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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 µg·g−1 to 1.33 µg·g−1, most of it in the form of sulphides. Concentrations of methylmercury (303.20-865.40 pg·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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## 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 ($Hg_{total}$) 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 of this, is available for the methylation process because most of Hg derived from mining occurs~~most of it ~~-~~in the form of sulphides. Concentrations of methylmercury (303.20–865.40 $pg \cdot g^{-1}$) are up to two orders of magnitude lower than the concentration of $Hg_{total}$. Total As concentration ($As_{total}$) is enriched compared to the background level for the area. ~~Speciation analyses indicate that negligible quantities of organic As species are present; rather, the inorganic species (As(III)) and As(V)) are dominant. As (III) concentrations range from values <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 $\mu g \cdot g^{-1}$.~~ The relative abundance of As(V) on As(III) ~~as a percentage of $As_{total}$ (%As (V))~~ 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. ~~a maximum of 2.1% of the $As_{total}$ is present as As (III). The clay fraction is the main grain-size sediment component that entraps Hg and As, and the port areas act as a sink for both elements. In spite of the high total concentrations detected for As compared to Hg, the speciation analysis, their grain-size, and their geochemical characteristics, together with evidence of bioaccumulation in the coastal food web, suggest that transference from~~

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

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

## 1. Introduction

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

The Asturias region (north of Spain) is ~~characterized characterised by~~ one of the most important coastal areas of the country and one ~~that~~which ~~i~~has not been ~~high~~significantly impacted by anthropogenic activities. Consequently, the monitoring and management of this coastal ecosystem is of special concern in maintaining a good level of ecological quality. S~~However, s~~everal estuarine areas along the Asturias coast are very sensitive to possible contamination by sources located inland. Among them, the Nalón estuary is the most important transitional environment, connecting the Cantabrian Sea (the Biscay Bay) and the Nalón River, which is the main hydrographical system of northern Spain. The Nalón estuary contains remarkable anthropogenic contributions of trace metal(oid)s, especially arsenic (As) and mercury (Hg) due to the long-term activity of two mining areas, which have been identified as ‘hotspots’ for these elements (Loredo et al., 1999; Loredo, 2000; Fernández-Martínez et al., 2005). Several studies have been conducted over the last two decades to clarify the sources, processes, and dynamics of As and Hg in different environmental segments, such as soils, mine tailings, and fresh and ground waters of the Nalón River basin (e.g. Loredo et al., 2010; Silva et al., 2014; Ordoñez et al., 2014). R~~However, r~~esearch into the impact of these elements in the Nalón River estuarine system has only recently begun. For instance, As and Hg profiles in saltmarsh sediments and in some boreholes in the main estuarine channel have been studied in detail to reconstruct the long-term contamination history of the area and to establish preliminary geochemical background values for both elements (Garcia-Ordiales et al. 2015, 2016, 2017). Prior to this research, there have been no published reports quantifying Hg and As abundances across the entire estuarine system and determining their areal distribution as well as their sources. The only exception is the measurements performed by the Asturias Regional Port Authority on recent estuarine sediments~~,~~ which demonstrated~~showed~~ significant concentrations of Hg (0.15–1.56 $\mu g \cdot g^{-1}$) and As (20.00–39.20 $\mu g \cdot g^{-1}$) in the period 2003–2011. However, the toxicity and mobility of As and Hg in estuarine sediments strongly depend on their specific chemical forms along with their binding with sediment particles (Eggleton and Thomas, 2004; Vidmar et al., 2017). In this context, our work~~s~~ aims to investigate not only the total concentration distribution of these two elements but also their speciation in surface sediments, as well as the relationships between sediment particles and the specific geochemical conditions of the study area. Such information may be helpful in understanding the mechanisms influencing metal mobility from sediments and may also help ~~to~~ provide preliminary predictions of the bioavailability, if any, of these two metal(oid)s (Pinedo-Hernández et al., 2015; Beckers and Rinklebe, 2017) with regard to possible effects of intervention~~s~~ and maintenance, such as dredging operations in the estuary for navigation purposes.

## 2. Material and methods

### 2.1 Environmental setting

The Nalón River estuarine system in the Asturias region encompasses only a small part of the entire hydrographical basin (~~covers an area of~~ 4.5 km$^2$~~,~~) ~~which is only a small part of the entire hydrographical basin, which~~and extends 4,777 km$^2$ inland. The estuary is over 6 km long and its upper limit is established according to the salt wedge extension~~,~~ which moves upstream following the tidal range. The main estuarine channel has retained its natural river banks~~,~~ with the exception of the lower section~~,~~ close to the inlet, where two small regional ports were built (San Juan de la Arena ~~y~~ and San Esteban de Pravia in Fig. 1), which altered the natural morphology and sedimentation dynamics of the outer part of the estuarine system (Flor-Blanco et al., 2015). The main channel is more than 2 m deep and is affected by an annual meso-tidal range between 1.0 and 4.2 m; in general~~,~~ the tides are over 2 m ~~during~~ for more than 70% of the year (Flor et al., 1998). ~~The profile of the estuary is sinuous, as meanders have developed throughout its length, which is typical for an estuary with a strong fluvial influence and transgressive sedimentary filling on the lower fluvial section. The dynamics of water circulation in the estuarine region strictly depend on the tidal regime. During neap tides, the horizontal salinity gradient is the key driving force for estuarine circulation, whereas during spring tides, almost total vertical mixing governs the estuary hydrodynamics (Flor et al., 1998).~~

~~Currently, t~~The main activity in the estuarine area is tourism, including recreational uses (fishing and yachting). ~~However, the estuary was an important industrial port for raw materials export purposes in the recent past. Upstream, in the Nalón River basin, are located s~~Several urban settlements and some agricultural and mining-industrial sites are located in the Nalón River basin. Among the mining-industrial activities, which have been active since the end of the eighteenth century, the most important are related to the ~~remarkable~~ ~~major~~significant deposits of coal, mercury, gold, and iron as well as other polymetallic ores containing copper, lead, and zinc found in the area. ~~Within~~ Among the metal~~s~~ extraction ~~activity~~industry, Hg mines have been especially important; ~~, as~~ Asturias is the second largest Hg producer in Spain.

The most notable Hg deposits in Asturias are La Peña-Terronal in Mieres and La Soterraña in Pola de Lena~~, which are located in the Nalón River basin~~. The main metal ore of these deposits is cinnabar [HgS], in association with low amounts of native Hg, as well as ~~important~~ significant amounts of As-bearing minerals such as realgar [AsS] and pararealgar [$As_4S_4$], orpiment [$As_2S_3$], and arsenic-rich pyrite (Ordoñez et al. 2013). Despite the cessation of mining activity several decades ago, drainage waters flowing out from ~~the~~ inactive mines where low remediation actions were implemented (Rodríguez-Pérez et al., 2014), ~~and~~ their tailings and residual deposits may still affect the quality of the fluvial waters and the sediments downstream of the sources (Loredo et al., 2003; Ordoñez et al., 2013). ~~and t~~The contamination has reached the estuarine environment where the historical accumulation of As and Hg in the saltmarsh and estuary channel has been correlated ~~with~~to the historical Hg mining activity located about 40 km upstream in the Nalón river drainage basin (Garcia-Ordiales et al., 2015, 2016, 2017).

## 2.2 Sampling and analysis

A total of 56 sediment samples were collected from the estuary (Fig. 1). When accessible, both sides of the river banks were sampled together with the main channel area, representing the whole estuarine sector of the active stream of the Nalón riverbed. Surface sediments (0-5 cm) were collected by means of a plastic shovel from the river banks while they were exposed to air during ebb tide conditions or by a stainless-steel Van Veen grab from the submerged parts of the estuary. ~~About~~ Approximately 1 kg of sediment~~s~~ was collected from each sampling point, homogenised in the field, stored in double zip-lock bags, and transported to the laboratory in a portable fridge. Each sample was divided into ~~split in~~ different representative subsamples, using a riffle-type sample splitter with a removable hopper. Grain size and total elemental content were determined in air-dried samples. For grain-size analysis, an aliquot of each sample was treated with a solution of 3% (v/v) $H_2O_2$ for 48 h to remove most of the organic matter. The sample was then wet sieved at 2 mm and analysed with a Fritsch ANALYSETTE MicroTec Plus 22. Grain-size data are ~~synthesized~~ synthesised using the classical sand-silt-clay notation according to the Udden-Wentworth scale. Major and trace elements were determined on 0.5 g freeze-dried samples, which were digested in a microwave ~~with~~ using a multi-acid solution (HCl–HNO$_3$–HF) and analysed by inductively coupled emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectroscopy (ICP-MS; Bureau Veritas, Vancouver, Canada). The accuracy of the results was verified by comparison against analysis of Standard Reference materials PACS-2 (marine sediment), RTC-CRM026-050 (sandy loam soil) and CRM042-056 (loam soil). Percentage recoveries for all elements considered ranged from 93% to 106%.

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

Twenty sediment samples were selected ~~For~~ for the Hg and As speciation analysis~~, twenty sediment samples were selected~~ (Fig. 1). These samples were chosen based on the results obtained from the total concentration analyses and following the hydrodynamic criteria, which were intended to cover the different sectors of the estuary and discover possible significant differences among them. For As species, 0.1 g of sediment was placed together with an extracting agent (1 M $H_3PO_4$ + 0.1 M ascorbic acid) in a microwave vessel. The extracts were diluted (1:5) and filtered (<0.45 µm). The As species were separated ~~by~~ using a mobile phase of 2 M phosphate buffered saline (PBS)/0.2 M EDTA (pH = 6.0) in a separation column with a 1260

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

Organic Hg was analysed using the methodology proposed by Válega et al. (2006). As organic mercury compounds other than methylmercury, such as dimethylmercury, have rarely been detected in sediments (Ullrich et al., 2001; Mason, 2013), the organic mercury measured may be considered ~~to be~~ methylmercury. In brief, sediment samples were first treated with an acid solution ($KBr/H_2SO_4/CuSO_4$), followed by extraction of the organic Hg halide with toluene and back-extraction with an aqueous sodium thiosulphate solution. The analyses were carried out using an HPLC-ICPMS (Agilent Technologies). The accuracy of the results was verified against the estuarine sediment IAEA-405 certified reference material (recovery range from 94% to 102%).

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

## 3. Results and discussion

### 3.1 General characteristics of sediments

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

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

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

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

In general, the distribution of the sulphur (S) (Fig. 3) concentration (0.27–2.18%) is closely associated with the fine grain-sized sediments ($r^2 = 0.838$, $p < 0.01$) (Fig.1 , supplementary material) since sulphur is primarily associated with iron sulphide in the Nalón estuary. Indeed, the main rivers of the drainage basin provide an abundant supply of iron-rich terrigenous siliciclastic debris (Freslon et al., 2014). On the other hand, ~~, showing a dispersion similar to that of the clay component across the entire estuary. Also,~~ the ~~S displays a~~ positive correlation~~s~~ between S and ~~with~~ $C_{org}$ ($r^2 = 0.802$, $p < 0.01$)~~,~~ and the average C/S ~~ratio~~ value ~~for the sediments~~ (3.43 ± 0.97~~%~~), suggest that sediments were deposited under oxydis~~z~~ing conditions~~genated~~ at the bottom~~ waters~~ ~~is comparable to that proposed for "normal" marine conditions (2.8 ± 1.5%) by other authors~~ (Berner 1982; Raiswell and Berner, 1985)~~; normal conditions correspond to the characteristics of an oxygenated environment~~. L~~However, l~~ow C/S values, usually associated with anoxic or semi-anoxic depositional environments (Burone et al., 2003) were detected ~~the obtained results with samples from~~in ~~in~~ the San Esteban port basin ~~displayed the lowest C/S ratio values~~ (2.40–2.81~~%~~), suggesting partial hypoxic or anoxic conditions would occur~~red~~ in this area.~~during deposition of sediments may have occurred in this area.~~ ~~Overall, Llow C/S ratios are associated with anoxic or semi-anoxic depositional environments, with potentially high sulphate reduction (Burone et al., 2003).~~ ~~Among the obtained results, samples from the San Esteban port basin displayed the lowest C/S ratio values (2.40–2.81%), suggesting that remineralization processes through sulphate-reduction under hypoxic or even anoxic conditions in the surface sediments may have occurred in this area.~~

### 3.2 Arsenic in surface sediments: occurrence and speciation

~~Total arsenic concentrations (As$_{tot}$) range from 20.10 to 68.10 µg·g$^{-1}$ (avg. 27.43 ± 9.96 µg·g$^{-1}$); asthe highest concentrations were found in the lower sector of the estuary, especially in the San Esteban port basin.~~

