, 1997). These results are consistent with the concentrations
228 detected in core profiles from the same area (Garcia-Ordiales et al., 2015, 2016, 2017). Due to
229 long-term extraction activity, the As_{tot} background values have significantly increased,
230 surpassing the consensus-based threshold levels (MacDonald et al., 2000) such as the
231 Threshold Effect Concentration (As TEC, $9.97 \mu\text{g}\cdot\text{g}^{-1}$), and the Probable Effect Concentration (As
232 PEC, $33.0 \mu\text{g}\cdot\text{g}^{-1}$), the latter of which is exceeded by 86% of the samples.
233
234 The concentration of As_{tot} in the sediments was closely related to the amount of the
235 corresponding clay fraction ($r^2 = 0.831$, $p < 0.01$) and S ($r^2 = 0.825$, $p < 0.01$) contents (Fig. 2,
236 supplementary material), suggesting that particle size and sulphide control the As retention in
237 the solid phase and its dispersion throughout the estuary. The lower sector of the estuary,
238 where a major proportion of fine particles and S contents occur, demonstrated the highest
239 concentrations of As in the sediments (Fig. 4), and this is especially remarkable in the San
240 Esteban port basin which acts as a sink for fine-sized particles.
241
242 Speciation analysis of As showed that the occurrence of the organic species
243 (monomethylarsonate and dimethylarsinate) was negligible; the inorganic arsenic species are
244 dominant in the sediments (Fig. 3, supplementary material). Moreover, within the inorganic As
245 species, arsenate was the main one found in the sediments due to the oxidising conditions in
246 the aquatic environment based on the C/S values. The concentration of As(V) falls in the range
247 of $16.89\text{--}64.96 \mu\text{g}\cdot\text{g}^{-1}$ (avg. $31.39 \pm 12.85 \mu\text{g}\cdot\text{g}^{-1}$). Its relative abundance in comparison to the
248 As_{tot} concentration in the sediments ranges from 97.6% to 100%. In the upper-middle sector of
249 the estuary, As (III) species were not detected possibly as a consequence of the redox
250 conditions in the sediments (avg. C/S 3.90 ± 1.40) which may have potentially produced As(III)
251 although below the detection limit. On the contrary, in the lower sector where marine
252 conditions occur, the majority of the samples showed detectable amounts of As(III). The

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253 arsenite component was significantly negatively correlated to the C/S value ($r^2 = -0.742$, $p <$
254 0.05) (Fig. 5a). This negative correlation suggests that the redox condition is the key factor of
255 the presence of arsenite entrapped in the sedimentary matrix. The relationship between redox
256 conditions and the amounts of the As(III) species in sediments has already been extensively
257 studied by various authors (e.g. Rochette et al. 1998, Foster, 2003; Mudhoo et al., 2011;
258 Shaheen et al., 2016). The same authors demonstrated that reducing conditions can increase
259 As(III) concentrations by converting As(V) into As(III). The low proportion of As(III) with respect
260 to the As_{tot} concentration (from 1.0% to 2.1%), despite the redox conditions (Frohne et al.,
261 2011), suggests that the reduction of As (V) to As(III) is inhibited, thus decreasing the potential
262 release of the most mobile and toxic As (III) (Pierce and Moore, 1982). In the Nalón estuary,
263 seawaters show more than 100 mg L^{-1} of total SO_4^{2-} at Eh levels greater than 100mV and it is
264 expected that large amounts of this SO_4^{2-} absorbed by the sediment potentially stabilise As by
265 forming complex ligands (Sparks, 1999; LeMonte et al., 2017). The preferential or concurrent
266 SO_4^{2-} reduction process may preserve occluded As (V) and resulting in an inhibition of As(V)
267 reduction (Burton et al., 2013), which is a possible explanation for the low proportion and
268 amounts of As(III) detected in the sediments.

269 270 **3.3 Mercury in surface sediments: occurrence and speciation**

271
272 The total mercury concentrations (Hg_{tot}) fall in the range of $0.10\text{--}1.33 \text{ }\mu\text{g}\cdot\text{g}^{-1}$ (avg. 0.41 ± 0.21
273 $\mu\text{g}\cdot\text{g}^{-1}$). Like As_{tot} , concentrations of Hg_{tot} exceed the estimated concentration of $0.2 \text{ }\mu\text{g}\cdot\text{g}^{-1}$ for
274 uncontaminated marine sediments (Salomons and Forstner, 1984) and the background level
275 estimated for local estuarine sediments ($0.012 \pm 0.001 \text{ }\mu\text{g}\cdot\text{g}^{-1}$, Garcia-Ordiales et al., 2016). In
276 addition, the Hg_{tot} concentrations were all above the Threshold Effect Concentration value
277 ($0.18 \text{ }\mu\text{g}\cdot\text{g}^{-1}$), but only 3% of the samples exceed the Probable Effect Concentration value (1.1
278 $\mu\text{g}\cdot\text{g}^{-1}$).

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280 The distribution of the metal concentration in the surface estuarine sediments (Fig. 6) is quite
281 similar to that observed for As_{tot} (Fig. 4) and the highest values for Hg_{tot} are also found in the
282 port basin of San Esteban de Pravia. The two elemental concentrations are strongly correlated
283 ($r^2 = 0.884$, $p < 0.01$) (Fig. 2, supplementary material). This relationship has already been
284 reported by Silva et al. (2014) for the sediments of the Nalón river drainage basin and by
285 Garcia-Ordiales et al. (2017) for the saltmarsh sediments of its estuary. This strong correlation
286 supports a mutual origin associated with the sources identified in the mining districts and the
287 subsequent common mechanism of dispersion along the river basin estuary. The correlations
288 observed between Hg_{tot} with grain sizes, C_{org} and S concentrations suggest the adsorption
289 mechanisms for Hg are different from those hypothesised for As_{tot} . Concentrations of Hg_{tot}
290 were closely related to the amount of C_{org} ($r^2 = 0.896$, $p < 0.01$), clay ($r^2 = 0.843$, $p < 0.01$), and S
291 ($r^2 = 0.782$, $p < 0.01$) (Fig. 2, supplementary material). These results demonstrated that the
292 organic fractions were likely the most significant factor controlling the distribution
293 concentrations of Hg in sediments together with the grain size, but also the presence of
294 sulphide species cannot be disregarded as reflect the high correlation between Hg_{tot} and S. These
295 correlations have already been observed in other global coastal environments impacted by Hg
296 mining activities (e.g. Covelli et al., 2001; Conaway et al., 2003) and also in the Asturias Hg
297 mining areas (Silva et al., 2014). In this geochemical context, Hg sulphide is the most common
298 species near the source but downstream Hg could be mainly found in the form of Hg^{2+} . This
299 species could be trapped in the sediment by a variety of processes such as complexing or
300 chelation with organic ligands, sorption onto colloids or Fe-Mn oxides and/or incorporation
301 into the crystal lattice of mineral grains (Biester et al., 2000; Covelli et al., 2001; Silva, 2014) as
302 is highlighted from the observed correlations.

