Contribution of fluorite mining waste to mercury contamination in coastal systems

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Abstract

Samples from 13 beaches along the northern Spanish coast, a region with a history of heavy industries, were first screened to identify signs of pollution. High concentrations of Hg on Vega beach (Asturias) correlated with Ba. Both elements belong to the paragenesis of fluorite ores mined in the surroundings. Samples of sandy beach and fluvial sediments, and nearby soils were collected in Vega beach area to address potential Hg pollution, its fate and sources. Most samples showed a similar pollutants fingerprint to that of beach samples, especially those taken from white dunes, registering notable Hg concentrations. Hg was enriched in the finer fractions, and overall the main input was attributed to the mining waste discharged along the coast. Although a specific risk assessment and study of the submerged sediments are advisable for this area, Hg bioavailability and methylation were low, thus indicating that this metal poses a reduced environmental risk.

Keywords: Mercury, beach, mining waste, Cantabrian Sea, sediments, pollution

1. Introduction

Environmental contamination by Potentially Toxic Elements (PTEs) receives special attention at local, regional and global scales. PTE contamination is a challenge because, in addition to being toxic, these compounds are non-biodegradable and persistent, tending to bioaccumulate in biota and thus implying a risk to ecosystems and human health (Beone et al., 2018, Cabrini et al., 2017, García-Ordiales et al., 2019, Landers et al., 2018, Yang et al., 2013). Within this context, mining industries are one of the productive sectors of most concern. Mines, mineral processing and mining-waste disposal are common sources of pollution that affect large areas comprising soils (Boente et al., 2019, Forján et al., 2018, García-Giménez et al., 2017), rivers, and even beaches (La Colla et al., 2019, Khan et al., 2017).

Mercury (Hg) is released into the environment through both natural and anthropogenic routes, and it has wide-ranging and marked effects on the health of animals and the ecosystem. Hg is a metal with global distribution, and it is listed as a high-priority environmental pollutant within the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention, 2004). Moreover, since the recently approved UN Minamata Convention on Mercury (2017), whose main objective was to raise global awareness of measures to control contamination by Hg (Evers et al., 2016), interest in this pollutant has grown. Hg and its compounds are classified as neurotoxic, mutagenic, teratogenic and carcinogenic, and they can have embryocidal, cytochemical, and histopathological effects (La Colla et al., 2019, Lyons et al., 2017).

The increase of Hg in beach sediments can affect the distribution and composition of benthic organisms and lead to a high concentration of this pollutant in sediment-dwelling fauna (Black et al., 2009, Bramha et al., 2014, Vetrimurugan et al., 2017). In this context, coastal regions are particularly important as they account for a small fraction of physical space in which all four spheres, namely the lithosphere, hydrosphere, atmosphere and biosphere, interact. Coastal regions are hotspots of environmental changes driven by natural events (changing sea level and storms), and in this regard, the footprint of urban expansion and industrial activities is left in narrow strips of land bordering the oceans (Hiller et al., 2016, Vetrimurugan et al., 2018).

Beaches are exposed to a wide range of marine, fluvial, and aeolian processes, although the most important suppliers of sand sediments to the shoreline are fluvial systems (Milliman and Farnsworth, 2011). These factors modify the mineralogy and geochemistry of beach sediments. Moreover, if the beaches are located along an urbanized coast or near industrial or mining activities, they can be contaminated by discharges and emissions. Therefore, beach sediments can be enriched in contaminants such as PTEs as a result of anthropogenic activities (Díaz et al., 2015, Khan et al., 2017).

Following the preceding considerations, this study started by screening 13 of the main beach/dune systems along the Cantabrian coast in northern Spain. This area has been highly industrialized in the last two centuries. Indeed, both in the past and today, industrial and mining activities are found very close to the coast and have left a clear pollutants fingerprint (Gallego et al., 2013; Irabien et al., 2008; Leorri et al., 2014; Sierra et al., 2014). The initial results from the screening revealed Hg contamination of a large coastal system (Vega beach and surroundings). Therefore, the main aim of this study was to study the fate and sources of Hg in the environmental compartments of Vega beach, and their link to the fluorite mining works that operated in the area for decades. The methodologies applied here can be extrapolated to similar case studies and the results can serve to increase awareness of the scientific community with respect to the potential hazards posed by Hg contamination in coastal systems.

