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Assessment of mercury pollution sources in beach sand and coastal soil by speciation analysis

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Abstract

Background: An essential requisite for controlling and monitoring mercury in the environment is to identify its species in different types of soils and sediments, as this will help not only to establish its mobility in the environment and ecosystem and the degree of its toxicity, but also to establish the source of contamination. The objective of this work was to identify the origin of mercury in beach sands and soil taken from a coastal region with previously high mining and industrial activity by characterizing the mercury species using the technique known as thermal desorption (HgTPD).

Results: Apart from quartz, the main mineral species identified in the raw sands and soil were calcite, fluorite and barite. The concentration of mercury ranges from 5 to 23 $\mu g\ g^{-1}$, and although it is distributed in different proportions in the function of the size, thermal desorption profiles demonstrated that the mercury species present in the samples do not vary with the mercury concentration and the particle size. By means of HgTPD, mercury oxide (HgO) was identified in the beach sands, whereas mercury sulfide (HgS) was found in the soil sample taken from the vicinity of the beach. Complementary methodologies foster the HgTPD conclusions and verify that mercury is present mostly in insoluble stable (HgS) or low-mobility (HgO) forms in the samples studied. Analyses by ICP-MS after sequential extraction and HPLC separation of mercury species show that inorganic mercury is the predominant form in the samples.

Conclusions: The technique HgTPD is a very useful tool to ascertain the origin of mercury in contaminated beach sands and shoreline soils. In the particular area studied in this work, the species identified indicate that previous mining activity was the source of the mercury and rule out the possibility that contamination is derived from coal combustion activities ongoing in the region.

Keywords: Mercury, Speciation, Thermal desorption

Background

Mercury is a heavy metal of great concern due to its high level of toxicity and the serious effects it has on health and the environment. Although all mercury species are toxic, certain species-specific toxic mechanisms have been demonstrated to have an effect on human organisms [26]. For instance, methylmercury, which is the species of mercury that can be incorporated into humans through food, may cause very serious harm to the central and peripheral nervous system [49]. The enormous alarm caused by mercury toxicity as a consequence of the presence of its compounds in the environment led to the Minamata Convention on Mercury, which came into force in August 2017 [48]. The Minamata Convention is the first global environmental agreement negotiated in the 21st millennium. The objective of the Convention is to protect human health and the environment from anthropogenic emissions and the release of mercury and mercury compounds, and it has set out a range of measures to meet this objective.

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Due to emissions of mercury to the atmosphere and their subsequent deposition onto the land and into the water as a result of the proximity of industrial activity zones or the transport process, some areas may contain high concentrations of mercury [32, 35]. In addition, point-source pollution associated with the inappropriate disposal of mining waste, metal smelters and other industrial activities have increased the environmental threat from mercury [9, 18, 31, 46]. Asturias, NW Spain, has had a long history of industrial activity, especially in the form of coal mining, but mercury mining and metallurgy were also important activities up until the end of the 1970s. This, coupled with other industrial processes, such as coal combustion, the production of steel and cement, exposed the region's soils, beaches and coastal environments to the risk of contamination (see e.g., [6, 42]), especially by mercury [21, 27, 34]. Local and regional studies based on geological records, such as peat bogs or estuarine sediments, have also revealed a dramatic increase in mercury accumulation over the last 200 years [15, 23, 25]. On a global scale, coal combustion and the production and processing of metals are the main anthropogenic sources of mercury emissions in Europe and the USA [11, 47]. The contamination of beaches by mercury comes mainly from anthropogenic sources such as industrial waste, stormwater runoff and sewage outfalls [10, 13, 29]. Chlor-alkali plants are also important sources of mercury, and the area surrounding these plants has been found to have high mercury concentrations [4]. Proximity to such industrial activities is in itself suggestive of the source of mercury contamination, but when several different activities occur in the same area or when the polluting species are transported by air or water from elsewhere, the origin of the mercury species is often difficult to pinpoint. Ascertainment of the source of mercury contamination will help to determine the risk of exposure, and being able to determine the chemical form (speciation) of the mercury present in the land is essential for understanding and modeling metal-contaminated systems since the way in which the mercury compounds are distributed determines their environmental mobility and bioavailability [14].