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304 The concentration values of MeHg in the sediments (Fig. 6) range from 303.20 to 865.40 $\text{pg}\cdot\text{g}^{-1}$,
305 and show significant positive relationships with Hg_{tot} ($r^2 = 0.886$, $p < 0.01$) and C_{org} ($r^2 = 0.700$, p
306 < 0.01). The importance of the microbial activity of sulphate-reducing bacteria in mercury
307 methylation processes has been demonstrated (e.g. Gilmour et al., 1992), and the most
308 important parameters controlling methylation rate are mercury, sulphate concentrations and
309 the amount of organic matter (e.g. Benoit et al., 1999), in accordance with the significant
310 correlations previously mentioned. The spatial dispersion of MeHg in the estuarine sediments
311 (Fig. 6) demonstrated that the highest levels of MeHg occurred in the San Esteban de Pravia
312 port area, whereas the lowest values were detected in the upper part of the estuary. An
313 examination of the relative abundance of MeHg versus Hg_{tot} allows additional insights
314 regarding the occurrence of MeHg among the different sectors of the estuary. The MeHg
315 component ($< 0.10\%$ MeHg) was similar to that of other estuaries impacted by Hg mining
316 activities (Table 1), which does not generally exceed 0.5% (Conaway et al., 2003; Hines et al.,
317 2006). In contrast, the percentage of MeHg was very low compared to other estuaries where
318 the primary sources of Hg in the aquatic environment are urban, industrial, agricultural, or
319 aerial depositions, for which the MeHg component may account for values near 100% (Haris et
320 al., 2017). The relationship between *in situ* Hg speciation and methylation is not easy to
321 represent as each sediment type shows a different methylation potential (Bloom et al., 2003).
322 In the estuary, the percentage of MeHg showed that only low amounts of the Hg_{tot} are
323 methylated, suggesting first the probable occurrence of Hg species such as cinnabar, not
324 readily available for methylation and second, a low biological activity which is in agreement
325 with the negligible concentrations of organic As species. This is apparent based on the
326 percentage values of MeHg, as they are quite similar to those detected for samples collected
327 both outside and inside the San Esteban port area in spite of the differences observed in the
328 Hg_{tot} contents. The relationships among the percentage of MeHg and the main factors
329 affecting methylation (Benoit et al., 1999), only appear significant for C_{org} ($r^2 = 0.825$, $p < 0.01$)

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330 and S ($r^2 = -0.651$, $p < 0.01$) although in an opposite manner (Fig. 5a and 5b). Organic matter is
331 well known for playing a key role for the metabolism of methylating bacteria at the water-
332 sediment interface (e.g. Ullrich et al., 2001; Hines et al., 2017 and references herein).
333 Conversely, the negative correlation of MeHg/Hg with sulphur suggests not only a greater
334 availability of Hg for methylation when present in forms not associated with sulphur but also
335 that this element acts as a limiting factor of methylation where sediments are highly anoxic
336 (Fig. 5b). It is indeed possible that high rates of SO_4 reduction in sediment near the surface,
337 especially in summer, produce sufficient sulphide to lower the availability of Hg for
338 methylation (Hines et al., 2006).

339

340 **4. Conclusions**

341

342 The correlation between the total As and Hg concentration in sediments revealed the
343 important parallel contributions derived from mine sites to the estuary. It is apparent that the
344 spatial distribution of the two elements is strictly correlated to decreasing grain size.
345 Consequently, the high levels of As and Hg are mainly restricted to the port areas where
346 artificial barriers have allowed the accumulation of fine sediments. The high presence of
347 sulphides and the redox conditions seem to govern the speciation cycles of As and Hg in the
348 sediments reducing the formation of the most toxic species of As(III) and MeHg. The resistant
349 sulphur complex ligands acts as an inhibitor for the biological and chemical speciation
350 processes, reducing the apparent environmental threat. Possible changes in environmental
351 conditions such as extreme hydrological events or eutrophication, could alter the current
352 status, thus limiting or enhancing the availability of metal(loid)s in the aquatic environment. In
353 addition, anthropogenic activities such as dredging operations could affect the remobilisation
354 of metal(loid)s from bottom sediments through resuspension, which could represent a
355 potential secondary pollution source not only within the estuary environment but also in the

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356 nearby Cantabrian sea coastal environments as a result of tidal flux exchange. Future research
357 in the Nalón estuarine environment should focus on exploring the effects of possible
358 resuspension of bottom sediments contaminated by Hg and As as well as estimating their
359 mobility and exchange between sediments and the water column at selected estuarine sites.

360

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362

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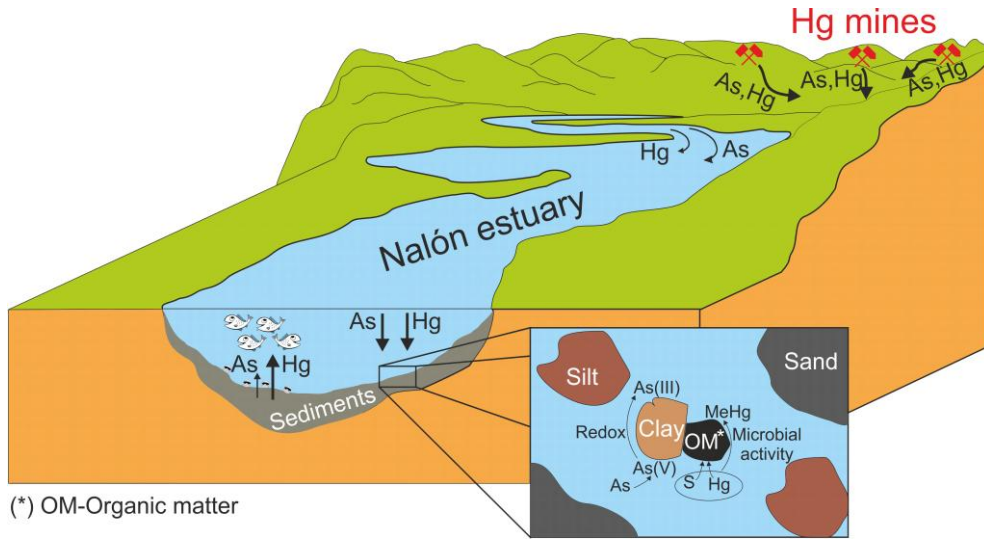
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587 **Graphical abstract**