Concentrations of $As_{tot}$ are well above the local background level estimated by Garcia-Ordiales et al. (2016) for the Nalón estuary (9.00 ± 0.94 $\mu g \cdot g^{-1}$) and the range of 5–15 $\mu g \cdot g^{-1}$ determined for uncontaminated nearshore marine and estuarine sediments (Moore and Ramamoorthy, 1984; Francesconi and Edmonds, 1997)~~, showing an important enrichment of this element in the surface sediments~~. These results are consistent with the concentrations detected in core profiles from the same area (Garcia-Ordiales et al., 2015, 2016, 2017)~~, where the relatively high concentrations of $As_{tot}$ in recent sediments were attributed to contributions from mining wastes located within the river basin~~. Due to ~~the~~ 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 $\mu g \cdot g^{-1}$), and the Probable Effect Concentration (As PEC, 33.0 $\mu g \cdot g^{-1}$), 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) ~~and $C_{org}$ ($r^2$ = 0.757, $p$ < 0.01)~~ contents (Fig. 2, supplementary material), suggesting that particle size and sulphide control the As retention in the solid phase and ~~as a consequence~~ its dispersion throughout ~~in~~ the estuary. The lower sector of the estuary, where a major proportion of fine particles and S contents occur, ~~showed~~demonstrated the highest concentrations of As in the sediments (Fig. 4), and this is especially remarkable in the San Esteban port basin ~~that~~ 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 ~~species~~ one found in the sediments due to the ~~oxidizing~~ oxidising conditions in the aquatic environment based on the C/S values. The ~~C~~concentration of As(V) falls in the range of 16.89–64.96 µg·g$^{-1}$ (avg. 31.39 ± 12.85 µg·g$^{-1}$). ~~, whereas i~~Its relative abundance in comparison to the $As_{tot}$ concentration ~~(%As(V))~~ in the sediments ranges from 97.6% to 100%. ~~This As(V) abundance provides relationships with $N_{tot}$ ($r^2$ = 0.813, $p$ < 0.01), $C_{org}$ (0.783, $p$ < 0.01), and clay contents ($r^2$ = 0.782, $p$ < 0.01) similar to those observed for $As_{tot}$; it also shows an analogous dispersion of their concentrations in the estuary. Whereas The As(III) concentrations range from <DL to 1.356 µg·g$^{-1}$ (avg. 0.78 ± 0.36 µg·g$^{-1}$). In the samples from~~ I~~i~~n the upper-middle sector of the estuary, ~~which is under the direct influence of the fluvial inputs, this~~ As (III) species ~~was~~ 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 arsenite component was significantly ~~and positively correlated to $As_{tot}$ ($r^2$ = 0.784, $p$ < 0.05), whereas a~~ negatively ~~relationship~~ correlated to~~with~~ the C/S ~~ratio~~ value ($r^2 = -0.742$, $p < 0.05$) ~~was detected~~ (Fig. 5a). This negative correlation suggests that the redox condition~~s~~ ~~of the sediments are~~is the key factor of the presence ~~seems to govern the amounts~~ of arsenite entrapped in the sedimentary matrix.~~, where As(III) reached its maximum in those samples wherein the C/S ratio is indicative of important anoxic or semi-anoxic conditions.~~ The relationship between redox conditions and the amounts of the As(III) species in sediments has already been extensively studied by ~~different~~ various authors (e.g. Rochette et al. 1998, Foster, 2003; Mudhoo et al., 2011; Shaheen et al., 2016). The same authors demonstrated that reducing conditions can increase As(III) concentrations by converting As(V) into As(III).

~~Conversely, the relative abundance of As(III) with respect to the $As_{tot}$ concentration in the samples, where detectable, range from 1.0% to 2.1% and depends on the C/S ratio ($r^2$ = −0.813, $p$ < 0.05) with a major proportion in the samples located at the San Esteban port basin.~~

T~~However, t~~he low proportion of As(III) with respect to the $As_{tot}$ concentration (from 1.0% to 2.1% ), despite the redox conditions (Frohne et al., 2011), suggests that the reduction of As (V) to As(III) is inhibited, thus decreasing the potential release of the most mobile and toxic As (III) (Pierce and Moore, 1982). In the Nalón estuary, seawaters show more than 100 mg $L^{-1}$ of total $SO_4^{2-}$ at Eh levels greater than 100mV and it is expected that large amounts of this $SO_4^{2-}$ absorbed by the sediment potentially stabilis~~z~~e As by forming complex ligands (Sparks, 1999; LeMonte et al., 2017). The preferential or concurrent $SO_4^{2-}$ reduction process may preserve occluded As (V) and resulting in an inhibition of As(V) reduction (Burton et al., 2013), which is a possible explanation for the low proportion and amounts of As(III) detected in the sediments.

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

### 3.3 Mercury in surface sediments: occurrence and speciation

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

~~-~~The distribution of the metal concentration in the surface estuarine ~~(Fig. 5)~~ sediments (Fig. 6) is quite similar to that observed for $As_{tot}$ (Fig. 4) and the highest values for $Hg_{tot}$ are also found in the port basin of San Esteban de Pravia. The two elemental concentrations are strongly correlated ($r^2$ = 0.884, $p$ < 0.01) (Fig. 2, supplementary material). This relationship has already been reported by Silva et al. (2014) for the sediments of the Nalón river drainage basin and by Garcia-Ordiales et al. (2017) for the saltmarsh sediments of its estuary. This strong correlation supports a mutual origin associated with the sources identified in the mining districts and the sub~~con~~sequent common mechanism of dispersion along the river basin estuary. T~~However, t~~he correlations observed between $Hg_{tot}$ ~~and the other geochemical parameters~~with grain sizes, $C_{org}$ and S concentrations suggest the adsorption mechanisms ~~of~~for Hg are different from those hypothesised for $As_{tot}$. Concentrations of $Hg_{tot}$ 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 ($r^2$ = 0.782, $p$ < 0.01) (Fig. 2, supplementary material). These results demonstrated that the organic fractions were likely the most significant factor controlling the distribution concentrations of Hg in sediments together with the grain size, but also the presence of sulphide species cannot be disre~~c~~gard as reflect the high correlation between $Hg_{tot}$ and S. These correlations have already been observed in other global coastal environments ~~of the world that have been~~ impacted by Hg mining activities (e.g. Covelli et al., 2001; Conaway et al., 2003) and also in the Asturias Hg mining areas (Silva et al., 2014). In this geochemical context, Hg sulphide is the most common species near the source but downstream Hg could be mainly found in the form of $Hg^{2+}$. This species could be trapped in the sediment by a variety of processes such as complexing or chelation with organic ligands, sorption onto colloids or Fe-Mn oxides and/or incorporation into the crystal lattice of mineral grains (Biester et el., 2000; Covelli et al., 2001; Silva, 2014) as is highlighted from the observed correlations.

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

~~As for $As_{tot}$, concentrations of $Hg_{tot}$ exceed the estimated concentration of 0.2 µg·$g^{-1}$ for uncontaminated marine sediments (Salomons and Forstner, 1984). In addition, the local background level estimated for the estuarine sediments is 0.012 ± 0.001 µg·$g^{-1}$ according to Garcia-Ordiales et al. (2016). In addition, the $Hg_{tot}$ concentrations were detected above the TEC value (0.18 µg·$g^{-1}$), but only 3% of the samples exceed the PEC value (1.1 µg·$g^{-1}$).~~ The concentration values of MeHg in the sediments (Fig. 6~~5~~) range from 303.20 to 865.40 pg·$g^{-1}$, and show significant positive relationships with $Hg_{tot}$ ($r^2 = 0.886$, $p < 0.01$~~),~~) and $C_{org}$ ($r^2 = 0.700$, $p < 0.01$). ~~, clay ($r^2 = 0.630$, $p < 0.01$), and S ($r^2 = 0.548$, $p < 0.01$). Although pore waters were not extracted from sediments to analyse hydrogen sulphide ($H_2S$), t~~T~~he estimated C/S ratio~~ ~~as oxic or anoxic sediments conditions, together with the strong characteristic odour emitted by some samples during field work, possibly due to the production of hydrogen sulphide ($H_2S$), suggest the occurrence of anoxic conditions where remineralization of the organic matter via~~

~~sulphate reduction is presumably involved, as stated above for As.~~ The importance of the microbial activity of sulphate-reducing bacteria in mercury methylation processes has been demonstrated (e.g. Gilmour et al., 1992), and the most important parameters controlling methylation rate are mercury~~ and~~, sulphate concentrations and the amount of organic matter (e.g. Benoit et al., 1999), ~~coincident~~ in accordance with the significant correlations previously~~already~~ mentioned. The ~~mapped~~ spatial dispersion of MeHg in the estuar~~y~~ine sediments (Fig. ~~5~~6) demonstrated~~showed~~ that the highest levels of MeHg occurred in the San Esteban de Pravia port area, whereas the lowest values were detected in the upper part of the estuary. An examination of the relative abundance of MeHg versus $Hg_{tot}$ ~~in the sediments~~ allows additional insights regarding the occurrence of MeHg among the different sectors of the estuary. The MeHg component ~~in the Nalón estuarine sediments~~ (< 0.10% MeHg) was similar to that ~~one from~~of other estuaries impacted by Hg mining activities (Table ~~2~~1), which does not generally exceed 0.5% (Conaway et al., 2003; Hines et al., 2006). In contrast, the ~~%~~ percentage of MeHg ~~detected in the estuary~~ was very low compared to other estuaries where the primary sources of Hg in the aquatic environment are urban, industrial, agricultural, or aerial depositions, for which the MeHg component may account for values near 100% (Haris et al., 2017). The relationship between *in situ* Hg speciation and methylation is not easy to represent ~~since~~ as each sediment type shows a different methylation potential (Bloom et al., 2003). In the estuary, the percentage of MeHg showed that only low amounts of the $Hg_{tot}$ are methylated, suggesting first the probable occurrence of Hg species such as cinnabar, not readily available for methylation and second, a low biological activity which is in agreement with the negligible concentrations of organic As species. ~~In Asturias (Esbri et al., 2010), similar to other Hg mining districts (e.g. Biester et al., 2000; Domagalski, 2001; Garcia-Ordiales et al., 2015), emissions from the mine sites are primarily dominated by solid mercury sulphides (HgS) as cinnabar or metacinnabar compounds, which are not readily available to the methylation processes. Thus, only low amounts of the $Hg_{tot}$ introduced from mine liabilities is really~~

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

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

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

## 4. Conclusions

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

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

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

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

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

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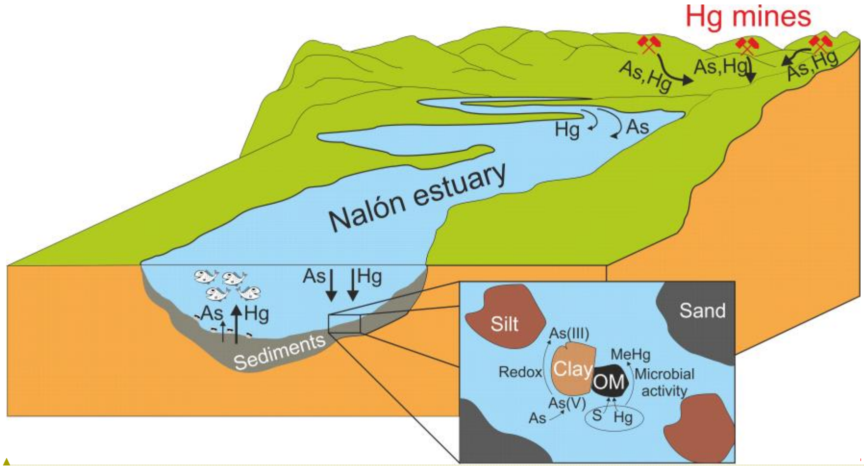
# Graphical Abstract_mark

## Graphical abstract



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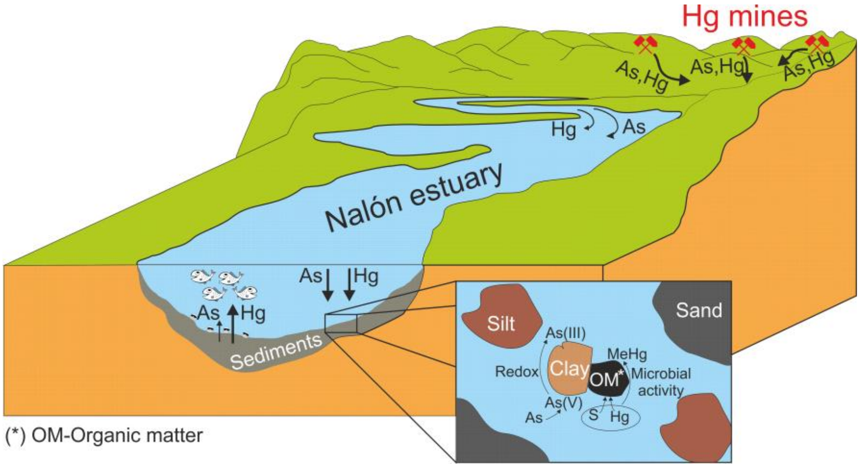