The objective of this study is to identify the mercury species present in samples of beach sands and soil taken from a coastal area of Asturias by the technique based on programmed temperature desorption (HgTPD) [3, 5, 36, 37]. Because the samples come from a region (Asturias), where different industrial activities have taken place, the study aims to relate the species of mercury to their source of origin.
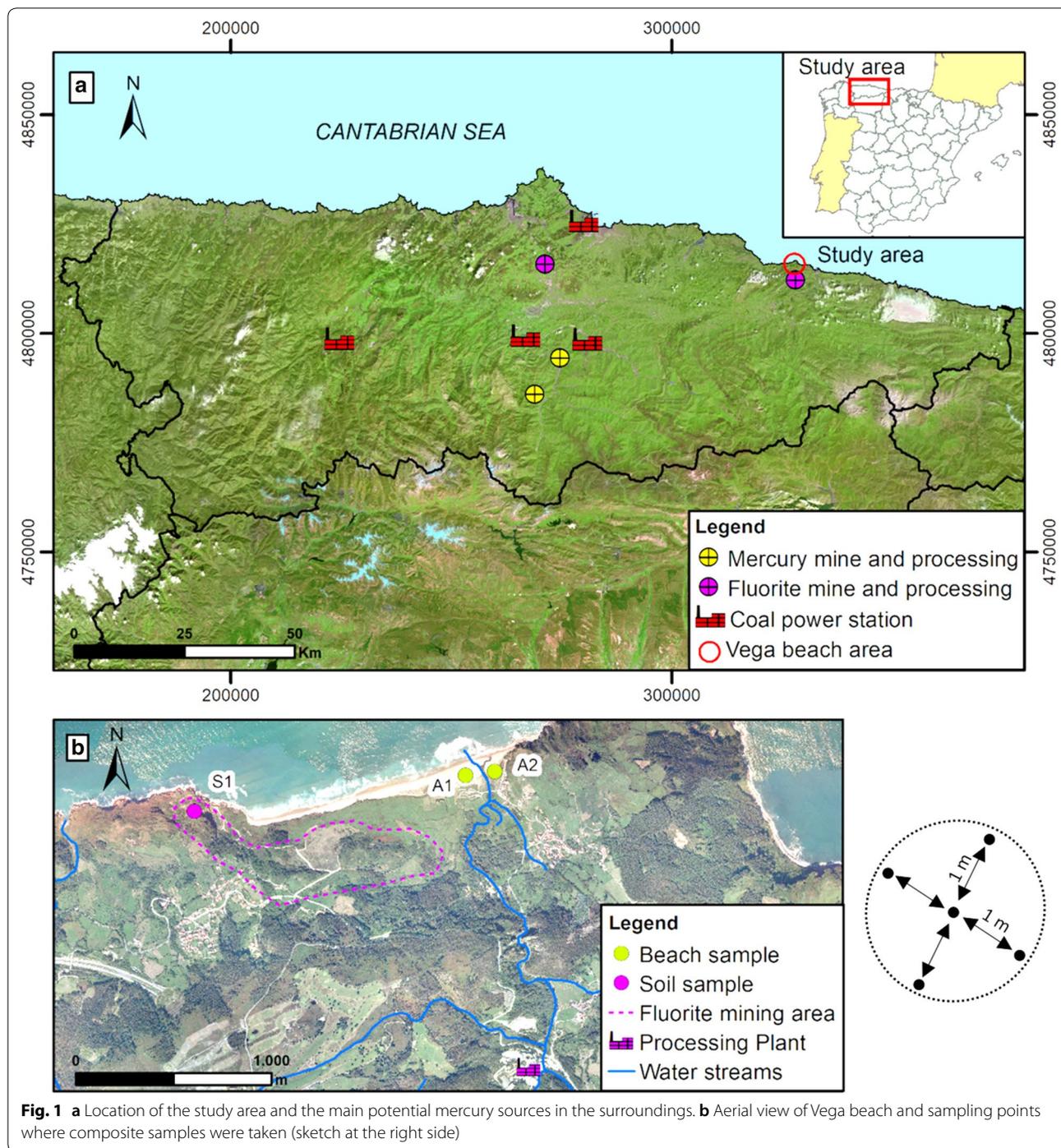
Experimental part
Site description and samples
During a sampling campaign of 13 sandy beaches with dunes in the Cantabrian area (unpublished data), it was found that sand samples from the Vega beach (Asturias, NW Spain) showed anomalously high mercury concentrations when compared to other areas sampled. The high mining and industrial activity in this region (Fig. 1a) suggests several possible sources for the presence of this heavy metal. Accordingly, three different composite samples were taken for a comprehensive addressing of mercury sourcing (Fig. 1b), namely A1 (supratidal sand), A2 (white dune) and S1 (coastal soil on the shoreline). Each sample was composed of five increases taken from each vertex of a 1 m edge square and its central point, from the top 30 cm of the material, using an Edelman Auger (Fig. 1b). In situ sieving of the samples through a 2-cm mesh screen was carried out to remove the large material and then the remaining samples were kept in plastic bags until their pre-treatment in the laboratory. Afterward, the samples were dried in an oven at 30 °C to prevent the volatilization of the mercury. The fractions smaller than 2 mm were separated by dry sieving, and the representative subsamples were generated using a riffler.