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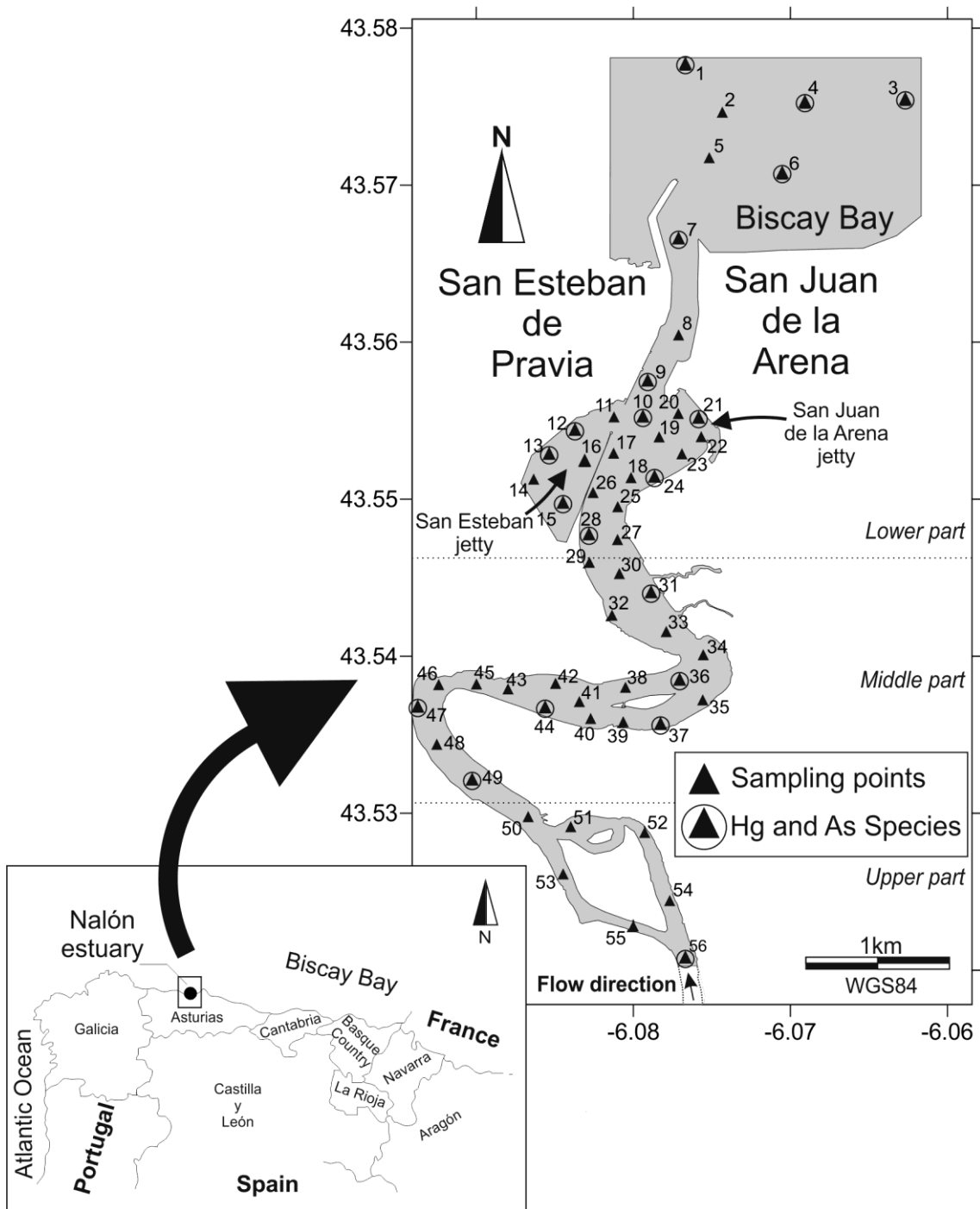


(*) OM-Organic matter

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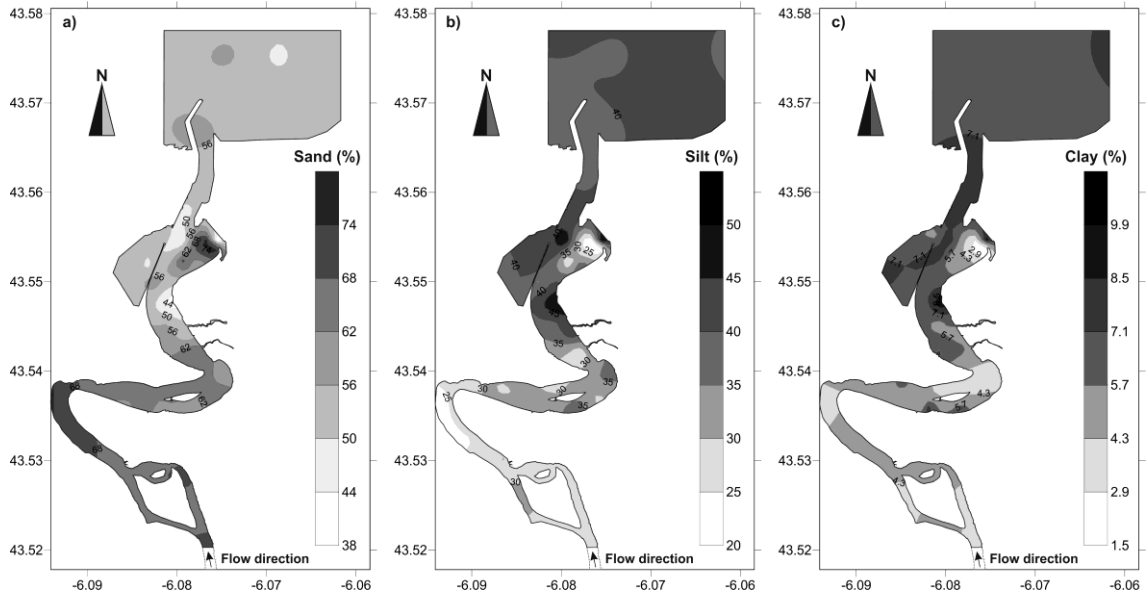


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594 *Figure 1. Index map of the Nalón River estuary along with location of the sediment sampling*

