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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 ($303.20\text{--}865.40 \text{ pg} \cdot g^{-1}$) 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.

18

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20

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).

33
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

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**

71

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

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} ,

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,

1984; Francesconi and Edmonds, 1997). These results are consistent with the concentrations detected in core profiles from the same area (Garcia-Ordiales et al., 2015, 2016, 2017). Due to long-term extraction activity, the As_{tot} background values have significantly increased, surpassing the consensus-based threshold levels (MacDonald et al., 2000) such as the Threshold Effect Concentration (As TEC, $9.97 \mu\text{g}\cdot\text{g}^{-1}$), and the Probable Effect Concentration (As PEC, $33.0 \mu\text{g}\cdot\text{g}^{-1}$), the latter of which is exceeded by 86% of the samples.

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

Speciation analysis of As showed that the occurrence of the organic species (monomethylarsonate and dimethylarsinate) was negligible; the inorganic arsenic species are dominant in the sediments (Fig. 3, supplementary material). Moreover, within the inorganic As species, arsenate was the main one found in the sediments due to the oxidising conditions in the aquatic environment based on the C/S values. The concentration of As(V) falls in the range 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 As_{tot} concentration in the sediments ranges from 97.6% to 100%. In the upper-middle sector of the estuary, As (III) species were not detected possibly as a consequence of the redox conditions in the sediments (avg. C/S 3.90 ± 1.40) which may have potentially produced As(III) although below the detection limit. On the contrary, in the lower sector where marine conditions occur, the majority of the samples showed detectable amounts of As(III). The

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 $\mu\text{g}\cdot\text{g}^{-1}$).

279

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.

303

304 The concentration values of MeHg in the sediments (Fig. 6) range from 303.20 to 865.40 $\mu\text{g}\cdot\text{g}^{-1}$,
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} ($r^2 = 0.825$, $p < 0.01$)

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

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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369

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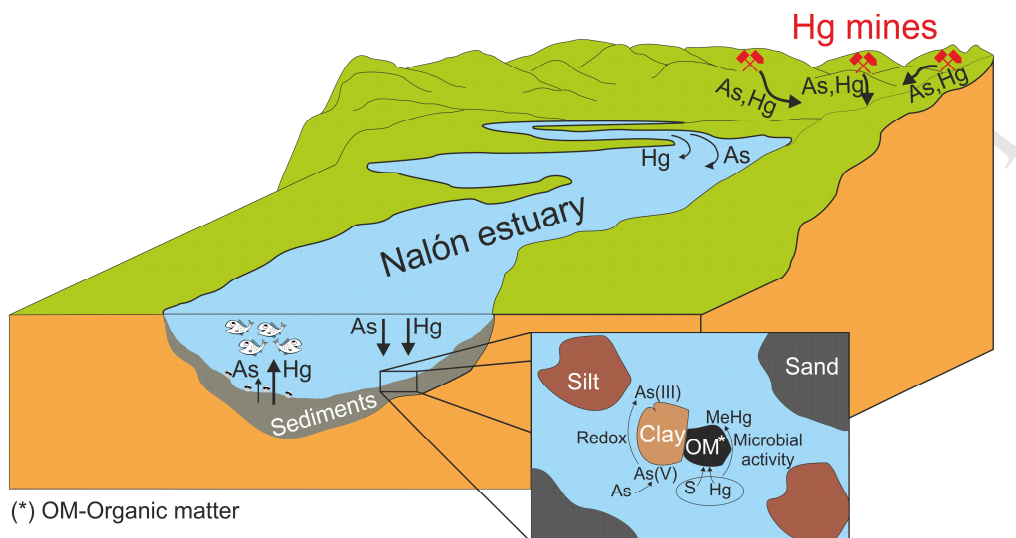
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587 Graphical abstract