Devices for mercury determination and speciation
The concentration of total mercury in the raw samples and in the sieved sub-size fractions (see below) was determined by means of a mercury analyzer (AMA 254). The mercury species were identified by temperature-programmed desorption (HgTPD) using a setup developed by the authors [38]. This device consists of a temperature-programmed furnace coupled to a PYRO 915 furnace from LUMEX and a continuous mercury analyzer (RA-915) [39]. The peculiarity of this device is that the mercury species are desorbed in the first furnace using N_2 as an inert gas, while at the same time O_2 is introduced into the PYRO furnace to ensure the total decomposition of volatile matter. Desorption profiles are obtained by heating the sample at a rate of 50 °C min^{-1} under a N_2 flow of 500 mL min^{-1}. The PYRO 915 unit is kept at approximately 800 °C under an O_2 flow of 500 mL min^{-1}. In this unit, all the mercury species that have been vaporized from the sample in an inert atmosphere are transformed into elemental gaseous mercury (Hg^0). As Hg^0 reaches the detector in the continuous analyzer, the software registers temperature or time versus mercury and records the desorption profiles that correspond to the evaporation of the mercury species present in the sample. Each desorption peak is assigned to a species of mercury in accordance with the reference database of pure mercury compounds prepared in concentration and with matrices

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Fig. 1 **a** Location of the study area and the main potential mercury sources in the surroundings. **b** Aerial view of Vega beach and sampling points where composite samples were taken (sketch at the right side)

similar to the selected samples. Mercury reference materials used in this study included HgS, HgO, Hg^0, $HgCl_2$ and mercury associated with humic acid (Hg-HA).

In addition to the total mercury content analyzed in the AMA equipment, the determination of the identified species was carried out in the HgTPD device. The equipment was calibrated for total mercury content by analyzing

reference samples containing different amounts of HgS in a pure commercial sand matrix. The detection limit of the system was 3 ng for a maximum sample weight of 100 mg (0.03 mg kg^{-1}), assuming that the release of all the Hg occurs in a single peak. Each mercury standard and sample were analyzed 2 to 4 times. The precision of the analysis was evaluated from the standard deviation

(SD) and relative standard deviations (%RSD). An RSD value < 10% was achieved.