595 *points*

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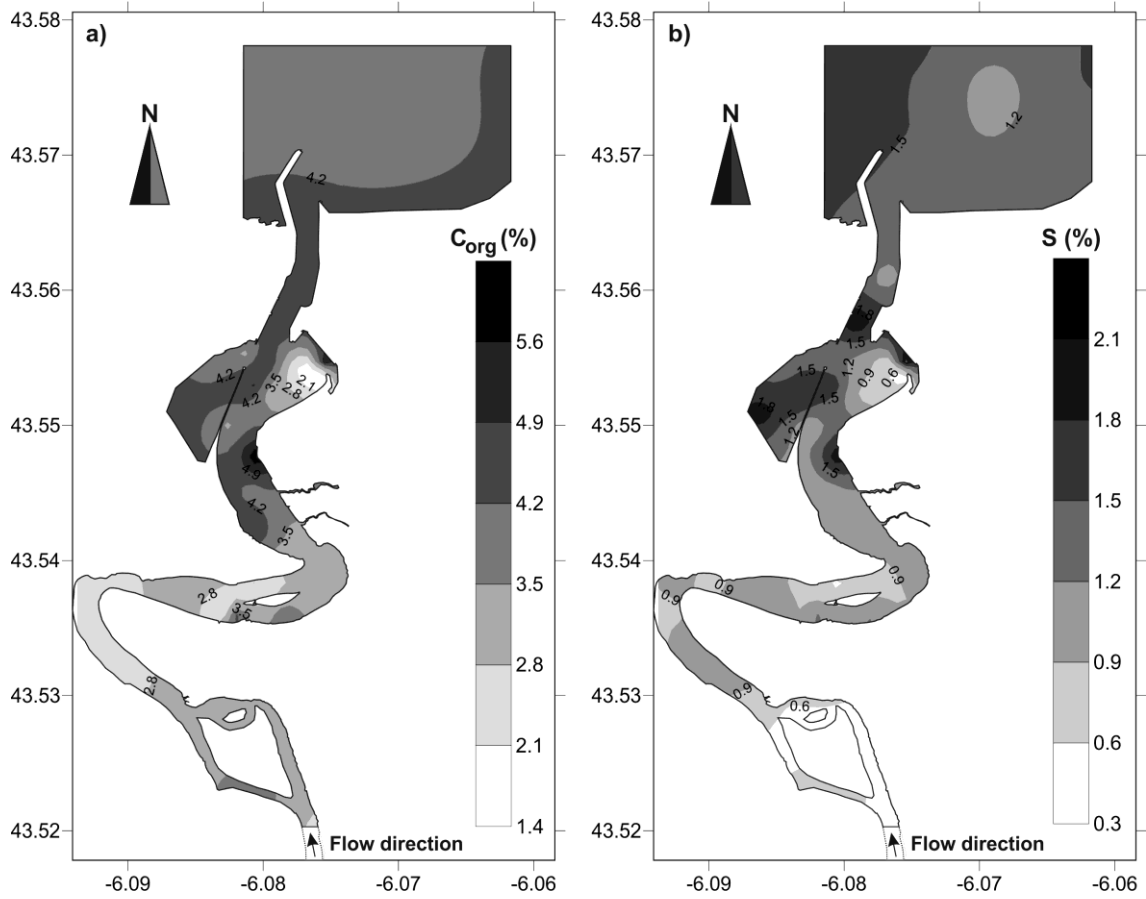


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598 *Figure 2. Spatial distribution of the sand (a), silt (b) and clay (c) fractions in the surface*

599 *sediments of the Nalón estuary.*

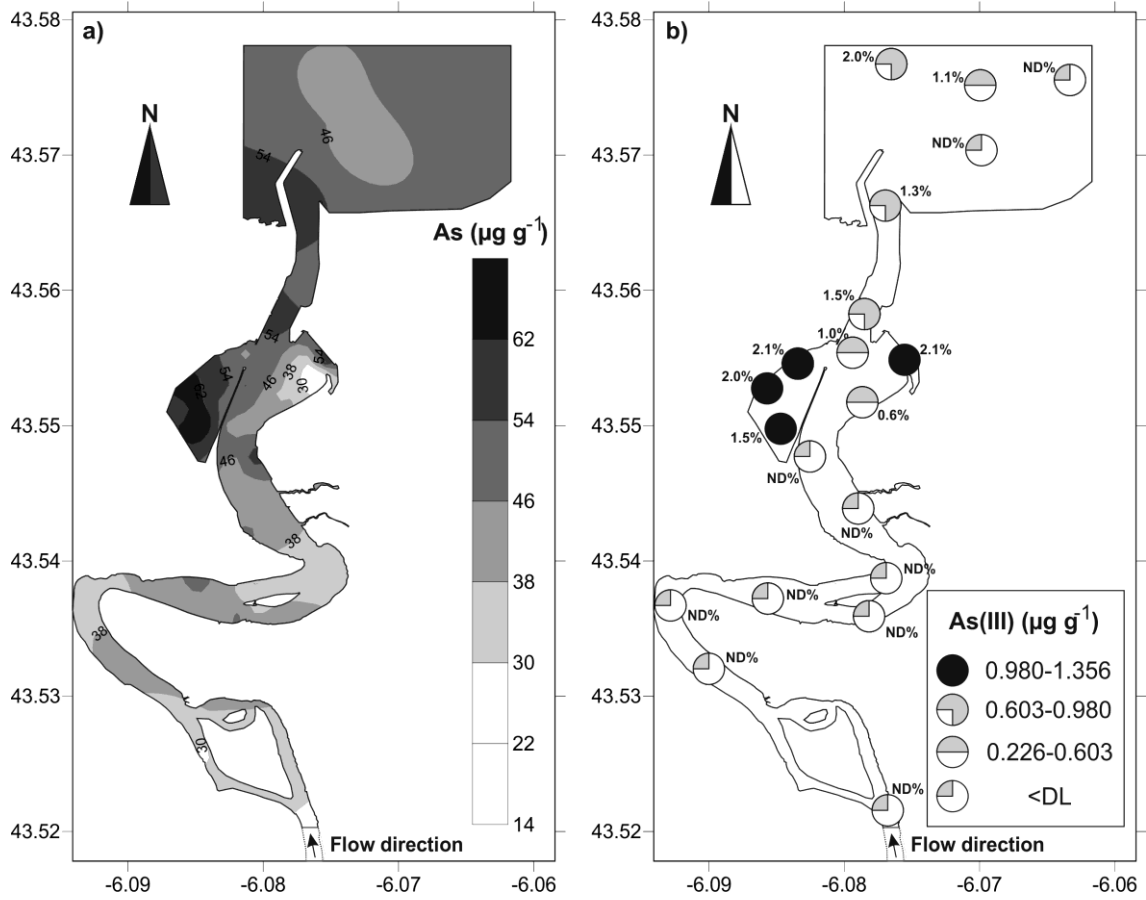
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602 *Figure 3. Spatial distribution of C_{org} (a) and S_{tot} (b) concentrations (%) in the surface sediments*
 603 *of the Nalón estuary.*