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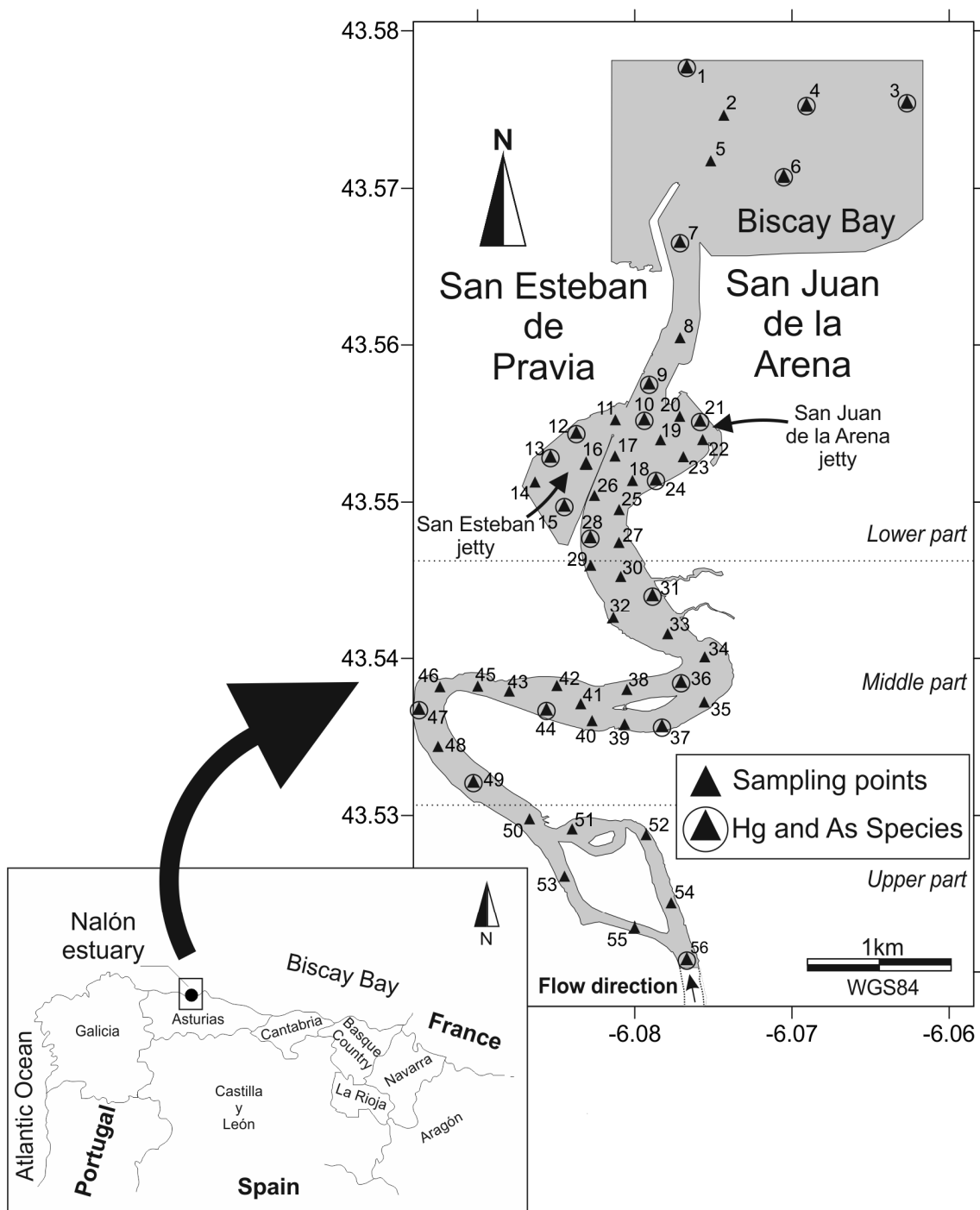
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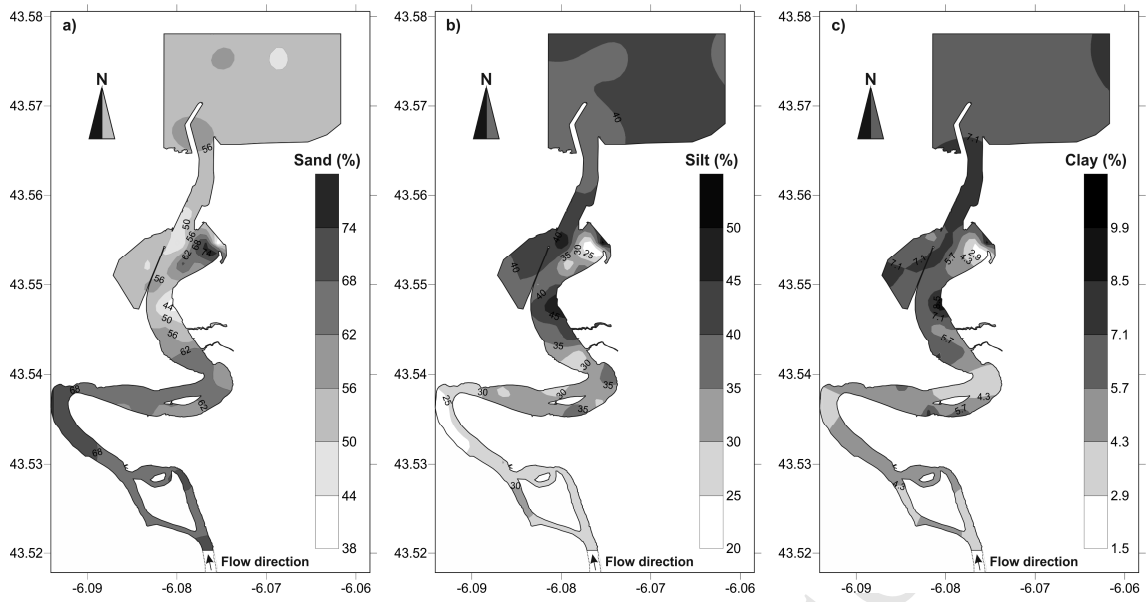
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594 *Figure 1. Index map of the Nalón River estuary along with location of the sediment sampling*595 *points*