To balance the HgTPD study, two supplementary techniques were applied. First, a sequential extraction [45] was conducted. In brief, extracts with solutions of increasing strengths were attained from subsamples of the samples under study; i.e., the following fractions were obtained: exchangeable (extracted in $MgCl_2$), carbonate-bound (extracted in a buffer of CH_3COONa/CH_3COOH), Fe–Mn oxide-bound (extracted in NH_2OH-HCl); organic matter-bound (extracted in several steps using H_2O_2, HNO_3 and NH_4NO_3); and the residual fraction (extracted in aqua regia); in all fractions, the supernatants were separated after centrifugation for 15 min at 8000 rpm, filtered and analyzed in an Agilent Technologies 7700 ICP-MS (inductively coupled plasma mass spectrometry). In addition, a second approach by chemical speciation was also performed after extraction of representative subsamples using a solution of 7.6% HCl and 10% 2-mercaptoethanol in an ultrasonic bath. The extract was then centrifuged and diluted. The determination was carried out in a 1260 Infinity HPLC coupled to a 7700 ICPMS, using a ZORBAX Eclipse XDB C18 (2.1 mm i.d. × 50 mm, 5 μm) column and 0.06 M ammonium acetate, 5% methanol and 0.1% 2-mercaptoethanol (pH = 6.8) as mobile phase.

Complementary analyses

Granulometric separation was performed in three fractions (800–224 μm, 224–125 μm, < 125 μm), to ascertain the distribution and speciation of mercury as a function of its size and composition. Fraction > 800 μm was rejected as no mercury was detected in this fraction. Before being examined, the material was cleaned to eliminate any possible remains of vegetal matter or fauna from the samples.

The mineral species of the samples were identified by X-ray diffraction (XRD), in a Bruker D8 Discover apparatus with Cu Kα radiation (λ = 1.54059 Å). The scan was performed between 10º and 90º (2θ) using a step size of 0.02º s^{-1} and a step time of 2 s.
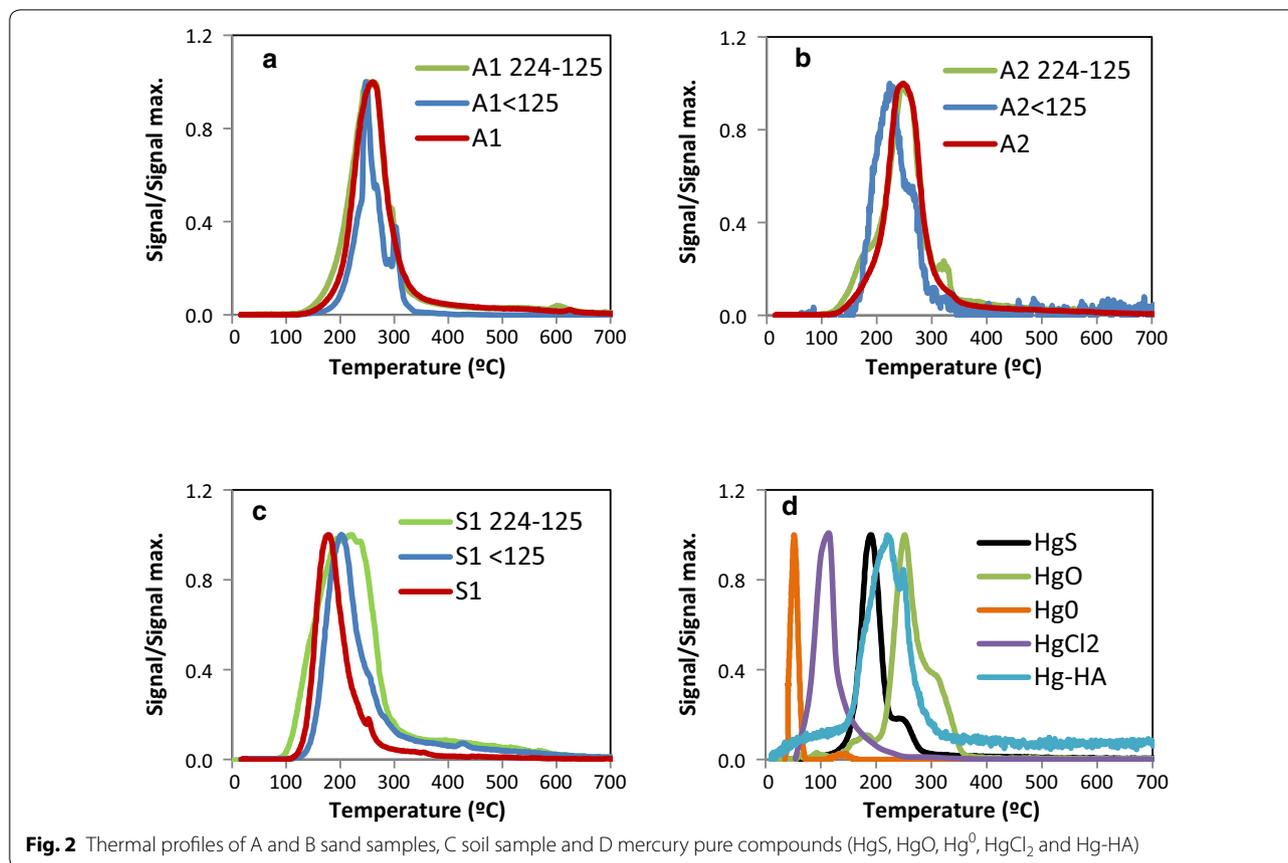
Results