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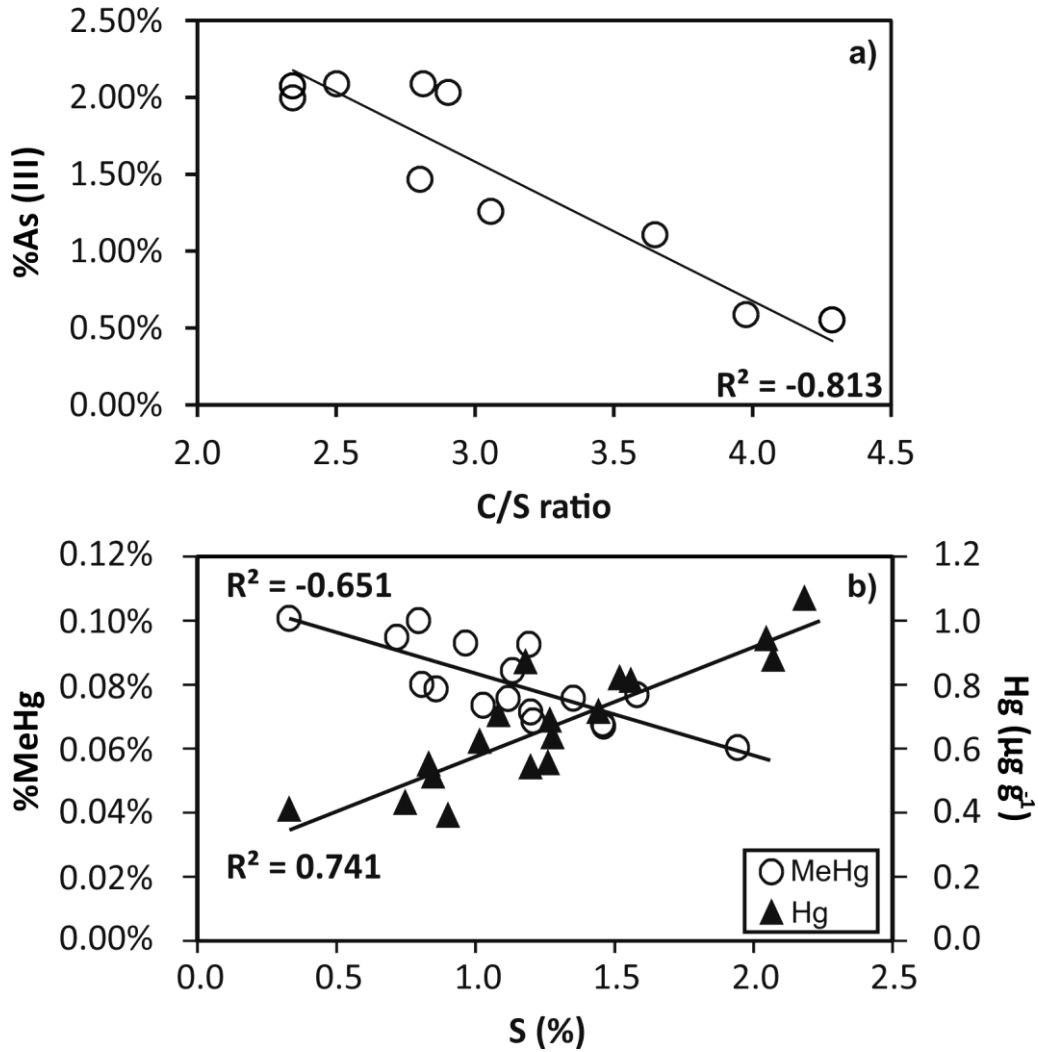


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607 *Figure 4. Spatial distribution of As_{tot} (a) and $As(III)$ (b) concentration ($\mu g g^{-1}$) in the surface*
 608 *sediments of the Nalón estuary. Percentage values represent the abundance of $As(III)$ with*
 609 *respect to the concentration of As_{tot} .*

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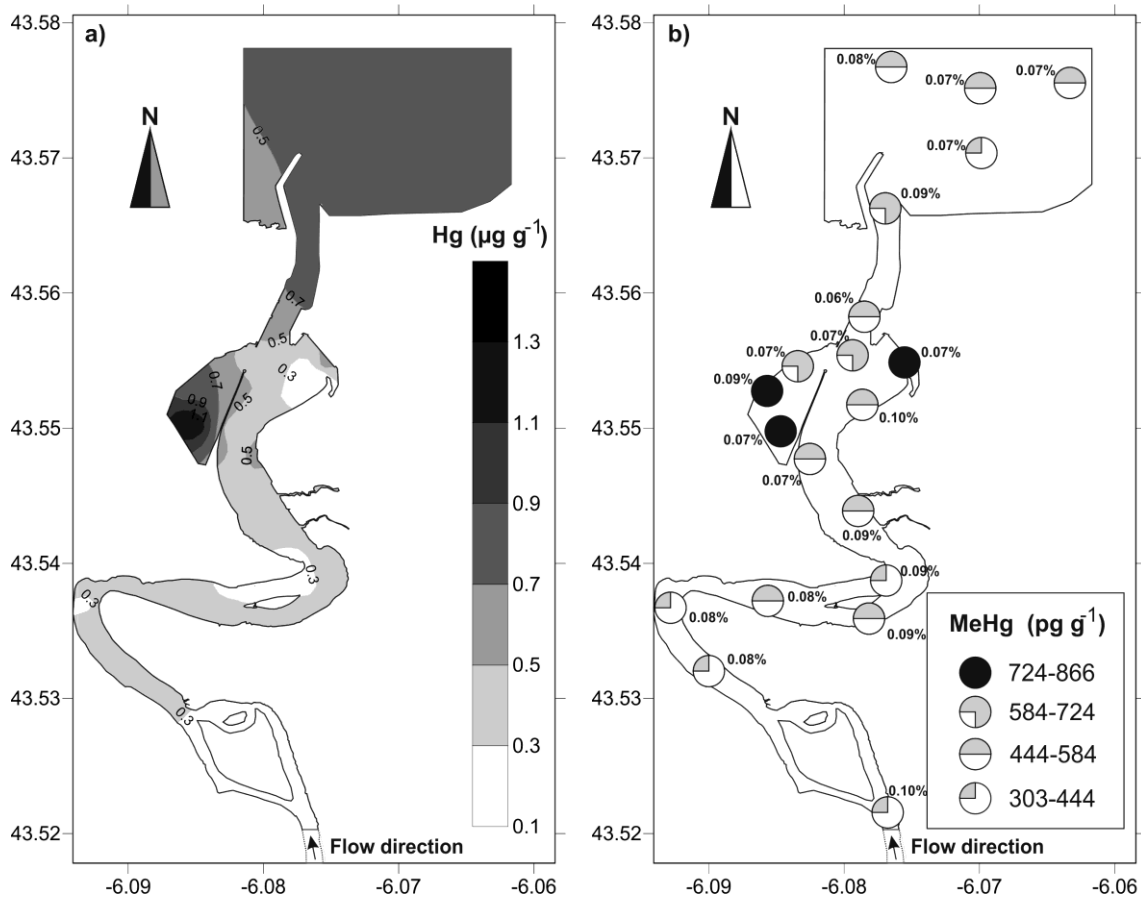
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613 *Figure 5. Scatterplots of %As(III) as a function of C/S ratio and Hg ($\mu\text{g g}^{-1}$) and %MeHg as a*
614 *function of S concentrations (%) in the surface sediments of the Nalón estuary.*

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616

617 *Figure 6. Spatial distribution of Hg_{tot} (a, in $\mu g g^{-1}$) and MeHg (b, in $pg g^{-1}$) concentration in the*
 618 *surface sediments of the Nalón estuary. Percentage values represent the abundance of the*
 619 *MeHg component with respect to the total concentration of Hg (Hg_{tot}).*

620

621 *Table 1. Ranges of mercury and arsenic concentrations reported in literature for coastal*
 622 *environments. (na- not available and <DL- Below detection limit).*