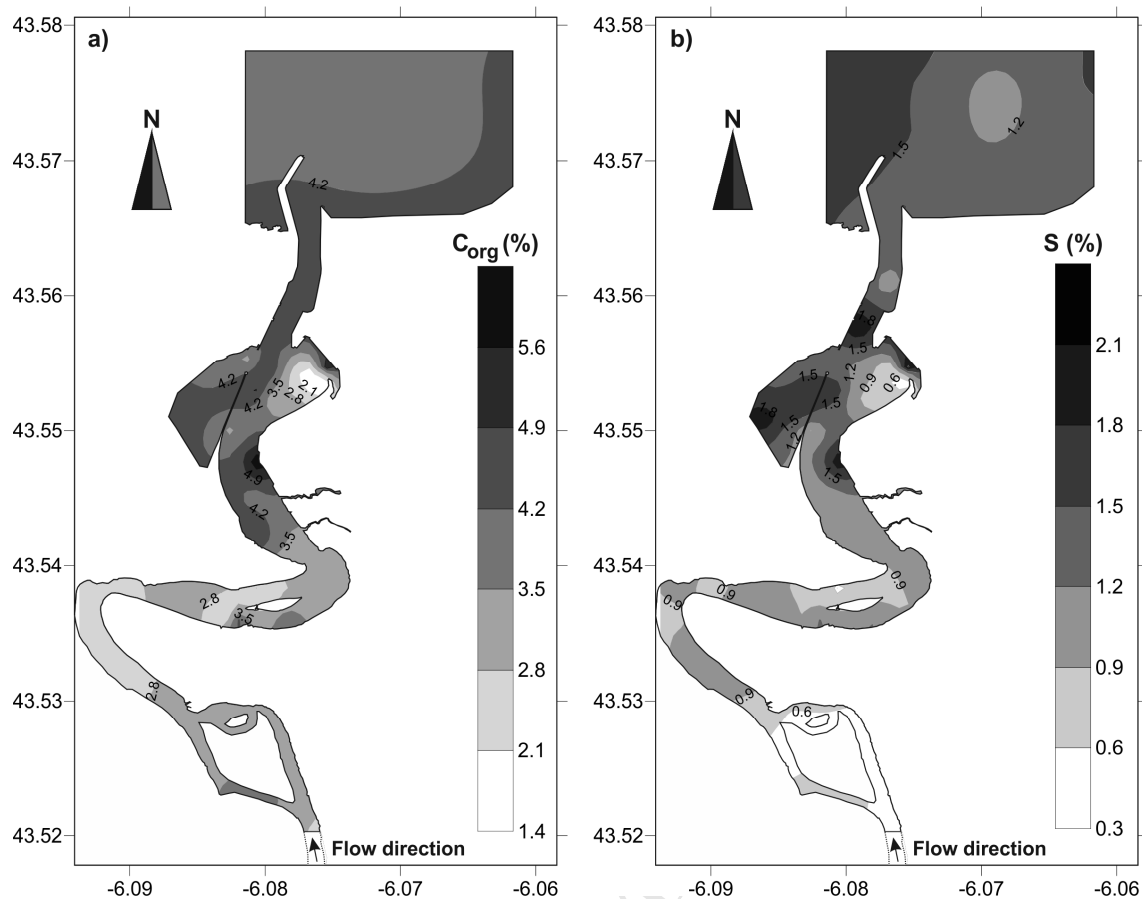
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598 *Figure 2. Spatial distribution of the sand (a), silt (b) and clay (c) fractions in the surface*599 *sediments of the Nalón estuary.*