The concentration of mercury in the raw sands and soil, and in the different size fractions together with the minerals identified by XRD, is shown in Table 1; note that mercury values found in the raw samples are well above the background/screening levels valid in the region [7]. As might be expected, the main mineral species identified was quartz in all the samples (Additional file 1: Figure S1). Calcite was also present in the sands and in the soil in different proportions. However, there was also an abundance of other minerals such as fluorite in all of the samples and of barite in two of them.

As can be appreciated from the data, the mercury content of the raw samples selected for this study ranges from 5 to 23 μg g^{-1}. Moreover, the mercury concentration is distributed in different proportions in the separated fractions (Table 1), the highest concentration being found in the fraction of the smallest particle size. As mentioned above, the objective of this work was restricted to identifying the mercury species and relating them to their origin in a particular area. Extensive samplings and analyses of the area are being carried out with the aim of creating a catalog of the type and level of contamination of this coastal area. Although the analyses performed for this study do not provide yet a conclusive picture about the pollution of the total area, as a preliminary study it may serve to identify the mercury species and to relate them to the source of contamination.

Figure 2 shows the thermal desorption profiles of the beach sands and soil together with the mercury standards used as reference materials. As shown in Fig. 2a–c,

Table 1 Mercury concentrations and mineral compositions of the raw samples and fractions

Sample	Fraction (μm)	% wt	Hg (μg g^{-1})		Mineral
			Fraction	**Raw sample**	
A1	800–224	31	0.16	10.9	Quartz (SiO_2) fluorite (CaF_2), calcite ($CaCO_3$)
	224–125	67	14.0		
	< 125	2	16.6		
A2	800–224	23	0.44	5.01	Quartz, fluorite, calcite, barite ($BaSO_4$)
	224–125	76	3.37		
	< 125	1	20.5		
S1	800–224	30	8.96	23.1	Quartz, fluorite, calcite, barite
	224–125	68	28.2		
	< 125	2	31.6		

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Fig. 2 Thermal profiles of A and B sand samples, C soil sample and D mercury pure compounds (HgS, HgO, Hg⁰, HgCl₂ and Hg-HA)

the maximum temperature peak of desorption is the same for each group of samples studied. Hence, the mercury species present in the samples do not vary with the mercury concentration and the particle size (Table 1). The thermograms of the mercury species from the beach sands (A1 and A2) analyzed show a maximum peak at 240 ± 10 °C. This peak corresponds to the HgO pure mercury compound (Fig. 2d). However, in the case of the soil sample (S1), the temperature of maximum desorption is at 180 ± 11 °C. This peak is assigned to HgS, the most abundant and stable mineral species of mercury in nature [43].

The analyses carried out by ICP-MS after sequential extraction and HPLC separation of mercury species show that inorganic mercury is the predominant form in the samples (Table 2). In fact, only in the soil sample very minor traces of organic mercury were found. In addition, Tessier's extracts of the samples revealed negligible amounts of mercury in all the fractions being the predominant fraction the residual one.