(*) OM-Organic matter

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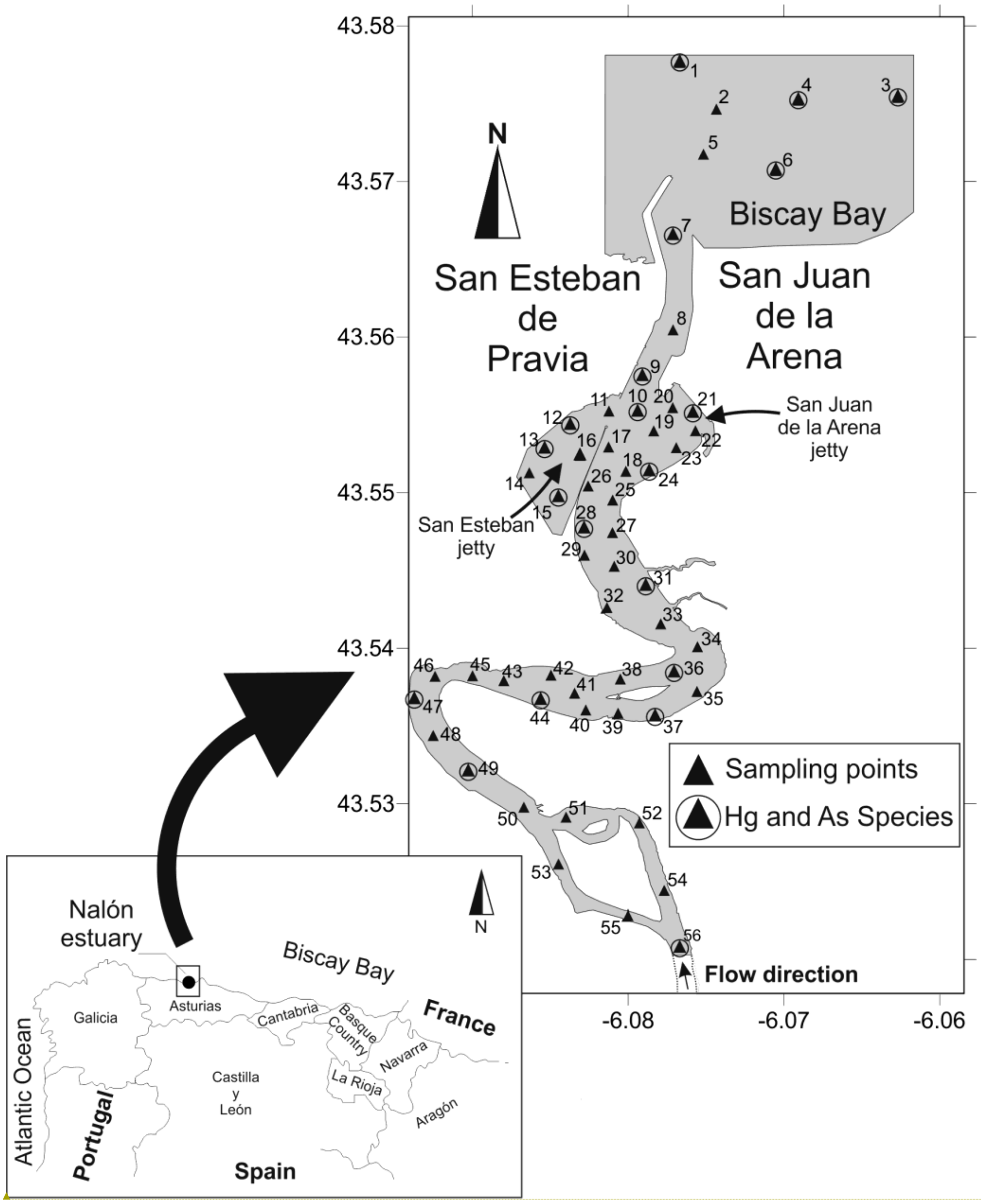
**Figures_mark**



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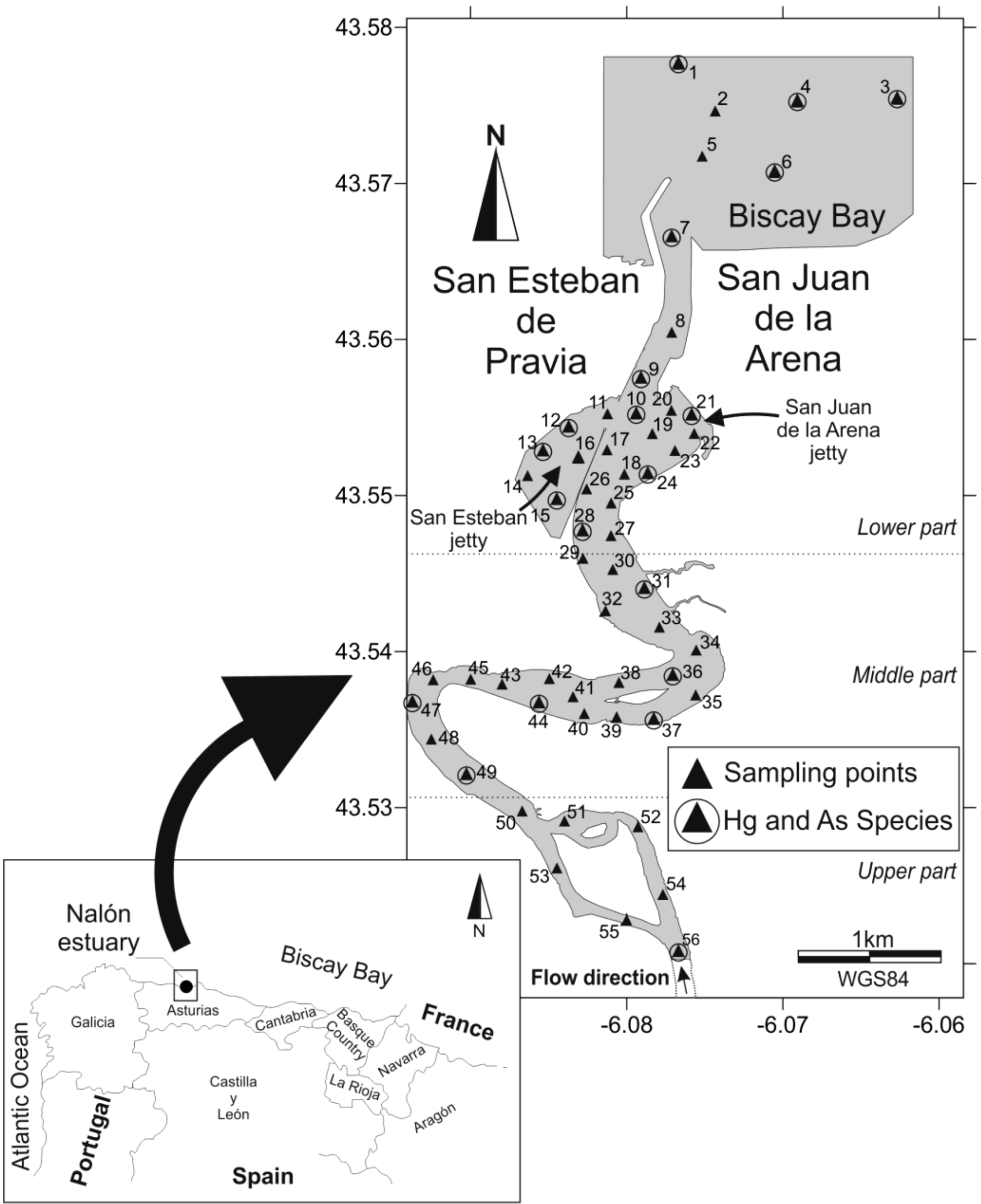

*Figure 1. ~~The study area~~Index map of the Nalon River estuary ~~and~~ along with location of the sediment sampling points*

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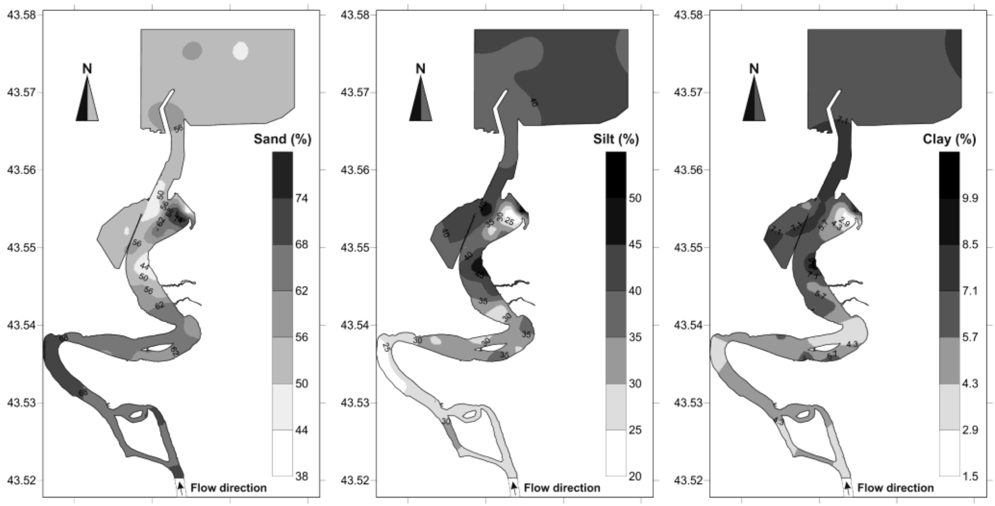

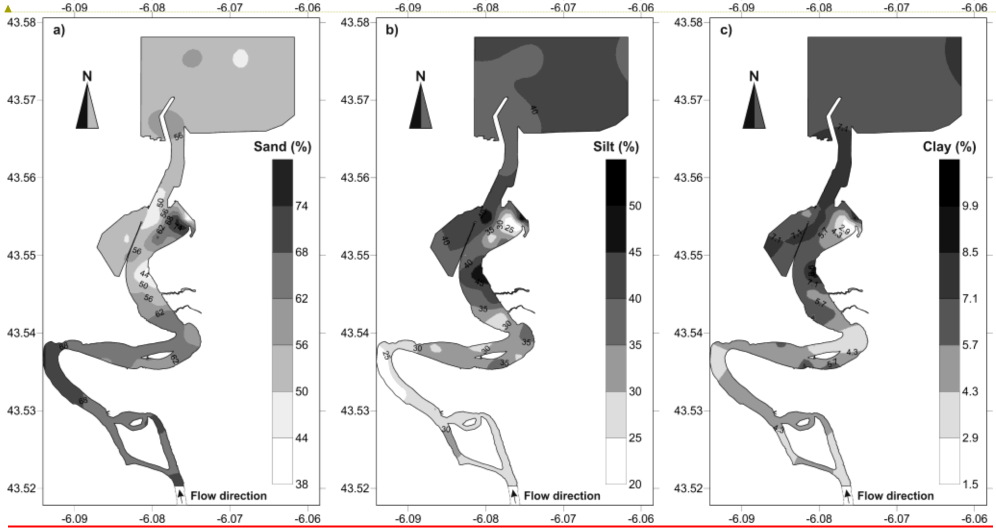

*Figure 2. Spatial distribution of the sand (a), silt (b) and clay (c) fractions in the surface sediments of the Nalón estuary.*