2. Material and methods

2.1. Initial screening

Sand samples were taken from 13 beaches along the Cantabrian coast, stretching from the Principality of Asturias to the Basque Country (Fig. 1). Specifically 8 samples were taken per beach in the intertidal and supratidal areas. 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, by means of an Edelman Auger. Samples were preserved in plastic bags until their pre-treatment in the laboratory. Samples were passed through a 2-cm mesh screen in order to remove large material. Afterwards, they were dried in an oven at 30°C to prevent the volatilization of Hg. Given the analytical results (see section 3.1), a more exhaustive sampling campaign on Vega beach was performed.

2.2. Study site (Vega beach)

The district of Berbes (approximately X: 326,027 m Y:4,816,009 m) was in the 20th century the most productive fluorite mining area not only of Asturias, but also of Europe (Levresse et al., 2019, Symons et al., 2017) because of the outcropping of important mineral ores along much of its perimeter (Fig. 2).

The paragenesis of the mineralization in this area is composed by fluorite (CaF_2) and abundant barite ($BaSO_4$) (Tejerina and Zorrilla, 1980). Furthermore, cinnabar (HgS) is occasionally present

in the form of fine inclusions in the fluorite and copper minerals (chalcopyrite, fahlore and Cu-carbonates are also abundant) (Iglesias and Loredo, 1994). Due to this singular mineralogy, the extraction and treatment of fluorite in this zone can cause Hg pollution. Other potential contaminants are arsenic (As), related to the iron and copper sulfides in the area, and phosphorus (P), which is present as fine apatite crystals from pre-fluorite silicified rocks (Iglesias and Loredo, 1994).

The main mineral deposits are found in an area of about 12 km^2 (Gutiérrez-Claverol, 2009) related to the unconformity between the ``Permo-Triassic cover´´ and the ``Palaeozoic basement´´. The deposits are present either as vein or stratabound ores (Fig. 2). The former can be found in fractures or in faults, while stratabound beds occur between Carboniferous basements and Permo-Triassic cover rocks, or within the Permo-Triassic sedimentary rocks (Iglesias and Loredo, 1994). In the second half of the 20th century, fluorite mining made a significant visual impact on the whole area due to the absence of strict environmental controls. In addition, waste discharge from fluorite mineral processing in the zone reached the shoreline through rivers (Gutiérrez-Claverol, 2009).

2.3. Sampling (Vega beach)

Twenty-nine sand samples were taken along the beach-dune system using a methodology very similar to that described above for the screening study. Each geomorphological division of the beach had representation in the sampling proportionally to its area; i.e., in the intertidal area, the largest one, 12 samples were gathered, while 6 samples were collected in the supratidal area, 8 in the white and grey dunes, and 3 in the embryo dunes. Finally, another sample was taken in the transition zone towards the soils contouring the beach (Fig. 3A).

In addition, soils from the surroundings of Vega beach were also examined. Samples from the former mining area (13 samples) and natural soils (11 samples) were taken, in order to verify whether the Hg pollution was attributable to the mining activities. These samples were subjected to the same preparation treatment as the sediments (Fig. 3C).

Finally, and given that mineral processing was commonly done in an area only a few kilometres upstream of the river mouth on the beach, 10 sediment samples were taken along the Vega River in order to evaluate environmental disturbance (Fig. 3B).