	As ($\mu\text{g g}^{-1}$)	Hg ($\mu\text{g g}^{-1}$)	MeHg (ng g^{-1})	Primary source	Authors
Nalón estuary (Spain)	20.10-68.10	0.10-1.33	0.30-0.87	Hg mining	This study
Tagus estuary (Portugal)	1.90-1022.00	0.20-66.70	<DL-6.70	Industry	Vale et al., 2008 Canario et al., 2007
Marano and Grado Lagoon (Italy)	na	0.68-9.95	0.47-7.85	Hg mining and industry	Acquavita et al., 2012
Venice Lagoon (Italy)	8.9-68.9	0.64-3.41	0.40-1.56	Industry	Giusti and Zhang, 2002
Gulf of Trieste (Italy)	6.40-18.20	0.10-23.30	0.20-60.10	Hg mining	Acquavita et al., 2010 Covelli et al., 2001
Northern Tyrrhenian Sea (Italy)	5.43-35.38	0.03-2.20	na	Hg mining	Piazzolla et al., 2015 Scanus et al., 2016
Kastela Bay (Croatia)	15.00-33.00	17.60-74.00	6.05-16.40	Industry	Orescanin et al., 2005 Kwokal et al., 2002
Aegean Sea (Turkey)	7.00-70.00	0.05-102.00	na	Hg mining	Ozkan et al., 2017
San Francisco Bay (USA)	2.25-13.50	0.03-2.65	0.01-10.3	Hg mining	Yee et al., 2017
Tomales Bay (USA)	na	0.05-3.10	0.30-70.00	Hg mining	Johnson et al., 2009
Honda Bay, Palawan (Philippines)	na	0.03-570.00	-	Hg mining	Benoit et al., 1994

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625 **Supplementary material**

626 *Table 1. Results of selected parameters determined in the sediments of the Nalón estuary.*