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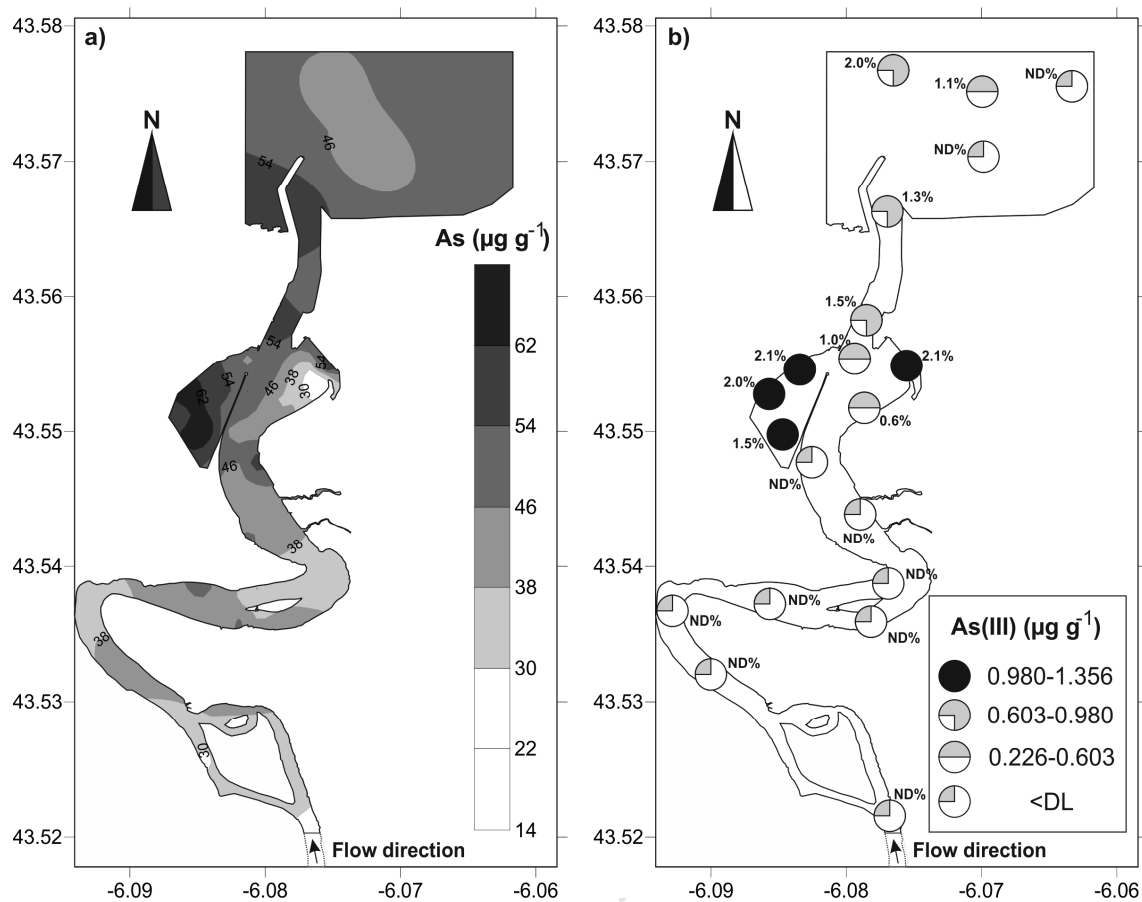