2.4. Laboratory analyses

2.4.1 Sample preparation and ICP-MS

All the samples, irrespective of their origin, were treated as follows: drying at a temperature below 30°C, separation of the fraction of less than 2 mm by dry sieving, and generation of representative subsamples by means of a Jones riffle splitter separator. An aliquot of each sample (fraction < 2 mm) was ground by an agate mill to a particle size of less than 100 microns. Then, 1-g representative sub-samples were sent to the ISO-9002 and ISO-17025 accredited Bureau Veritas Laboratories (Vancouver, Canada). These laboratories are specialized in the analysis of ores and samples from mining environments. The method selected was "Ultratrace 2", which consists of an aqua regia digestion and analysis of 25 elements by ICP-MS (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mn, Na, Ni, Pb, REE (heavy and light), S, Sb, Sr, V, Y and Zn). The samples were analyzed using strict quality controls. Five blanks, five duplicates and ten analyses of standard reference materials (internal standards and OREAS45EA) were inserted into the sequences of samples, thus providing a measure of background noise, accuracy, and precision. In addition, pH was measured by means of a Crison pH 25 device on the suspension supernatant of a 1: 2.5 mixture of sediment / water. Electrical conductivity was measured by a Crison CM 35 device on the same sample used for pH determination, modifying the proportion of the suspension to a sediment / water ratio of 1: 5. The percentage of Organic Matter (% MO) and Organic Carbon (% CO) was determined by ignition at 450°C.

2.4.2 Grain-size analyses.

The grain-size of aliquots of the samples taken on the beaches was analyzed. To this end, the material was cleaned in order to eliminate the possible remains of plant matter, as well as fauna. Subsequently, the sand was washed to eliminate salt, which could precipitate during sample drying. The samples were dried in an oven at 30°C ± 2°C in order to prevent the loss of volatile compounds such as Hg. Once the material had been dried, particle size distribution was measured by laser diffraction spectroscopy using the Aqueous Liquid Module of a LS 13320 Beckman Coulter system (accuracy from 0.040 μm to 2000 μm). In addition, some samples with the highest Hg content (see results) were fractionated by means of wet sieving, in order to obtain several fractions (2000-500 mm, 500-250 mm, 250-125 mm, <125 mm), which were then subjected to multi-element analysis in Actlabs.

2.4.3 Bioavailability and chemical speciation.

The potential effects of PTE pollution (Hg in our case) cannot be assessed through a single quantification, as this would imply that all the chemical forms of a given PTE have the same impact on the environment. Therefore, selective extraction of the specific fractions of given samples was carried out, using the extraction procedure proposed by Tessier et al. (1979). In all fractions, the supernatant of each extraction was separated after centrifugation for 15 min at 8,000 rpm. The supernatant was then filtered for further analysis by ICP-MS.

In addition, chemical speciation (inorganic vs. organic Hg) was also addressed after extraction using a solution of 7.6% HCl and 10% 2-mercaptoethanol in an ultrasonic bath. The extract was then centrifuged and diluted. Hg 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. x 50 mm, 5 µm) column and 0.06 M ammonium acetate, 5% methanol and 0.1% 2-mercaptoethanol (pH = 6.8) as mobile phase.

2.5. Statistical Analysis

The data obtained were treated using version 19.0 of the SPSS statistical programme for Windows. Analysis of variance (ANOVA) and a test of homogeneity of variance were carried out. In the case of homogeneity, a post-hoc least significant difference (LSD) test was carried out. When no homogeneity was detected, Dunnett's T3 test was performed.

A hierarchical clustering analysis was done with the multi-element results of samples from Vega beach. The procedure applied was Ward's algorithm with Squared Euclidean distance. This method maximizes the existing variance between groups and minimizes it between members of the same group, thus making it ideal for geochemical studies (Murtagh and Legendre, 2014). A bivariate analysis (Pearson correlation) was also carried out between soil concentrations of Hg and As, Ba, Cu and Sb.

3. Results and discussion

3.1 PTE distribution on beaches of the northern coast of Spain

The results of the metal(oid)s analyzed did not reveal any notable anomaly (Table S1), with the exception of Vega beach, which showed values of Hg exceeding the regional RBSSL for Asturias (BOPA, 2014), and Muskiz and Zarautz beaches, where samples exceeded the As value for regional levels for the Basque Country (BOPV, 2015).

In addition to the Hg anomaly detected, Ba content was also significant on Vega beach, (Fig. 4). In fact, Ba (in form of Barite, see Fig. S1) is present in the paragenesis of the exploited ore deposits (Iglesias and Loredo, 1994) and it can therefore be used as a geochemical tracer of F (not

measured in the ICP-MS analyses). Consequently, given the high Ba concentrations detected, it is reasonable to associate Hg anomalies with the fluorite mining works. In view of this anomaly, a detailed characterization study was carried out on Vega beach.