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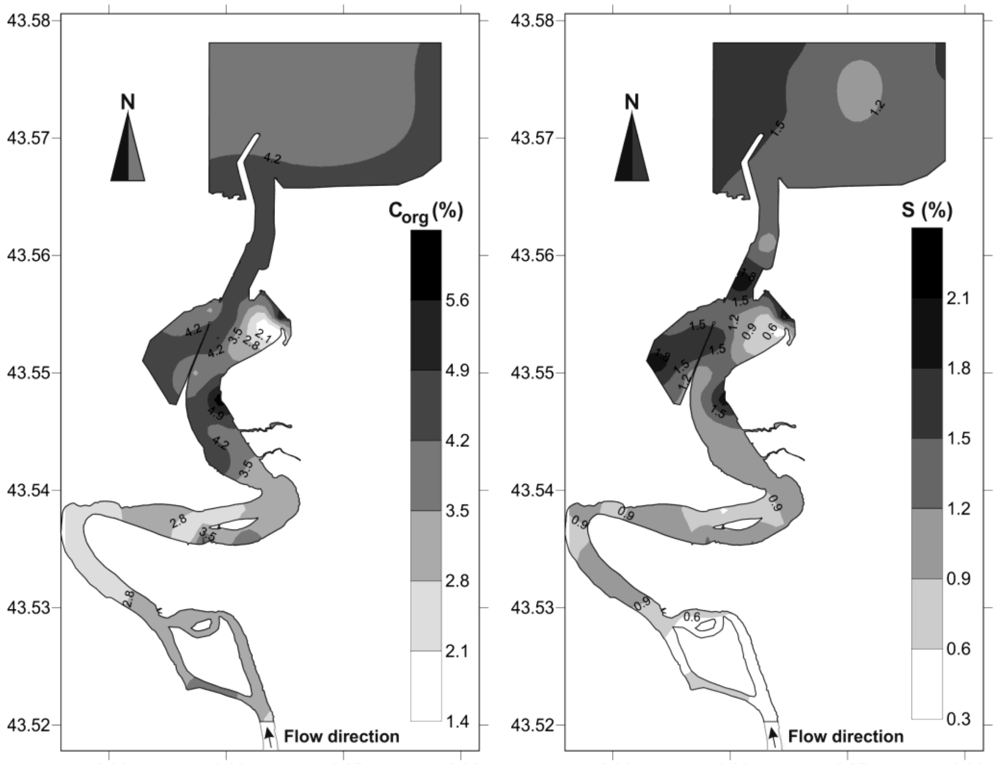


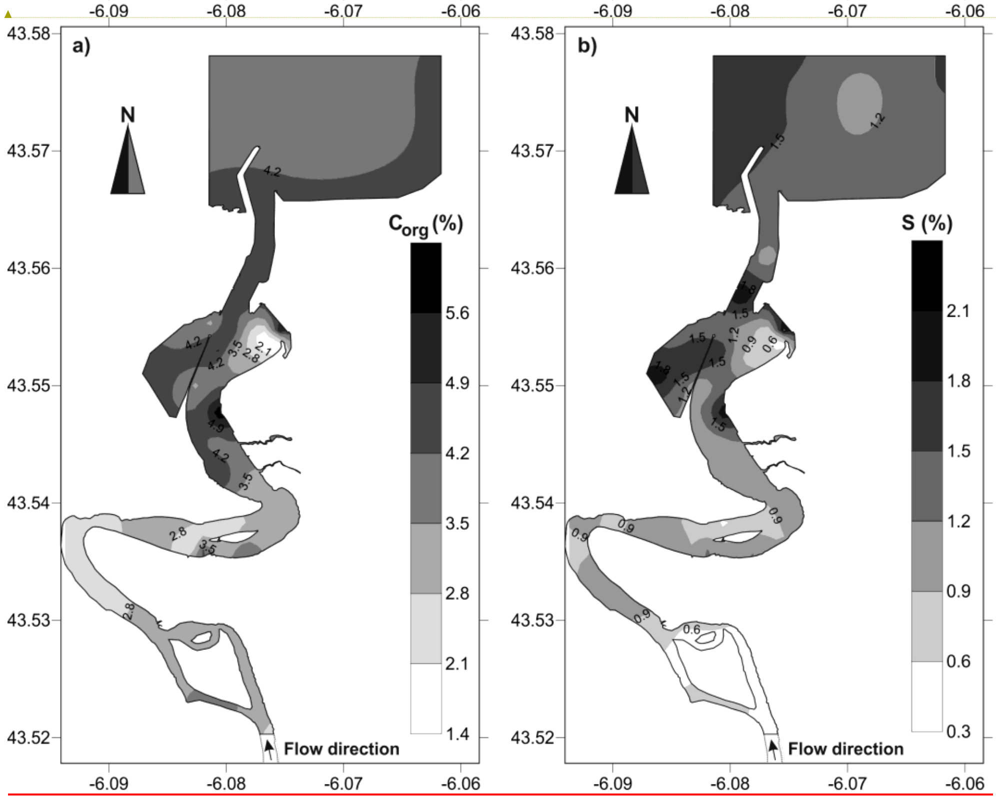
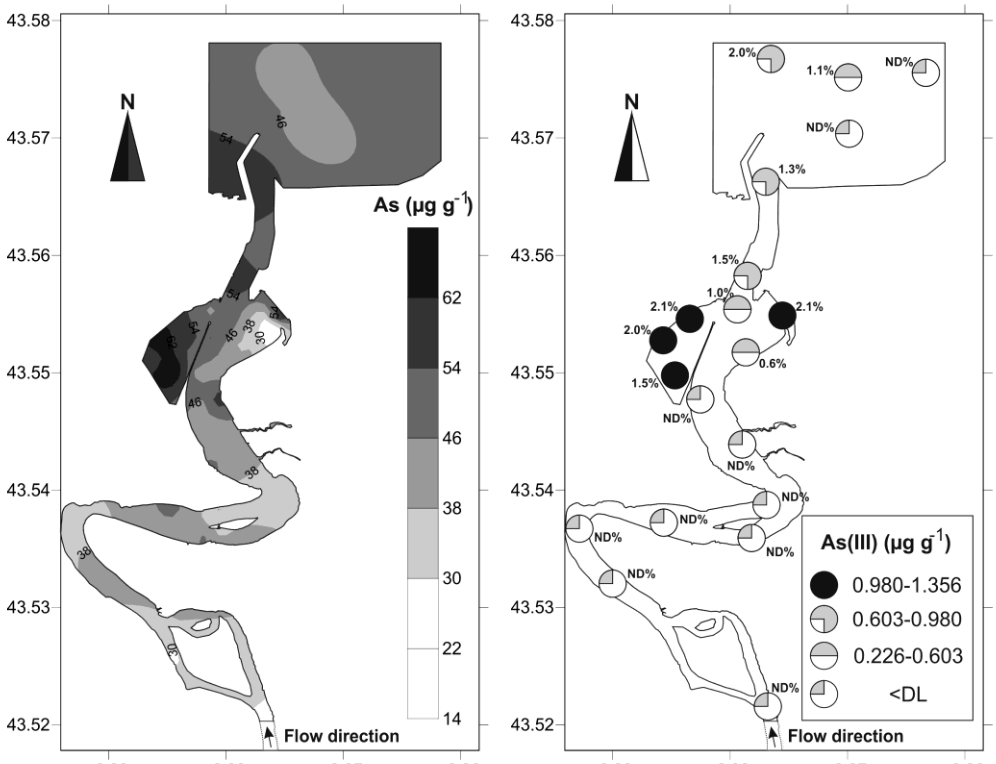


*Figure 3. Spatial distribution of $C_{org}$ (a) and $S_{tot}$ (b) concentrations (%) in the surface sediments of the Nalón estuary.*



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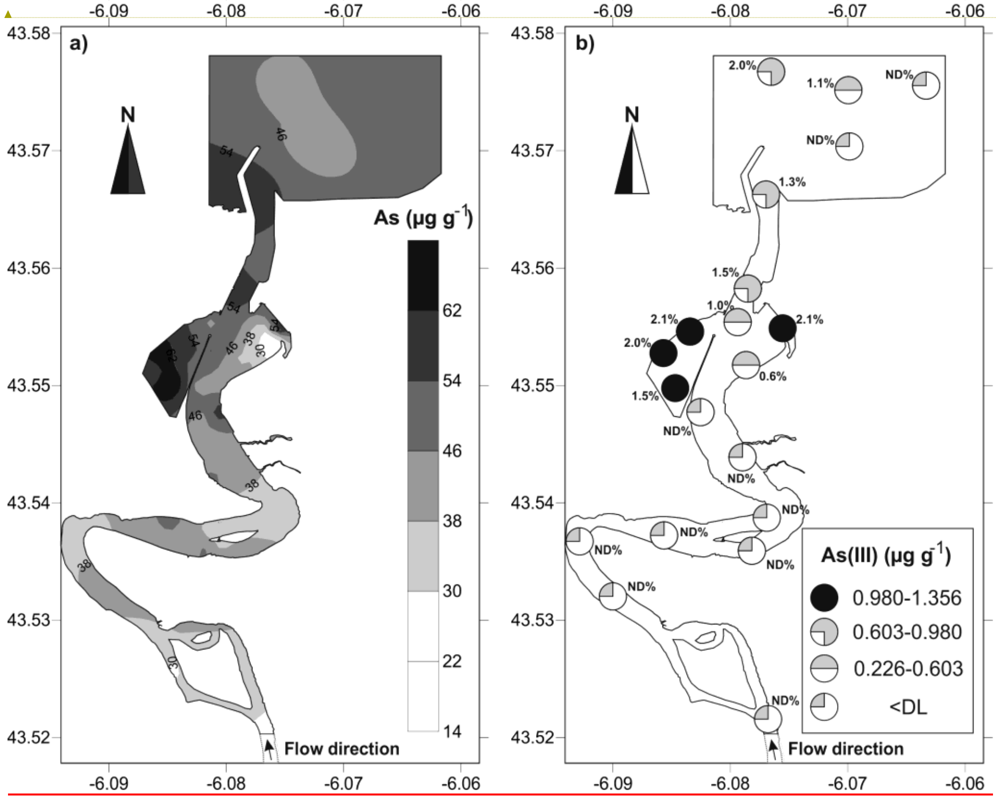
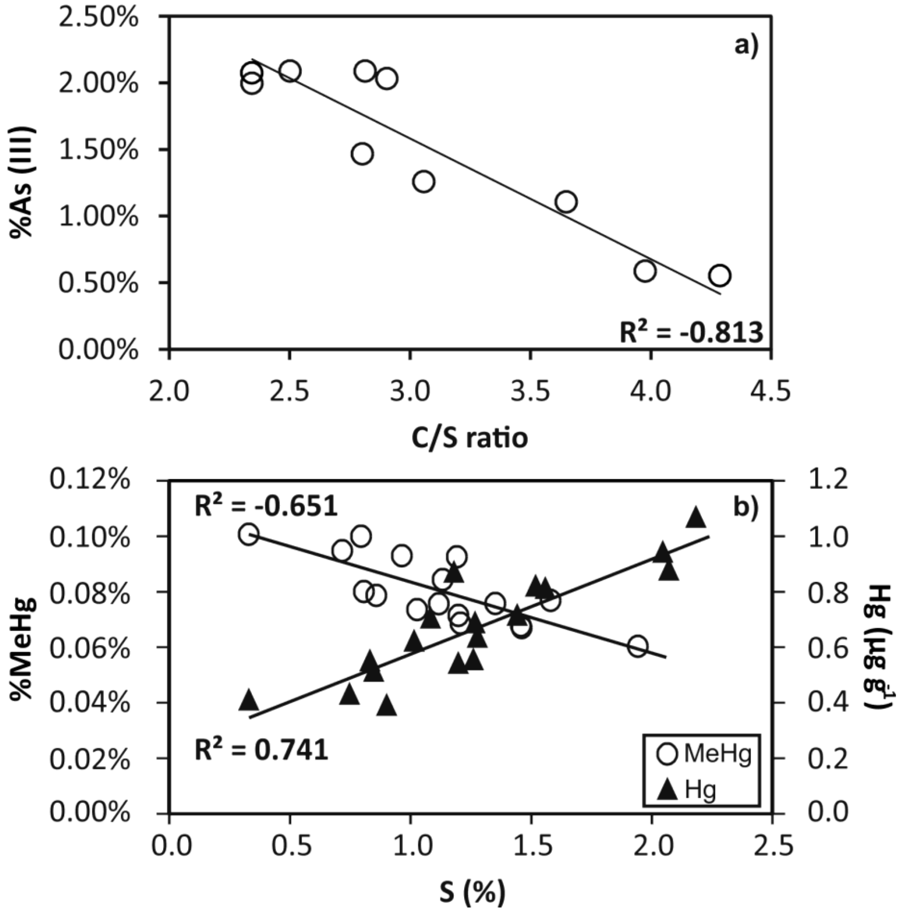
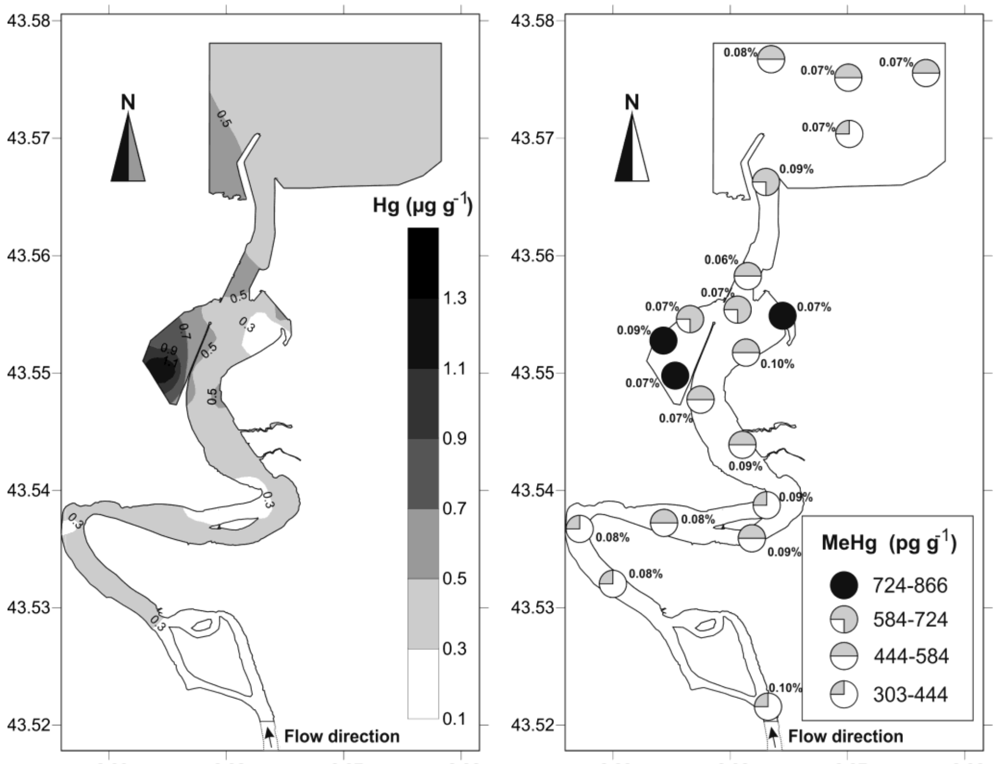