Table 2 (Left) Percentages of the five fractions obtained in the Tessier sequential extraction results; EX (exchangeable), CB (carbonate bound), OX (Fe/Mn oxides bound), OM (organic matter bound), and immobile fraction (residue), (Right) percentages of inorganic vs. organic mercury in the samples studied

Sample	% Hg (sequential extraction)					% Chemical speciation	
	EX	CB	OX	OM	Residue	Hg inorganic	Hg organic
A1	n.d	n.d	n.d	n.d	100	100	n.d
A2	n.d	n.d	n.d	n.d	100	100	n.d
S1	1.6	0.3	9.1	9.3	79.7	99.1	0.9

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Discussion

The HgTPD method has already demonstrated its capability for the identification of mercury species in different types of solids [3, 5, 36, 37]. However, its potential to explore the sources of contamination on a beach surrounded by mines and industries is a new issue. The identification of mercury species in similar samples was already been carried out by using other methods of analysis [2, 8, 50], and in all cases the results were of great relevance from the environmental and social point of view. However, the HgTPD method entails some advantages when compared with X-ray absorption spectroscopy (EXAFS) and classic extraction methods, such as its low detection limit and high selectivity. The application of the HgTPD technique has been shown to be an effective means of identifying mercury species in two environmental compartments that are difficult to assess using more conventional techniques based on Hg chemical extraction. In fact, soils in former mining areas, and especially sandy sediments in coastal areas, usually present abundant refractory complex minerals such as silicates together with sulfides and oxides, leading to difficulties in the quantification or speciation of metals linked to them and requiring very strong acidic extractions. This problem was overcome in this study by the application of HgTPD.

The results obtained by HgTPD technique and confirmed by ICP-MS after sequential extraction and HPLC separation verify that mercury is present mostly in insoluble stable (HgS) or low-mobility (HgO) forms in the samples studied, while other possible mercury species such as $HgCl_2$, Hg^0 and mercury associated with humic acids (Hg-HA) are virtually absent.

On the basis of the mercury species identified in the samples and the industrial activities carried out in the zone studied, the possible sources of mercury contamination to be considered are the following:

HgS, one of the mercury species identified in this study (Fig. 2), is found associated with different types of particles, such as airborne particulate matter [1, 12] and fly ash particles [40]. Given that in Asturias there are four coal-fired power plants currently operating at less than 100 km from the Vega beach (Fig. 1a) and that coal power plants are the main source of anthropogenic mercury emissions, the particles emitted from coal combustion should be considered as one potential source of mercury in this particular area. However, in the samples analyzed in this study it cannot be confirmed whether the mercury came from coal or the particles produced by the process itself. If the contamination had come from air deposits, then the soil and the beach sand should have been similarly affected given their close proximity to each other but no HgS was detected in the beach sands (Fig. 2). Neither

were any other mercury species, such as $HgCl_2$, $HgSO_4$ or HgO which are often present in coal fly ashes, detected [28, 40]. It is also significant that the levels of mercury found in other beaches closer to the coal power plants than Vega beach were much lower (0.13 ± 0.01 μg g^{-1} as an average value).

A second hypothesis could be the influence of former Hg mining and metallurgy activities that were carried out in the region up until the 1970s and the subsequent abandonment of huge amounts of Hg waste. This is highly likely in the case of the sites known as La Soterraña [30], El Terronal [16] and their surroundings (Fig. 1a), as a consequence of which the river sediments in the hydrographic basin where these sites are located were also affected [19]. The effects are especially noticeable in the river mouth of the Nalón River, the main river in the region (see e.g., [17]). However, the distance between the Hg mining cores and the studied area, which is located in a different basin, would seem to rule out any possible relationship. In addition, previous studies on mercury speciation in the mining and metallurgy waste of the above-mentioned Hg sites of central Asturias [41] present different profiles to those of the mercury species obtained here, i.e., several mercury species such as metacinnabar, $HgCl_2$, Hg-FeS$_2$ or even Hg(0) were present in Rumayor's study but not in this study of the Vega beach. Therefore, the second hypothesis seems very unlikely in the case of the present study.