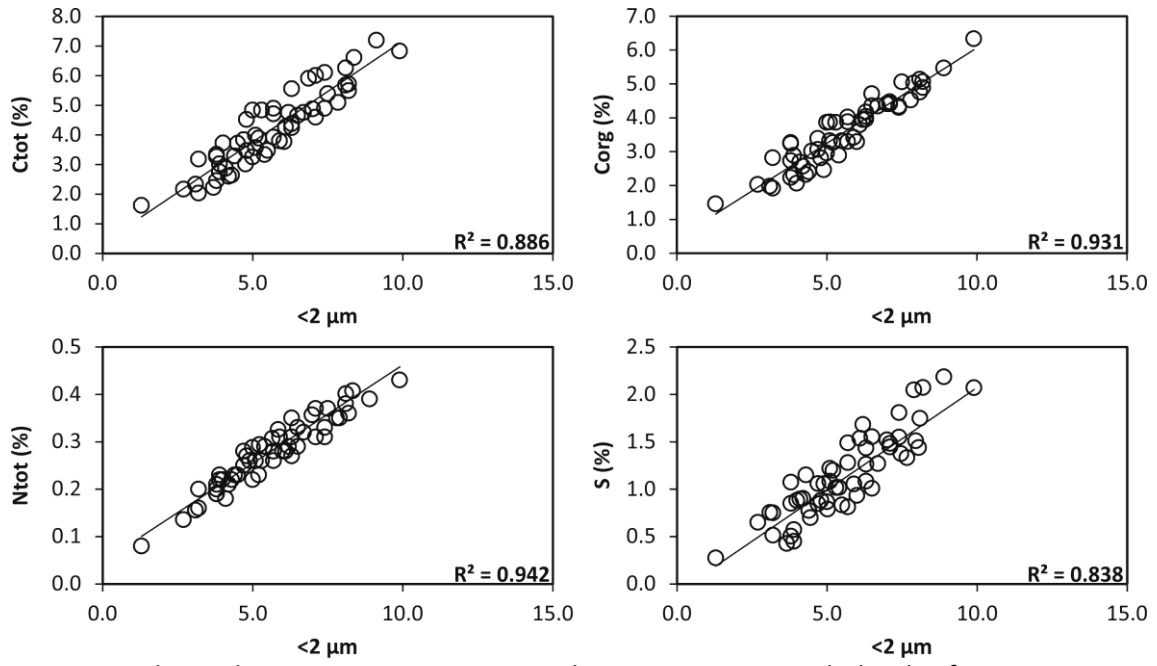
627 *Note: <DL-Below detection limit*

Sample	Lat	Long	Sand (%)	Silt (%)	Clay (%)	TC (%)	TOC (%)	N (%)	S (%)	As ($\mu\text{g g}^{-1}$)	As(V) ($\mu\text{g g}^{-1}$)	As(III) ($\mu\text{g g}^{-1}$)	% As(III)	Hg ($\mu\text{g g}^{-1}$)	MeHg (pg g^{-1})	% MeHg
1	-6.076	43.578	49.40	44.40	6.20	4.76	3.94	0.29	1.68	46.10	44.20	0.90	2.0%	0.65	492.20	0.08%
2	-6.075	43.576	58.90	35.40	5.70	4.71	4.02	0.28	1.49	41.70	-	-	-	0.70	-	-
3	-6.062	43.576	54.00	38.60	7.40	6.10	4.30	0.31	1.55	50.30	48.90	<DL	ND	0.74	487.00	0.07%
4	-6.069	43.575	49.20	44.50	6.30	5.56	3.96	0.35	1.08	54.10	53.50	0.60	1.1%	0.71	509.20	0.07%
5	-6.076	43.572	53.10	40.80	6.10	4.26	3.79	0.28	1.53	46.70	-	-	-	0.57	-	-
6	-6.073	43.571	52.60	41.70	5.70	4.89	3.88	0.26	1.28	38.10	37.90	<DL	ND	0.64	426.80	0.07%
7	-6.077	43.567	57.50	35.40	7.10	4.59	4.41	0.37	1.44	59.20	58.46	0.74	1.3%	0.72	642.60	0.09%
8	-6.077	43.561	52.70	39.50	7.80	4.84	4.52	0.35	1.10	49.70	-	-	-	0.83	-	-
9	-6.079	43.558	48.50	43.30	8.20	5.71	4.89	0.42	2.07	59.20	58.30	0.91	1.5%	0.88	512.20	0.06%
10	-6.080	43.555	39.70	52.10	8.20	5.49	5.06	0.36	1.18	53.20	52.69	0.51	1.0%	0.87	647.00	0.07%
11	-6.081	43.555	54.80	40.10	5.10	3.57	3.32	0.32	1.22	43.30	-	-	-	0.63	-	-
12	-6.084	43.554	51.20	42.50	6.30	4.24	4.04	0.31	1.43	61.50	60.22	1.28	2.1%	0.82	610.80	0.07%
13	-6.086	43.552	54.20	38.80	7.00	4.87	4.41	0.39	1.52	66.80	65.44	1.36	2.0%	0.94	824.60	0.09%
14	-6.086	43.551	54.70	37.40	7.90	6.74	5.02	0.35	2.05	56.70	-	-	-	1.17	-	-
15	-6.085	43.550	53.50	40.00	6.50	4.65	4.35	0.33	1.55	68.10	67.10	1.00	1.5%	1.33	865.40	0.07%
16	-6.083	43.552	49.20	43.40	7.40	4.64	4.33	0.33	1.81	52.90	-	-	-	0.81	-	-
17	-6.081	43.553	50.20	41.70	8.10	5.67	5.13	0.43	1.75	55.40	-	-	-	0.69	-	-
18	-6.079	43.552	71.50	24.40	4.10	2.87	2.69	0.18	0.90	36.80	-	-	-	0.40	-	-
19	-6.078	43.554	71.20	25.00	3.80	2.45	2.23	0.19	0.85	34.50	-	-	-	0.29	-	-
20	-6.077	43.555	76.00	21.30	2.70	2.17	2.03	0.12	0.65	29.50	-	-	-	0.24	-	-
21	-6.076	43.555	38.40	52.70	8.90	7.29	5.47	0.39	2.18	63.50	62.18	1.32	2.1%	1.07	779.40	0.07%
22	-6.076	43.554	80.00	18.70	1.30	1.62	1.45	0.08	0.27	20.10	-	-	-	0.10	-	-
23	-6.076	43.553	69.10	27.80	3.10	2.33	1.98	0.14	0.75	26.50	-	-	-	0.23	-	-
24	-6.078	43.552	55.30	39.20	5.50	3.47	3.32	0.33	0.83	38.70	38.47	0.23	0.6%	0.55	549.80	0.10%
25	-6.081	43.549	49.90	43.00	7.10	6.00	4.47	0.31	1.48	45.80	-	-	-	0.73	-	-
26	-6.083	43.550	60.20	34.10	5.70	3.92	3.29	0.35	0.81	43.70	-	-	-	0.50	-	-
27	-6.081	43.548	39.60	50.50	9.90	6.83	6.33	0.43	2.07	62.40	-	-	-	1.03	-	-
28	-6.082	43.547	48.50	44.80	6.70	4.75	4.34	0.32	1.27	43.50	43.32	<DL	ND	0.69	481.60	0.07%
29	-6.083	43.546	54.10	39.40	6.50	6.20	4.71	0.29	1.01	44.20	-	-	-	0.79	-	-
30	-6.081	43.545	56.80	38.10	5.10	3.99	3.87	0.26	1.08	41.30	-	-	-	0.59	-	-
31	-6.079	43.544	51.20	43.50	5.30	4.83	3.86	0.26	1.02	40.80	41.10	<DL	ND	0.62	574.80	0.09%
32	-6.081	43.542	60.80	31.70	7.50	5.39	5.06	0.37	1.24	47.10	-	-	-	0.77	-	-
33	-6.078	43.542	67.30	26.80	5.90	3.55	3.42	0.31	1.05	40.50	-	-	-	0.58	-	-
34	-6.075	43.539	59.60	36.60	3.80	4.10	3.24	0.20	1.07	32.70	-	-	-	0.53	-	-
35	-6.076	43.537	66.70	28.50	4.80	3.46	2.81	0.27	0.88	37.80	-	-	-	0.39	-	-
36	-6.077	43.539	64.50	32.30	3.20	3.18	2.82	0.16	0.75	31.80	31.50	<DL	ND	0.43	407.00	0.09%
37	-6.078	43.536	55.20	38.50	6.30	4.38	4.17	0.27	1.26	45.10	44.70	<DL	ND	0.56	510.80	0.09%
38	-6.081	43.538	68.40	28.40	3.20	2.03	1.92	0.20	0.51	28.20	-	-	-	0.22	-	-
39	-6.081	43.536	61.00	33.60	5.40	3.33	2.89	0.29	1.02	38.40	-	-	-	0.48	-	-
40	-6.082	43.536	56.20	35.70	8.10	6.25	4.75	0.38	1.31	50.10	-	-	-	0.70	-	-
41	-6.083	43.536	66.20	29.80	4.00	2.18	2.06	0.22	0.88	38.20	-	-	-	0.20	-	-
42	-6.085	43.538	62.50	31.50	6.00	3.52	3.29	0.28	0.93	45.30	-	-	-	0.58	-	-
43	-6.086	43.537	66.50	28.80	4.70	4.75	3.39	0.25	1.06	39.60	-	-	-	0.59	-	-
44	-6.086	43.536	58.80	36.00	5.20	3.88	3.27	0.23	1.20	40.30	36.70	<DL	ND	0.54	452.40	0.08%
45	-6.090	43.538	66.20	29.40	4.40	3.29	2.40	0.23	0.77	37.50	-	-	-	0.35	-	-
46	-6.093	43.538	70.30	25.40	4.30	2.64	2.32	0.22	1.15	32.50	-	-	-	0.31	-	-
47	-6.093	43.535	71.20	24.60	4.20	2.60	2.57	0.21	0.90	37.70	39.60	<DL	ND	0.39	303.20	0.08%
48	-6.090	43.532	70.50	24.60	4.90	2.53	2.46	0.26	1.06	40.10	-	-	-	0.31	-	-
49	-6.086	43.530	65.10	30.20	4.70	3.83	3.06	0.28	0.85	35.20	33.70	<DL	ND	0.52	410.60	0.08%
50	-6.084	43.529	68.20	26.80	5.00	3.25	2.96	0.22	0.58	38.80	-	-	-	0.43	-	-
51	-6.079	43.529	69.30	26.20	4.50	3.71	3.02	0.23	0.52	37.30	-	-	-	0.49	-	-
52	-6.084	43.526	64.10	32.10	3.80	3.34	3.26	0.19	0.50	32.10	-	-	-	0.54	-	-
53	-6.078	43.524	66.20	29.90	3.90	3.02	2.89	0.23	0.45	32.40	-	-	-	0.45	-	-
54	-6.094	43.537	72.50	23.60	3.90	2.75	2.32	0.22	0.57	30.10	-	-	-	0.34	-	-
55	-6.080	43.523	67.20	27.80	5.00	4.84	3.86	0.30	0.87	35.20	-	-	-	0.58	-	-
56	-6.077	43.520	69.30	26.90	3.80	3.27	2.73	0.21	0.33	32.30	30.20	<DL	ND	0.41	412.40	0.10%