*Figure ~~4~~4. Spatial distribution of $As_{tot}$ (a) and As(III) (b) concentration~~s~~ ($\mu g\ g^{-1}$) in the surface sediments of the Nalón estuary. Percentage values represent the abundance of As(III) with respect to the ~~the~~ concentration of $As_{tot}$ ~~concentrations~~.*



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



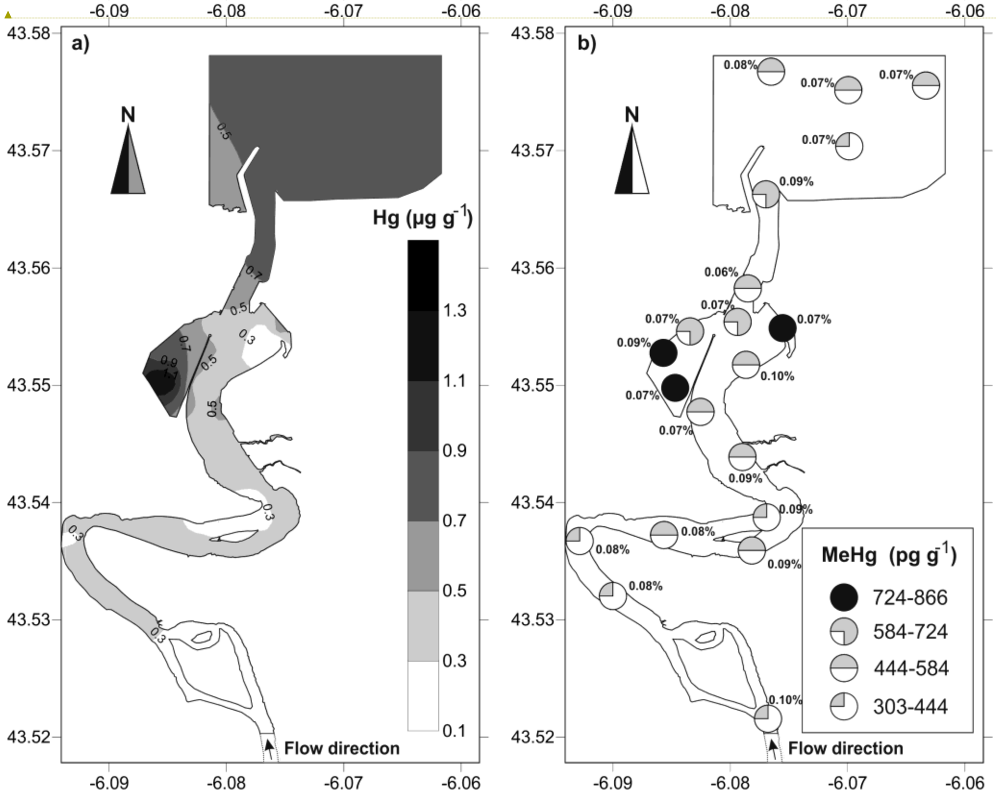


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*Figure ~~5~~6. Spatial distribution of Hg$_{tot}$ (a, in µg g$^{-1}$) and MeHg (b, in pg g$^{-1}$) concentration~~s~~ in the surface sediments of the Nalón estuary. Percentage values represent the abundance of the MeHg component with respect to the total concentration of Hg (Hg$_{tot}$).*

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

*~~Note: <DL-Below detection limit~~*

| ~~Sample~~ | ~~Lat~~ | ~~Long~~ | ~~Sand (%)~~ | ~~Silt (%)~~ | ~~Clay (%)~~ | ~~TC (%)~~ | ~~TOC (%)~~ | ~~N (%)~~ | ~~S (%)~~ | ~~As (µg g$^{-1}$)~~ | ~~As(V) (µg g$^{-1}$)~~ | ~~As(III) (µg g$^{-1}$)~~ | ~~% As(III)~~ | ~~Hg (µg 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%~~ |

*Table ~~2~~1. Ranges of mercury and arsenic concentrations reported in literature for ~~in other~~ coastal environments. (na- not available and <DL- Below detection limit).*

| | **As** (μg g$^{-1}$) | **Hg** (μg 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<br>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<br>Covelli et al., 2001 |
| Northern Tyrrhenian Sea (Italy) | 5.43-35.38 | 0.03-2.20 | na | Hg mining | Piazzolla et al., 2015<br>Scanus et al., 2016 |
| Kastela Bay (Croatia) | 15.00-33.00 | 17.60-74.00 | 6.05-16.40 | Industry | Orescanin et al., 2005<br>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 |

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

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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 ($Hg_{total}$) 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 sulphides. Concentrations of methylmercury (303.20–865.40 $pg \cdot g^{-1}$) are up to two orders of magnitude lower than the concentration of $Hg_{total}$. Total As concentration ($As_{total}$) 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.

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

## 1. Introduction

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

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

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

## 2. Material and methods

### 2.1 Environmental setting

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

The main activity in the estuarine area is tourism, including recreational uses (fishing and yachting). Several urban settlements and some agricultural and mining-industrial sites are located in the Nalón River basin. Among the mining-industrial activities, which have been active since the end of the eighteenth century, the most important are related to the significant deposits of coal, mercury, gold, and iron as well as other polymetallic ores containing copper, lead, and zinc found in the area. Among the metal extraction industry, Hg mines have been especially important; Asturias is the second largest Hg producer in Spain. The most notable Hg deposits in Asturias are La Peña-Terronal in Mieres and La Soterraña in Pola de Lena. The main metal ore of these deposits is cinnabar [HgS], in association with low amounts of native Hg, as well as significant amounts of As-bearing minerals such as realgar [AsS] and pararealgar [$As_4S_4$], orpiment [$As_2S_3$], and arsenic-rich pyrite (Ordoñez et al. 2013). Despite the cessation of mining activity several decades ago, drainage waters flowing out from inactive mines where low remediation actions were implemented (Rodríguez-Pérez et al., 2014), their tailings and residual deposits may still affect the quality of the fluvial waters and the sediments downstream of the sources (Loredo et al., 2003; Ordoñez et al., 2013). The contamination has reached the estuarine environment where the historical accumulation of As and Hg in the saltmarsh and estuary channel has been correlated to the historical Hg mining activity located about 40 km upstream in the Nalón river drainage basin (Garcia-Ordiales et al., 2015, 2016, 2017).

## 2.2 Sampling and analysis

A total of 56 sediment samples were collected from the estuary (Fig. 1). When accessible, both sides of the river banks were sampled together with the main channel area, representing the whole estuarine sector of the active stream of the Nalón riverbed. Surface sediments (0-5 cm) were collected by means of a plastic shovel from the river banks while they were exposed to air during ebb tide conditions or by a stainless-steel Van Veen grab from the submerged parts of the estuary. Approximately 1 kg of sediment was collected from each sampling point, homogenised in the field, stored in double zip-lock bags, and transported to the laboratory in a portable fridge. Each sample was divided into different representative subsamples, using a riffle-type sample splitter with a removable hopper. Grain size and total elemental content were determined in air-dried samples. For grain-size analysis, an aliquot of each sample was treated with a solution of 3% (v/v) $H_2O_2$ for 48 h to remove most of the organic matter. The sample was then wet sieved at 2 mm and analysed with a Fritsch ANALYSETTE MicroTec Plus 22. Grain-size data are synthesised using the classical sand-silt-clay notation according to the Udden-Wentworth scale. Major and trace elements were determined on 0.5 g freeze-dried samples, which were digested in a microwave using a multi-acid solution ($HCl–HNO_3–HF$) and analysed by inductively coupled emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectroscopy (ICP-MS; Bureau Veritas, Vancouver, Canada). The accuracy of the results was verified by comparison against analysis of Standard Reference materials PACS-2 (marine sediment), RTC-CRM026-050 (sandy loam soil) and CRM042-056 (loam soil). Percentage recoveries for all elements considered ranged from 93% to 106%.

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

Twenty sediment samples were selected for the Hg and As speciation analysis (Fig. 1). These samples were chosen based on the results obtained from the total concentration analyses and following the hydrodynamic criteria, which were intended to cover the different sectors of the estuary and discover possible significant differences among them. For As species, 0.1 g of sediment was placed together with an extracting agent (1 M $H_3PO_4$ + 0.1 M ascorbic acid) in a microwave vessel. The extracts were diluted (1:5) and filtered (<0.45 µm). The As species were separated using a mobile phase of 2 M phosphate buffered saline (PBS)/0.2 M EDTA (pH = 6.0) in a separation column with a 1260 Infinity high-performance liquid chromatograph (HPLC) coupled to a 7700 ICP-MS (Agilent Technologies). The accuracy of the results was verified by comparing the total arsenic concentration with the sum of all species concentrations determined. The recovery of As speciation ranged from 95% to 106%.

Organic Hg was analysed using the methodology proposed by Válega et al. (2006). As organic mercury compounds other than methylmercury, such as dimethylmercury, have rarely been detected in sediments (Ullrich et al., 2001; Mason, 2013), the organic mercury measured may be considered methylmercury. In brief, sediment samples were first treated with an acid solution (KBr/$H_2SO_4$/$CuSO_4$), followed by extraction of the organic Hg halide with toluene and back-extraction with an aqueous sodium thiosulphate solution. The analyses were carried out using an HPLC-ICPMS (Agilent Technologies). The accuracy of the results was verified against the estuarine sediment IAEA-405 certified reference material (recovery range from 94% to 102%).