3.2. Vega beach

3.2.1 Presence and distribution of Hg on Vega beach.

Fluorite mining in the basin of Vega River, which flows into Vega beach, started in 1957 (Gutiérrez-Claverol, 2009). From 1974 to 1989, silty-sand waste from fluorite processing (mainly obtained by flotation, see Boaretto et al., 2018; Zhang et al., 2018 and references therein) was released onto Vega beach (Gutiérrez-Claverol, 2009). From the 1990s until now, the discharge has been done through a marine outfall that was initially located 660 m away from the low tide line but is now 1000 m away (isobaths 15 and 22 m respectively). Thus, we hypothesized that Hg has experienced strong dispersion throughout the beach area as a result of the historical direct release of mineral processing waste on the shoreline and, perhaps secondarily, of the more recent use of the marine outfall. Old waste-dumping practices in the river and the abandonment of some mining areas without undertaking a restoration plan may also have contributed to the dispersion of this PTE.

Regarding the general characterization of sandy beach sediments, all the samples showed average values of pH, EC (Electrical Conductivity), %OM (Organic Matter) and %OC (Organic Carbon) of 9.11, 547, 0.28 and 0.20, respectively. Thus, an alkaline pH was observed, the conductivity of the samples increased with proximity to the sea, and the content of OM was low. These values are common for beach sand (Chadwick et al., 1990).

Regarding the presence and distribution of Hg, white dunes presented the highest concentrations, whereas the other areas were partially depleted of this metal (Fig. 5). In fact, the differences in Hg concentrations between the distinct environments may be related to multiple factors, such as tides, wind and fluvial dynamics, as well as the age of the sediment deposition or grain-size distribution, among others. In our case, a detailed revision of aerial view information (from 1945 to the present) revealed that some sediments belonging to white dunes were incorporated during the decades of intensive fluorite mining activity in the area (1970s and 1980s), whereas others are much more recent. On the contrary, the sediments of the grey dunes were partially incorporated to the system before the start of fluorite mining. Finally, the other study zones (inter, supratidal and embryonic) were formed much more recently, which might suggest a minor accumulation of Hg-rich materials after the marine outfall construction, or may simply echo the effect of tidal washing (removal and transport of fine sediments).

To address Hg behavior in greater detail, we performed a grain-size analysis (Table 1). No clear relationships between the presence of Hg and the textural parameters of the samples were observed, since the parameters and sorting obtained were similar in the zones studied.

However, a chemical study using grain-size fractions in some samples with high Hg content revealed a marked enrichment in the finest fraction (<125 microns), although this fraction was the least abundant in weight with respect to the others (Table 2). These results point to beach sediments receiving contributions of fine sands, and silty or even clayey components, the latter likely related to mine waste given the high Hg content found.

The multi-element features of the sand samples (Table S2) were studied using cluster analysis. Fig. 6 reveals three clusters. Cluster 1 is the predominant group and it is related to lithogenic elements that appear naturally in sands, including Al, light and heavy rare earths (REE) and V. On the other hand, cluster 2 presents Hg, Ba and other minority elements (As, Sb, Cu) that are present in the mineral paragenesis of the fluorite deposits in the area, as described and referenced above. Cluster 3 groups those elements more clearly linked to marine influence, such as Ca, Na and S (biological carbonates, salts, etc.). Interestingly, the statistical distance between clusters 2 and 3 suggests a potential link of the contaminant sources (Hg, specifically) with the remobilization of shoreline sediments rather than with the direct supply of fluvial sediments.

3.2.2. Presence of Hg in fluvial sediments

Total Hg contents in the fluvial sediments were well below the maximum values found in the beach sand. However, samples tended to show increasing concentrations as distance to the mouth of the Vega River shortened (Fig. 7), with the only exception of the sample taken in the vicinity of the current mineral treatment plant. However, the concentrations of Hg in fluvial sediments were not especially high. This could be explained by the fact that the first marine outfall was built 26 years ago, as described above, thus marking the end of direct discharge into the river. These results strongly support a relationship between fluorite mining, in particular mineral treatment, with the anomalous concentrations of Hg in the area, but rule out any recent relevant discharge apart from that of the outfall system.