601

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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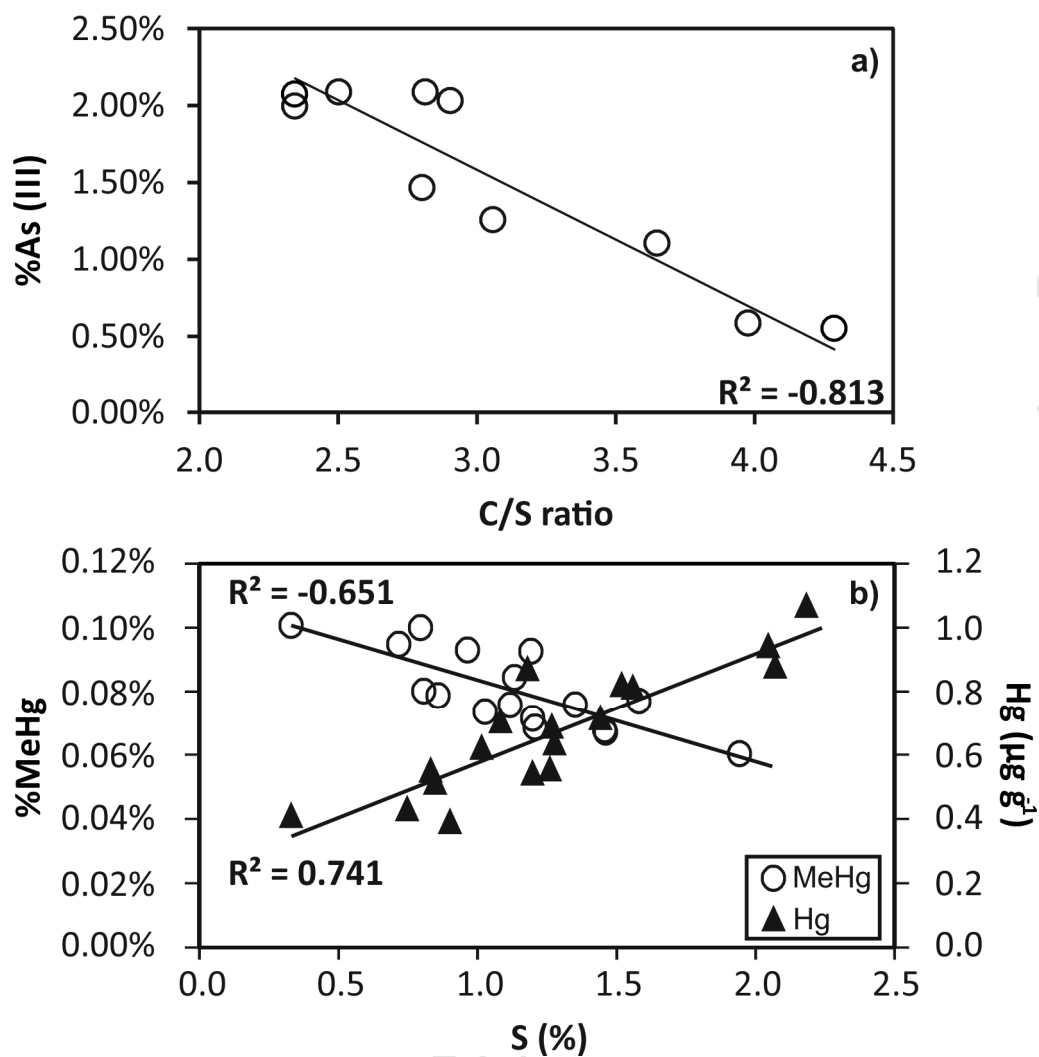