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

## 3. Results and discussion

### 3.1 General characteristics of sediments

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

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

Concentrations of $C_{tot}$ (1.62–7.29%), $N_{tot}$ (0.08–0.43%), and $C_{org}$ (1.45–6.33%) (Fig. 3) are strongly correlated to the clay percentage in the sediments ($r^2 = 0.886$, $r^2 = 0.931$, and $r^2 = 0.942$, respectively, $p < 0.001$)(Fig. 1, supplementary material), as the finest fraction easily adsorbs organic compounds in the bottom sediments. As a consequence, the highest concentrations of these parameters were detected in the inner part of the San Esteban port basin and in the San Juan de la Arena port where carbon and nitrogen preferably tend to accumulate. Conversely, the lowest concentrations are progressively found in the upper section of the estuary where the coarse component appears to be more relevant. Similarly, in the marine area in front of the estuary, a decrease in concentration occurs since the sediment grain size is coarse due to the action of the marine currents and wave motion (Flor et al., 1998). Carbon in the particulate matter ($C_{tot}$) is mainly organic, $C_{org}$ (avg. 87.1 ± 0.08%), from a minimum of 70% to a maximum value of 99%. The correlation between $C_{org}$ and sediment grain-size can be partially explained by the similar settling velocity (i.e. hydrodynamics) of the particulate organic constituents and the fine-grained mineral particles (Tyson 1995). Total nitrogen ($N_{tot}$) is significantly related to $C_{org}$ ($r^2 = 0.866$, $p < 0.01$), and plotting $N_{tot}$ against $C_{org}$ results in an intercept of 0.047, which indicates the percentage of $N_{tot}$ at 0% value of $C_{org}$, showing that there is a significant fraction of total $N_{org}$ in the samples. Calculated $C_{org}/N_{tot}$ ratios, commonly quoted as C/N values together with $\delta^{13}C$ and $\delta^{15}N$, are widely used as a tool for discriminating marine from terrestrial organic matter in sediments (Xu et al., 2017). At this point, some assumptions can be made merely on the basis of the C/N ratio (Covelli et al., 2012 and references therein). In the estuary sediments, the C/N ratio ranges from 9.38% to 18.18% (avg. 13.02 ± 2.18%), which suggests that the organic matter in these sediments is prevalently terrigenous, according to Meyers (1997). This result is in agreement with the dynamics of the estuary as described by Flor et al. (1998), where the supply of material from the river basin is the predominant source of sediments and organic matter into the estuary.

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

## 3.2 Arsenic in surface sediments: occurrence and speciation

Concentrations of $As_{tot}$ are well above the local background level estimated by Garcia-Ordiales et al. (2016) for the Nalón estuary (9.00 ± 0.94 $\mu g \cdot g^{-1}$) and the range of 5–15 $\mu g \cdot g^{-1}$ determined 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 $\mu g \cdot g^{-1}$), and the Probable Effect Concentration (As PEC, 33.0 $\mu g \cdot g^{-1}$), 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 16.89–64.96 $\mu g \cdot g^{-1}$ (avg. 31.39 ± 12.85 $\mu g \cdot g^{-1}$). 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 arsenite component was significantly negatively correlated to the C/S value ($r^2 = -0.742$, $p < 0.05$) (Fig. 5a). This negative correlation suggests that the redox condition is the key factor of the presence of arsenite entrapped in the sedimentary matrix. The relationship between redox conditions and the amounts of the As(III) species in sediments has already been extensively studied by various authors (e.g. Rochette et al. 1998, Foster, 2003; Mudhoo et al., 2011; Shaheen et al., 2016). The same authors demonstrated that reducing conditions can increase As(III) concentrations by converting As(V) into As(III). The low proportion of As(III) with respect to the $As_{tot}$ concentration (from 1.0% to 2.1% ), despite the redox conditions (Frohne et al., 2011), suggests that the reduction of As (V) to As(III) is inhibited, thus decreasing the potential release of the most mobile and toxic As (III) (Pierce and Moore, 1982). In the Nalón estuary, seawaters show more than 100 mg $L^{-1}$ of total $SO_4^{2-}$ at Eh levels greater than 100mV and it is expected that large amounts of this $SO_4^{2-}$ absorbed by the sediment potentially stabilise As by forming complex ligands (Sparks, 1999; LeMonte et al., 2017). The preferential or concurrent $SO_4^{2-}$ reduction process may preserve occluded As (V) and resulting in an inhibition of As(V) reduction (Burton et al., 2013), which is a possible explanation for the low proportion and amounts of As(III) detected in the sediments.

### 3.3 Mercury in surface sediments: occurrence and speciation

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

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

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

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

## 4. Conclusions

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

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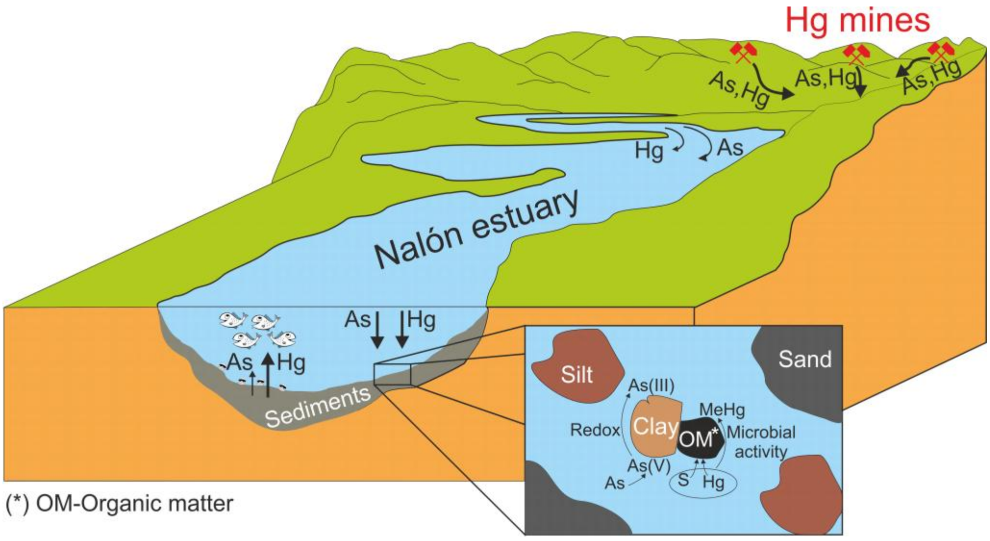
## Graphical abstract



(*) OM-Organic matter

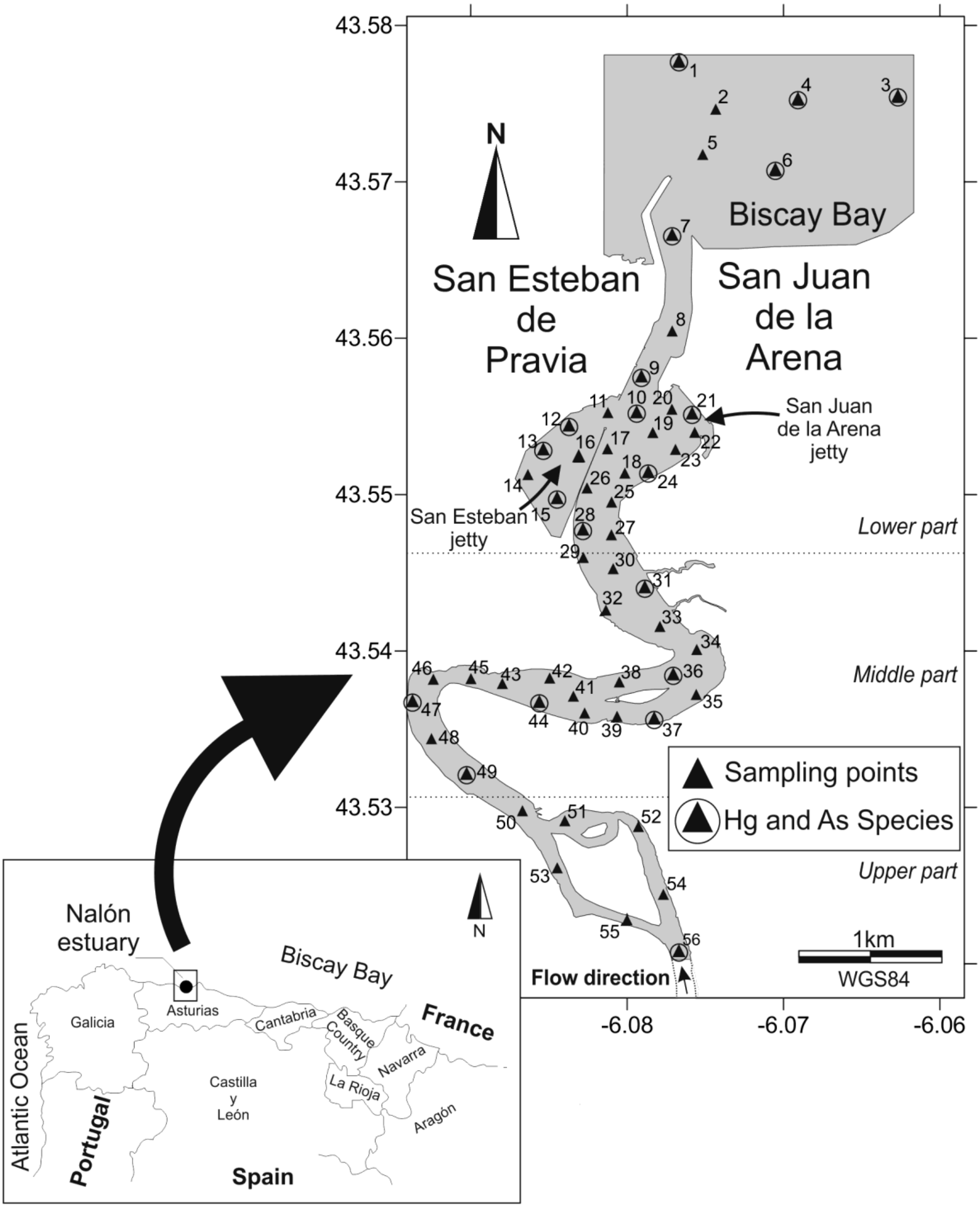


*Figure 1. Index map of the Nalon River estuary along with location of the sediment sampling points*

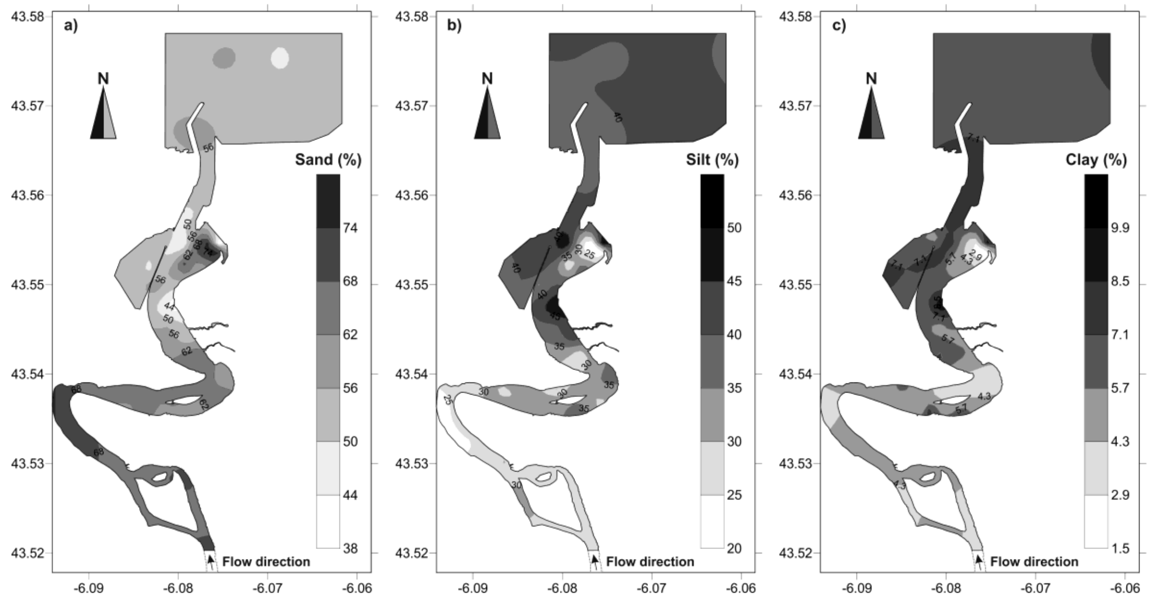


*Figure 2. Spatial distribution of the sand (a), silt (b) and clay (c) fractions in the surface sediments of the Nalón estuary.*