As mentioned in the Results section, X-ray diffraction data of both the soil and the sand samples indicate the abundant presence of fluorite (Table 1, Additional file 1: Figure S1). This is clearly related to the proximity of several fluorite mines in the vicinity of the studied area, i.e., the so-called Caravia-Berbes mining district (Fig. 1b) where the paragenesis of the mineralization involves fluorite (CaF_2) and abundant barite ($BaSO_4$) [22, 44], in coincidence with the minerals found in this study (Table 1, Additional file 1: Figure S1). Furthermore, cinnabar (HgS) is present in the form of fine inclusions in the fluorite and copper minerals that are also plentiful in the area [22]. It is possible therefore that the extraction and treatment of fluorite in this zone could lead to contamination by mercury.

Furthermore, the differences in the speciation observed between the soil sample (HgS) and those of the beach (HgO) (Fig. 2) could be due to two different sources. On the one hand, the soils have been affected by the uncontrolled abandonment of nearby mining areas and therefore reflect the original mercury mineralogy, whereas on the other hand, the main source of mercury in the beach could have been the dumping (for decades) of mineral processing waste into the Vega river which flows into the sea next to the Vega beach [20]. The processing of fluorite

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which is mainly performed by means of flotation (see [51] and references therein) may cause a separation of HgS and HgO species in different fractions. In addition, although mercury is usually found as HgS, other minerals such as montroydite (HgO) may also be present in mine wastes [24], as is the case of the studied area. These facts would explain the differences found between the soil and sand samples. Stable and insoluble forms of mercury, such as HgS, show a different mobility pattern in soils to that of other more reactive species of mercury, and this determines the potential impact on groundwater and hence on the health of human beings [33].

Conclusions

Use of the HgTPD technique has made it possible to identify the presence of HgO in the beach sands and HgS in shoreline soil, while discarding the presence of other possible mercury species such as $HgCl_2$, Hg^0 or mercury associated with humic acids. The results have been corroborated by sequential extraction and HPLC-ICP-MS.

The mercury concentration is higher in the samples of the smallest particle size, but the thermal profiles are similar for the different fractions, suggesting that there is no change in the speciation of mercury.

Based on the mercury species identified and the industrial activities carried out in the area, the results suggest that the main source of pollution is the previous local fluorite mining activity. Other sources such as coal combustion or other practices involved in the exploitation of coal, and also mercury, in the region are unlikely.

In addition to contribute to understanding the behavior and the presence of mercury in the environment, this study is a relevant contribution to the validation of the desorption technique at programmed temperature.

Supplementary information

> **Additional file 1: Figure S1.** X-ray diffraction patterns of sand samples (A1 and A2) and soil sample (S1).

Abbreviations

Å: Angstrom; A1: supratidal sand; A2: white dune; AMA: Advanced Mercury Analyzer; B: barite ($BaSO_4$); BOPA: Bulletin of Asturias (Spain) legislation; °C: Celsius degrees; C: calcite ($CaCO_3$); CB: fraction bound to carbonates; CSIC: Consejo Superior de Investigaciones Científicas. (Spanish National Research Council); Cu Kα radiation: $\lambda = 1.54059$ Å; E-PRTR: European Pollutant Release and Transfer Register; EX: fraction exchangeable; F: fluorite (CaF_2); g: grams; Hg^0: elemental gaseous mercury; HgTPD: mercury temperature-programmed desorption; HPLC: high-performance liquid chromatography; INDUROT: Institute of Natural Resources and Territorial Planning (University of Oviedo); ICP-MS: inductively coupled plasma mass spectrometry; km: kilometer; λ: wavelength; μg: microgram; μm: micrometer; min: minutes; mL: milliliter; mm: millimeter; n.d: non-detectable; OM: fraction bound to organic matter; OX: fraction bound to Fe and Mn oxides; Q: quartz (SiO_2); s: second; S1: coastal soil on the shoreline; UNEP: United Nations Environmental Program; URICI: Unit of Information Resources for Research; WHO: World Health Organization; % wt: weight percentage; XRD: X-ray diffraction; 2θ: angle between the diffracted and transmitted X-ray.

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