606

607 *Figure 4. Spatial distribution of As_{tot} (a) and $As(III)$ (b) concentration ($\mu\text{g g}^{-1}$) 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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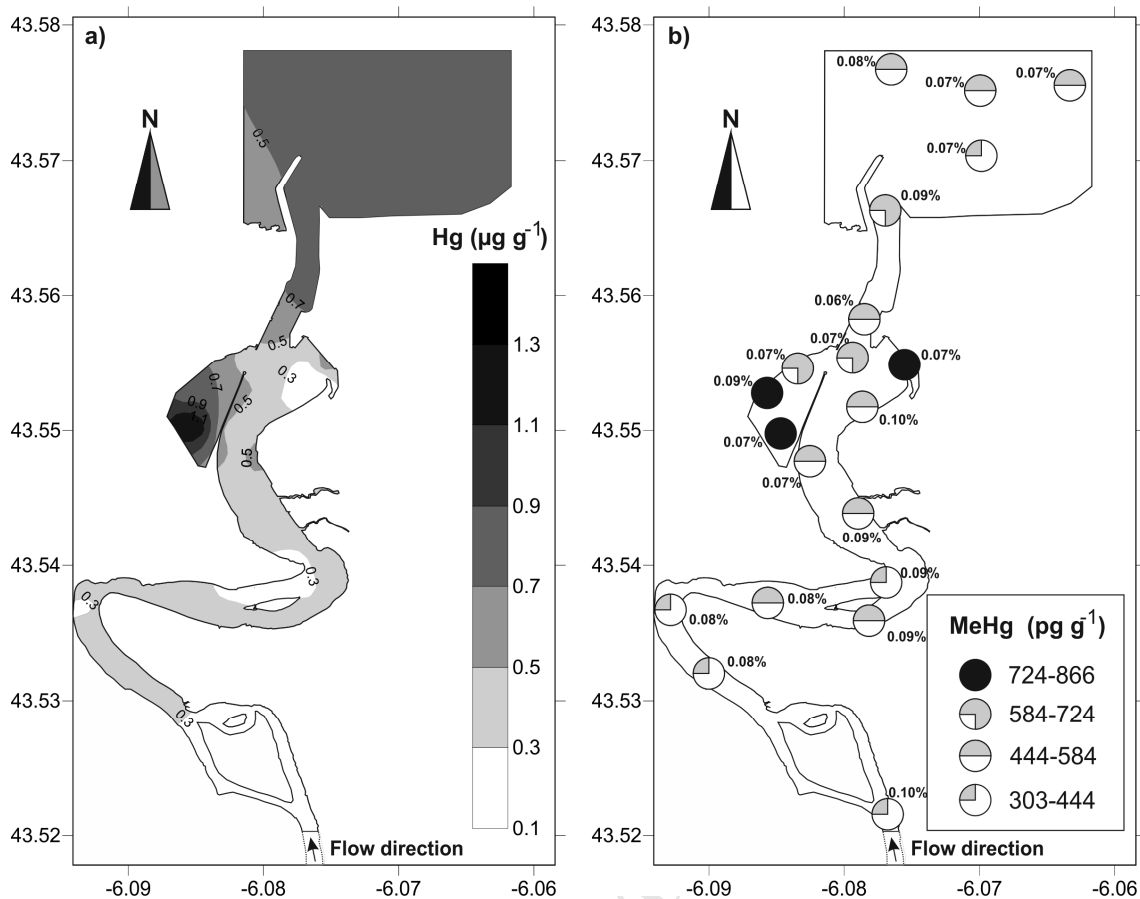
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613 *Figure 5. Scatterplots of %As(III) as a function of C/S ratio and Hg ($\mu\text{g g}^{-1}$) and %MeHg as a*
 614 *function of S concentrations (%) in the surface sediments of the Nalón estuary.*

615



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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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