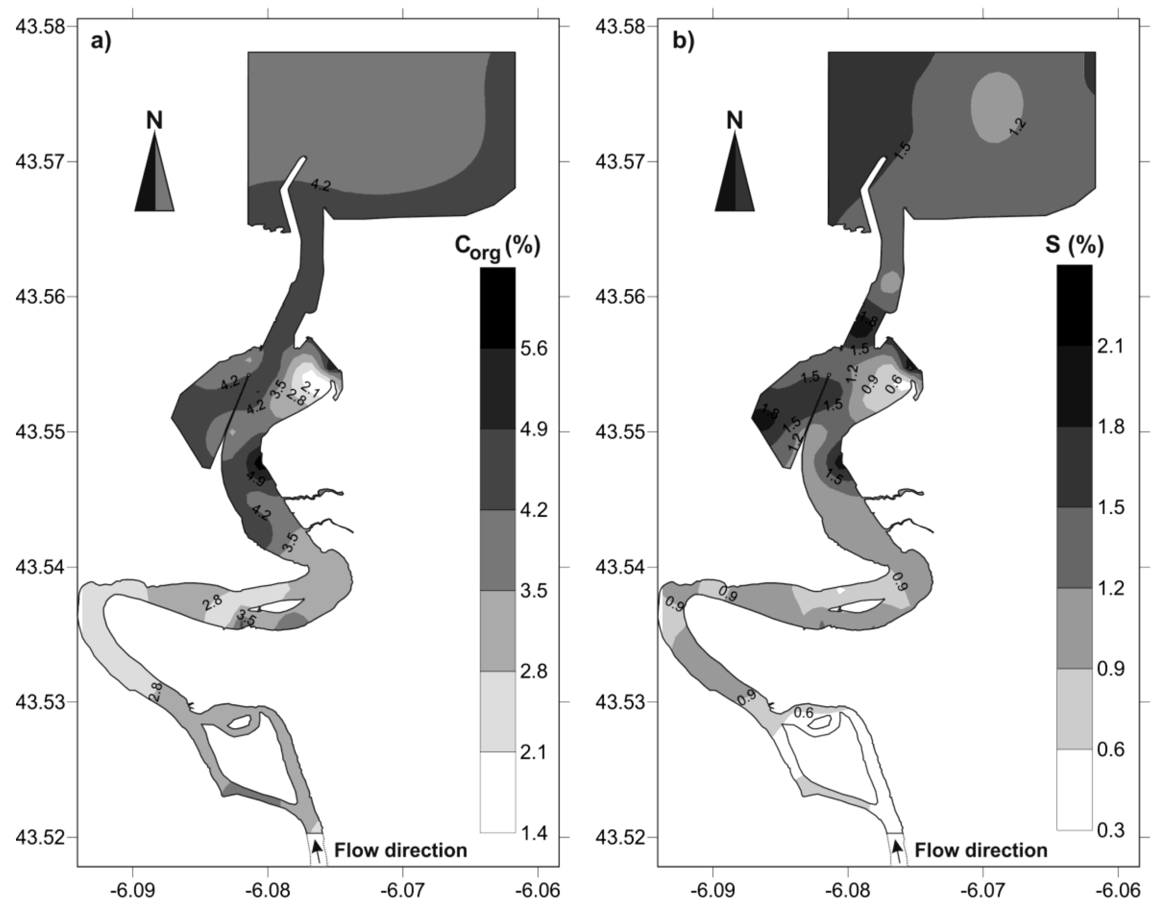


*Figure 3. Spatial distribution of $C_{org}$ (a) and $S_{tot}$ (b) concentrations (%) in the surface sediments of the Nalón estuary.*

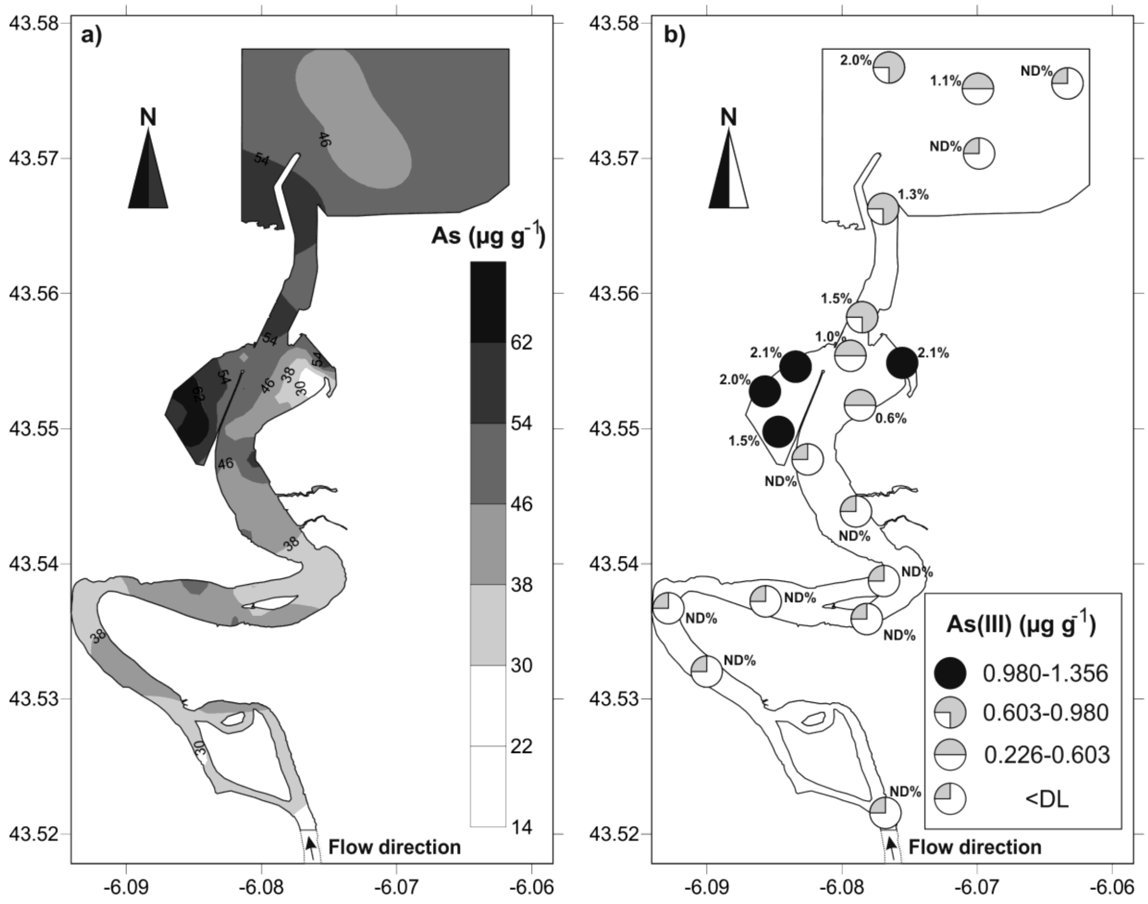


*Figure 4. Spatial distribution of* $As_{tot}$ *(a) and As(III) (b) concentration (µg* $g^{-1}$*) in the surface sediments of the Nalón estuary. Percentage values represent the abundance of As(III) with respect to the concentration of* $As_{tot}$*.*

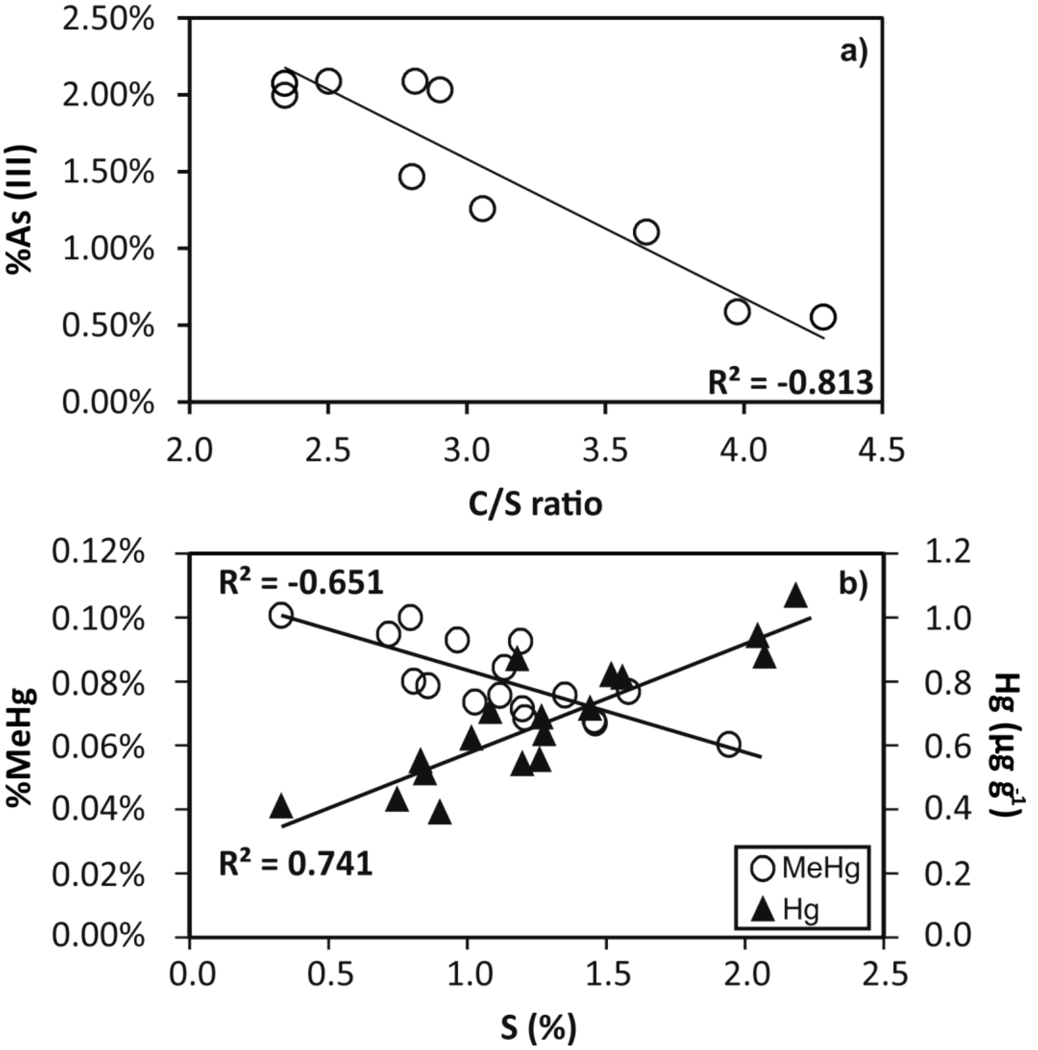


*Figure 5. Scatterplots of %As(III) as a function of C/S ratio and Hg (µg g$^{-1}$) and %MeHg as a function of S concentrations (%) in the surface sediments of the Nalón estuary.*

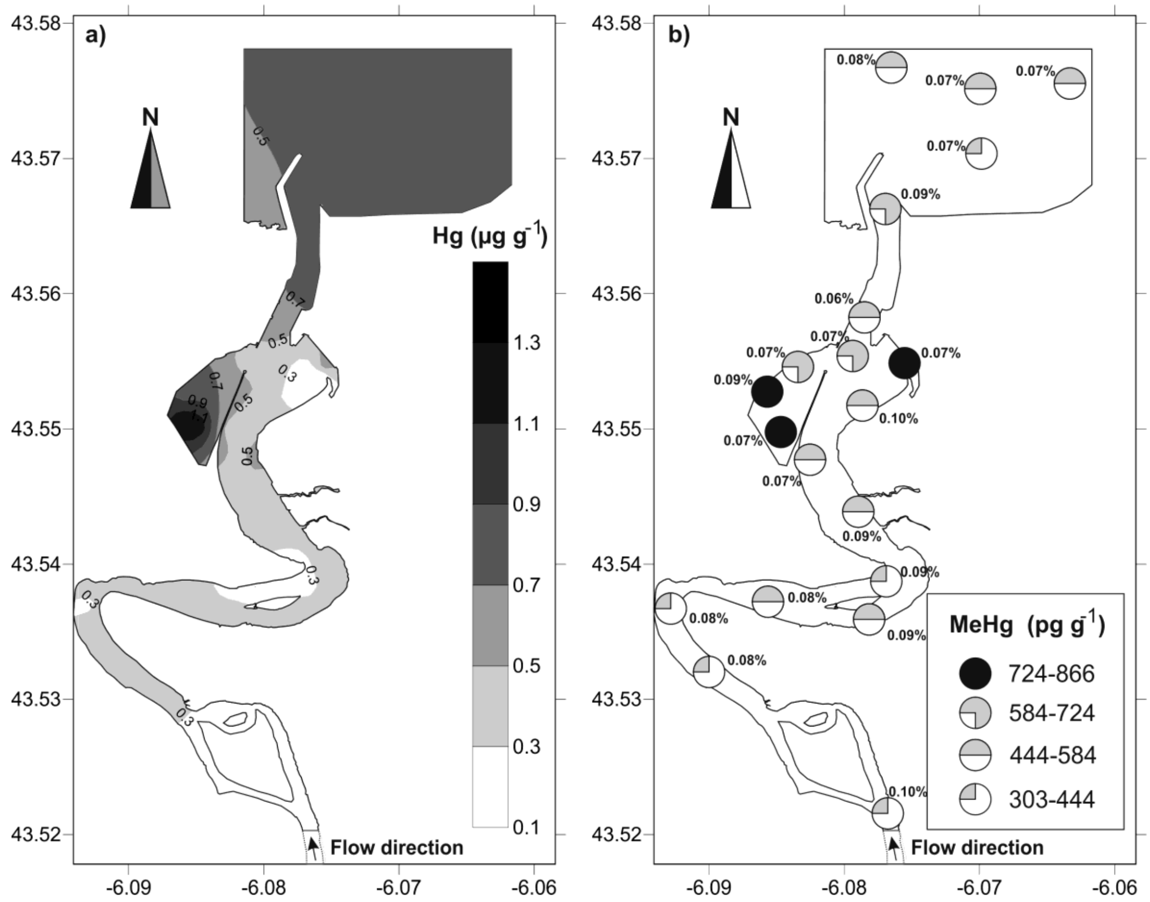


*Figure 6. Spatial distribution of $Hg_{tot}$ (a, in µg $g^{-1}$) and MeHg (b, in pg $g^{-1}$) concentration in the surface sediments of the Nalón estuary. Percentage values represent the abundance of the MeHg component with respect to the total concentration of Hg ($Hg_{tot}$).*