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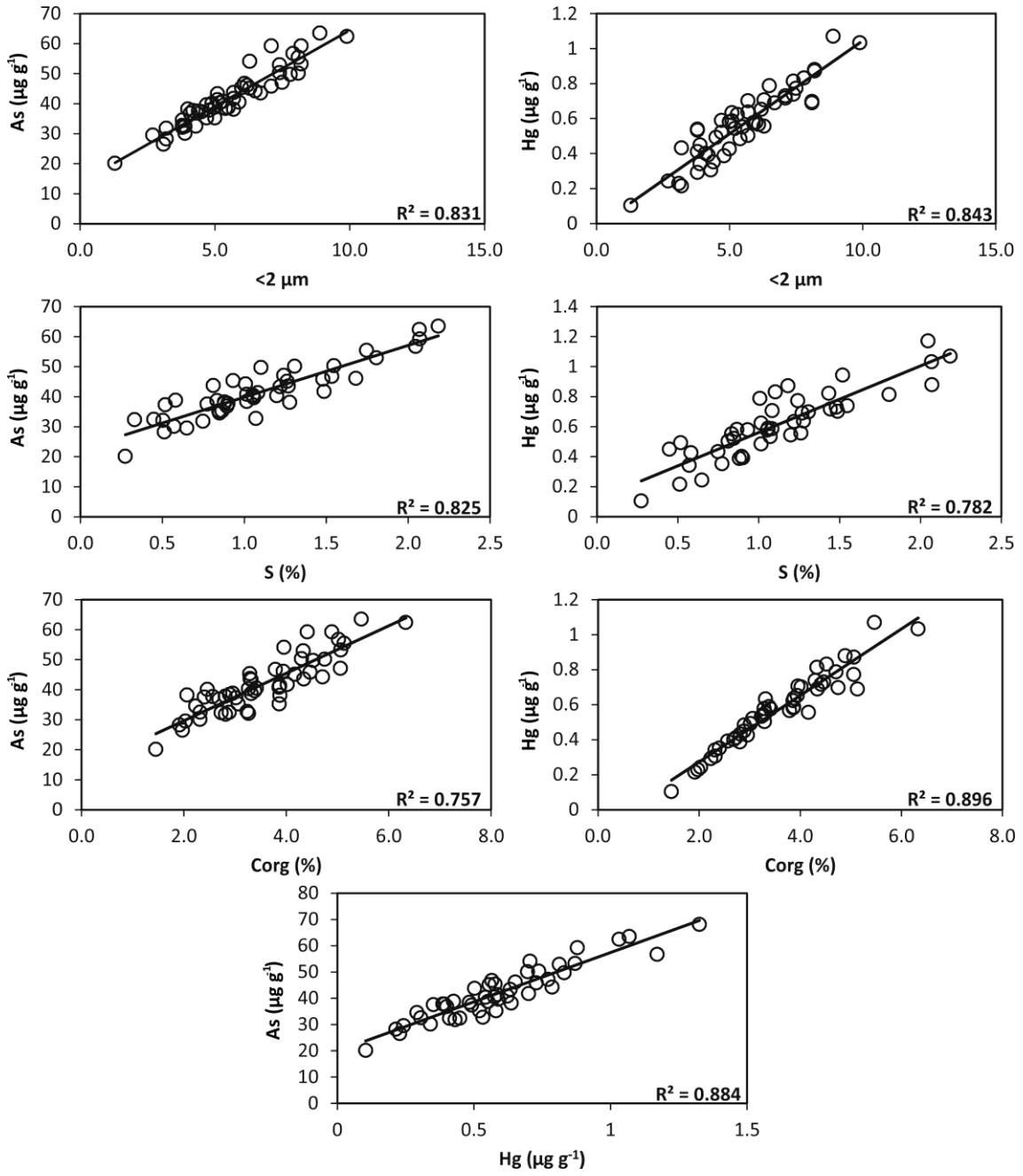
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631
 632 *Figure 1. Relationships among C_{tot} , C_{org} , N_{tot} and S concentrations with the clay fraction.*

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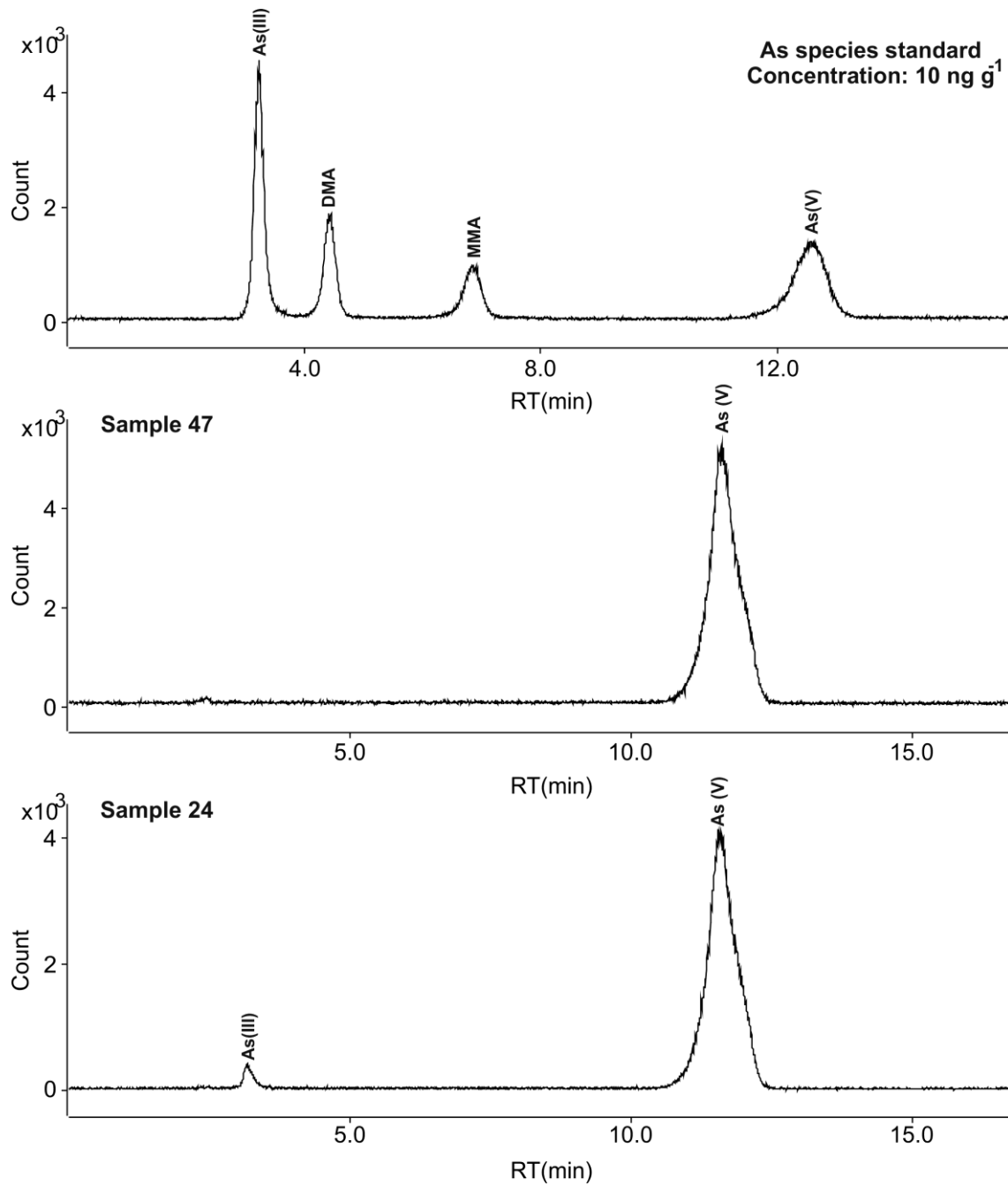
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636 *Figure 2. Relationships among As_{tot} and Hg_{tot} concentrations with the most significant*
637 *geochemical parameters of the surface sediments (clay fraction, C_{org} and S).*

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639
 640 *Figure 3. Examples of different chromatograms obtained from the As speciation analysis*

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Highlights

- Dispersion and speciation of As and Hg in the Nalón estuary sediments were studied.
- As and Hg correlate with clay fraction, organic matter and sulphur.
- As speciation is governed by sediment redox conditions
- Sulphur content seems to be a limiting factor for Hg speciation in sediments