3.2.3. Presence of Hg in soils

The soil samples collected in former mining areas in the surroundings of Vega beach presented high concentrations of Hg and also of As, Ba, Cu and Sb (Table S3). In this context, Pearson's correlation analysis ($P < 0.01$) showed a strong correlation of Hg with Cu (0.864), As (0.837), Sb (0.824) and Ba (0.585), which all belong to the paragenesis ore of the mineral deposit. These

results are consistent with data found in the multivariate study of the beach samples (Fig. 5). However, in the beach environment, only Ba and Hg were significantly enriched, thereby suggesting a higher geochemical mobility of Cu, As and Sb once released into environmental compartments.

Moreover, four of the samples showed Hg concentrations that exceeded the limit of quantification of the analytical method (10 mg / kg); i.e., ten times higher than the current RBSSL (BOPA, 2014) for the soil use in the region. These anomalies were located in the former mining exploitation areas very close to the ore veins and therefore could be considered part of the geological background (Fig. 8).

In turn, Hg concentrations in soils not subjected to mining activities presented lower values (Fig. 8), thereby suggesting that the high presence of Hg is limited to former mined sites. However, some natural soil samples to the west of the study area (Fig. 7) showed slightly anomalous concentrations. These samples were close to the mining areas and may have acquired Hg contamination by mechanical dispersion as a consequence of civil works, dust deposition or transfer by proximity to the mineral transportation tracks used by heavy machinery. However, given the absence of human activity in the former mined areas, a more detailed soil pollution study is not critical.

3.2.4. Hg bioavailability and speciation (Vega beach)

As described above, soil, sediment and fluvial sediments showed frequently anomalous Hg contents; however, we identified the main concern to be the beach. In fact, the Hg concentrations on Vega beach indicate potential risks to the environment and to human health. In this regard, the bioavailability study (Tessier method) of the samples with a higher concentration of Hg revealed the absence of the two main Hg fractions with greatest availability (Table 3). Likewise, the additional analyses carried out by HPLC-ICP-MS showed the predominance of inorganic Hg in the beach samples and no trace of methyl- or ethyl- Hg. All together, these data reasonably reduce the potential risks derived from the presence of Hg anomalies on Vega beach and point to the presence of Hg may be in mineral form (cinnabar), which is probably included in the crystalline network of other minerals, as reported by Iglesias and Loredo in 1994.

4. Conclusion

Here we initially sought to evaluate the degree of PTE pollution on several beaches along the northern coast of Spain. Our results revealed notable Hg concentrations on Vega beach that

surpassed the RBSSL in Asturias (1 mg/kg). We propose that these high Hg values are linked to former and current fluorite mining. This industrial activity has induced the presence of Hg, Ba and other trace elements in the study area, as a result of inappropriate disposal of mine processing waste (silty sands released onto the shoreline). To the best of our knowledge, this is the first study to establish a relationship between fluorite mining and Hg pollution.

Beach sand, fluvial sediments and the surrounding soils of Vega beach revealed a similar pollutant fingerprint. Analyses of fluvial sediment samples taken from the Vega river, which flows into the beach after crossing the mining areas and the mineral treatment plant, showed a slight increase in Hg content when approaching the beach. The highest Hg concentrations were found in mined soils, although these are attributable to proximity to ore veins. More significantly, notable Hg concentrations were found on the beach, especially in white dunes but also in the other geomorphological units studied. Hg was found to be enriched in the finer grain-size fractions (below 125 microns) of beach sediments and, overall, the main input of this metal was attributed to the mining waste that was discharged directly onto the coast for decades (and in recent years by means of a marine outfall). Hg bioavailability and methylation were negligible, thus reducing potential risks to the environment and human health. Nevertheless, on the basis of our findings, we recommend that a specific risk assessment and study of the submerged sediments be undertaken in the Vega beach area.

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