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

| | **As** (μg g$^{-1}$) | **Hg** (μg 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<br>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<br>Covelli et al., 2001 |
| Northern Tyrrhenian Sea (Italy) | 5.43-35.38 | 0.03-2.20 | na | Hg mining | Piazzolla et al., 2015<br>Scanus et al., 2016 |
| Kastela Bay (Croatia) | 15.00-33.00 | 17.60-74.00 | 6.05-16.40 | Industry | Orescanin et al., 2005<br>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 |

## Supplementary material

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

*Note: <DL-Below detection limit*

| Sample | Lat | Long | Sand (%) | Silt (%) | Clay (%) | TC (%) | TOC (%) | N (%) | S (%) | As ($\mu g\ g^{-1}$) | As(V) ($\mu g\ g^{-1}$) | As(III) ($\mu g\ g^{-1}$) | % As(III) | Hg ($\mu g\ g^{-1}$) | 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% |

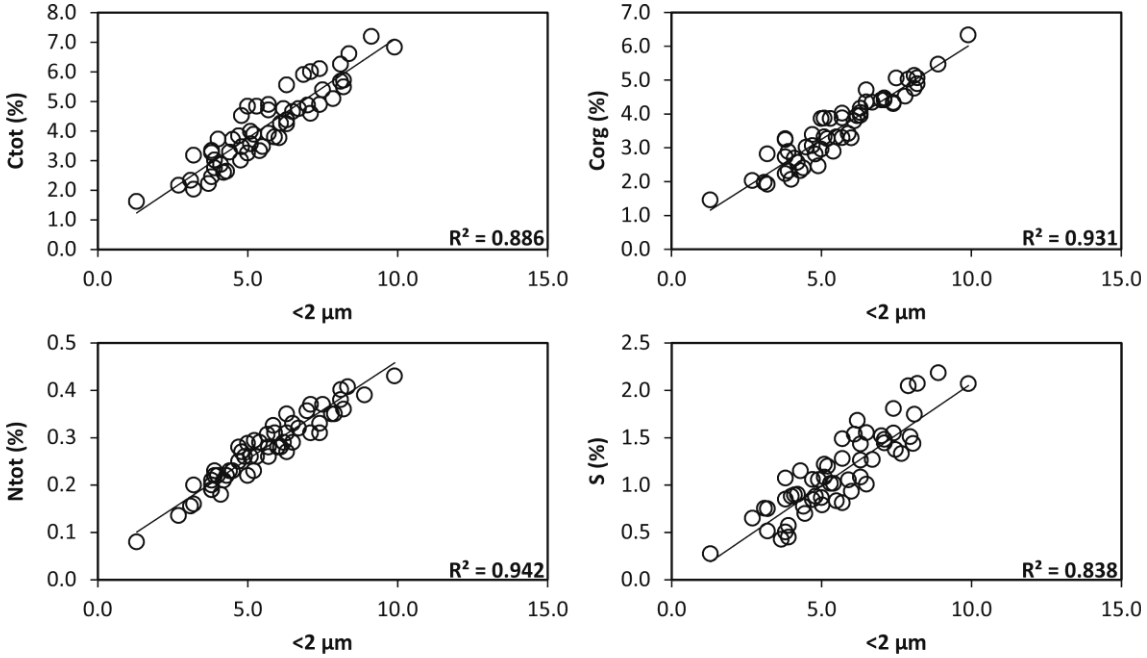


*Figure 1. Relationships among $C_{tot}$, $C_{org}$, $N_{tot}$ and S concentrations with the clay fraction.*

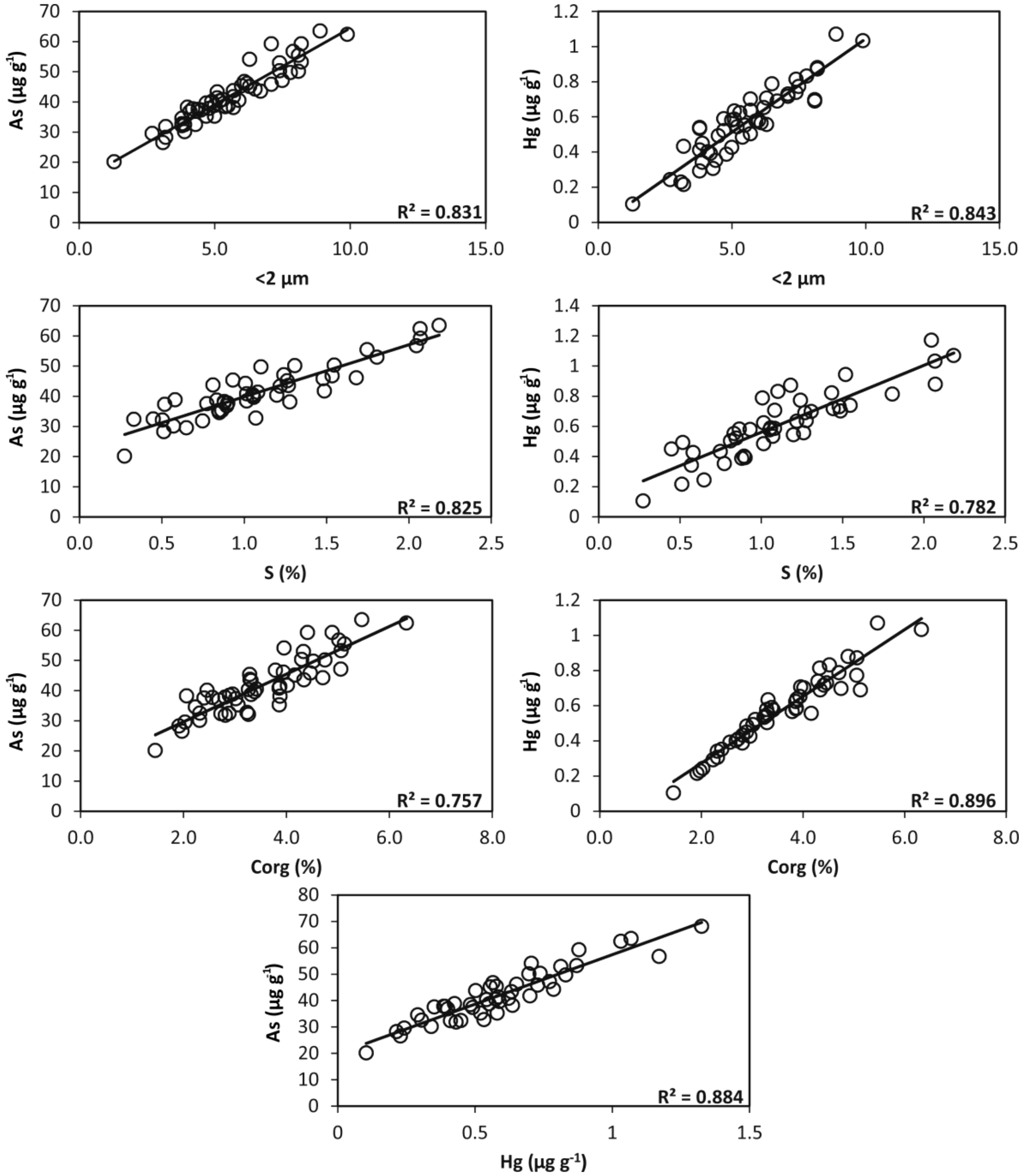


*Figure 2. Relationships among As$_{tot}$ and Hg$_{tot}$ concentrations with the most significative geochemical parameters of the surface sediments (clay fraction, C$_{org}$ and S).*

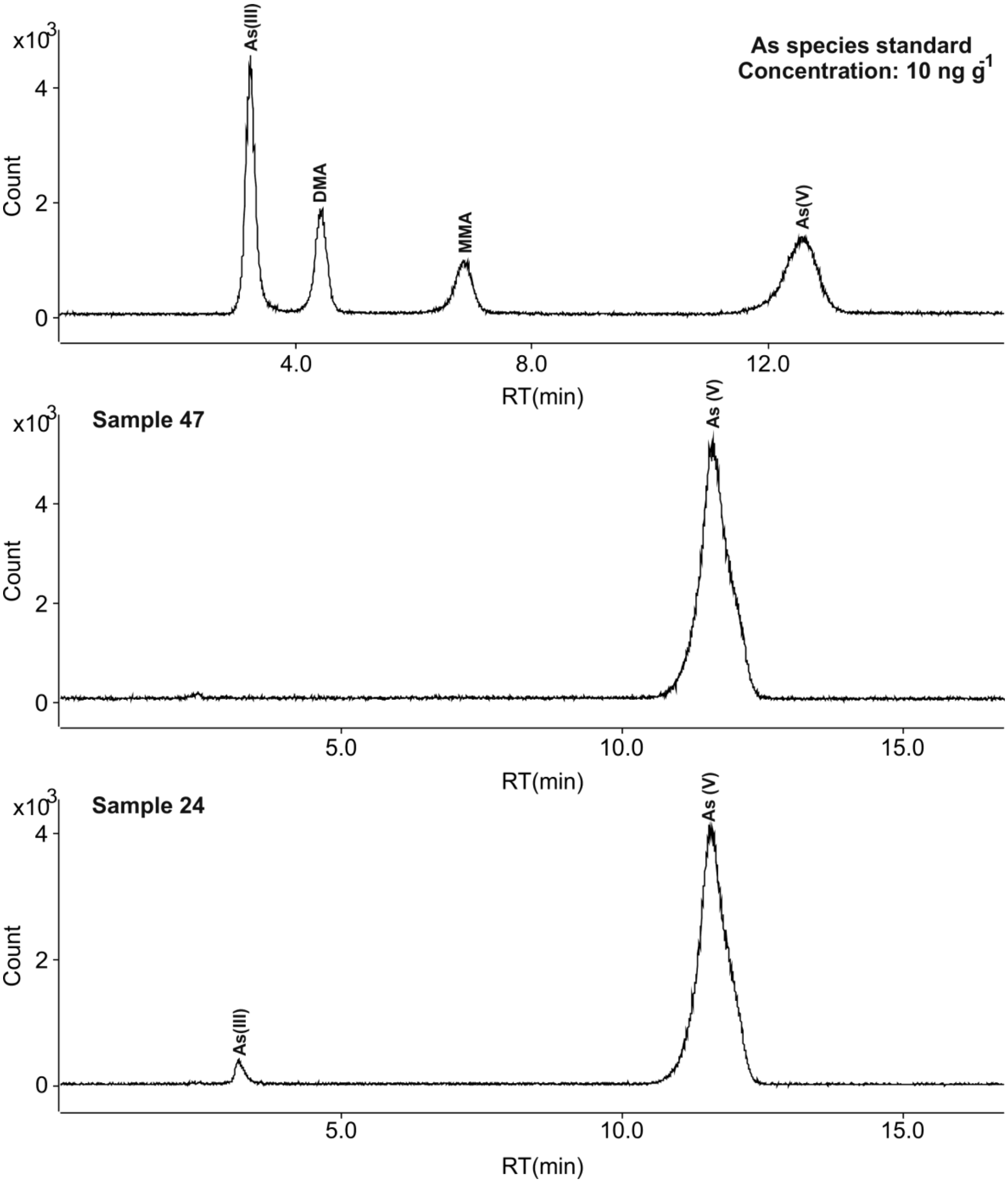


*Figure 3. Examples of different chromatograms obtained from the As speciation analysis*

**Highlights (3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

## 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