



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



Efrén García-Ordiales ^{a,*}, Stefano Covelli ^{b,c}, Jose Manuel Rico ^d, Nieves Roqueñí ^a, Giorgio Fontolan ^{b,c}, German Flor-Blanco ^e, Pablo Cienfuegos ^a, Jorge Loredo ^a

^a ISYMA Research Group, Mining, Energy and Materials Engineering School, University of Oviedo, Oviedo, Spain

^b Department of Mathematics and Geosciences, University of Trieste, Trieste, Italy

^c Co.N.I.S.Ma. Consorzio Nazionale Interuniversitario per le Scienze del Mare, Piazzale Flaminio 9, 00196, Rome, Italy

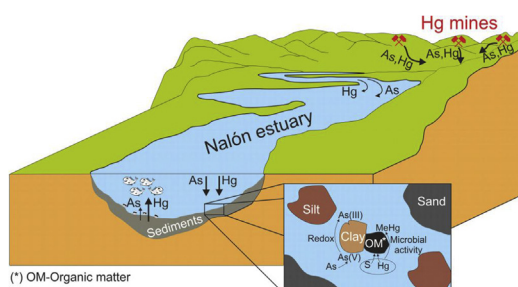
^d Department of Organisms and Systems Biology, University of Oviedo, Oviedo, Spain

^e GeoQUO Research Group, Department of Geology, University of Oviedo, Oviedo, Spain

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.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 November 2017

Received in revised form

18 January 2018

Accepted 27 January 2018

Keywords:

Mercury
Arsenic
Sediments
Estuary
Speciation
Mining

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 $0.20 \mu g g^{-1}$ to $1.33 \mu g g^{-1}$, most of it in the form of sulphides. Concentrations of methylmercury ($303.20\text{--}865.40 \mu g g^{-1}$) 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.

© 2018 Published by Elsevier Ltd.

1. Introduction

Among aquatic environments, coastal areas are particularly fragile and are very often threatened by significant direct and

* Corresponding author.

E-mail address: garciaefren@uniovi.es (E. Garcia-Ordiales).

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 Ael 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; Ordóñez 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 (García-Ordiales et al., 2015, 2016a, b, 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 ($0.15\text{--}1.56\ \mu\text{g g}^{-1}$) and As ($20.00\text{--}39.20\ \mu\text{g g}^{-1}$) 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 ($4.5\ \text{km}^2$) and extends $4777\ \text{km}^2$ 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 [As₄S₄], orpiment [As₂S₃], and arsenic-rich pyrite (Ordóñez 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; Ordóñez 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 (García-Ordiales et al., 2015, 2016a, b, 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) H₂O₂ 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–HNO₃–HF) and analysed by inductively coupled emission spectroscopy (ICP-ES) and inductively coupled plasma mass

Download English Version:

<https://daneshyari.com/en/article/8851969>

Download Persian Version:

<https://daneshyari.com/article/8851969>

[Daneshyari.com](https://daneshyari.com)