Assessment of the zinc diffusion rate in estuarine zones

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ARTICLE INFO

ABSTRACT

Industrial pressures suffered by estuarine zones leave a pollution record in their sediment. Thus, high concentrations of many heavy metals and some organic compounds are often found in estuarine sediment. This work aims to contribute to the enhancement of water quality management strategies in these zones by studying in detail the diffusive processes that take place between the water and sediment using a two-pronged approach: experimental practice and numerical simulation. To provide an example of the practical application of the methodologies proposed in this paper, the Suances Estuary (northern Spain) was selected as the study zone. This estuary exhibits significant historical pollution and its sediment acts as a continuous internal source of zinc, mainly due to diffusive processes derived from the concentration gradient between the interstitial water at the solid particles of the sediment and the bottom of the water column. The experimentally obtained results, based on 6 case studies, demonstrated the buffering capacity of the system and allowed the determination of the required time for the mass transfer processes to reach an equilibrium state. Furthermore, the diffusion rate of zinc was approximately modeled taking into consideration the high concentration variability observed in sediment along the entire estuary. The convergence between the modeled and the experimental results indicated the required contact time to reach an equilibrium state in a real field situation.

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1. Introduction

Industrial and transport activities in estuarine zones are crucial for local economic development, but the establishment of an efficient management system becomes essential to balance socio-economic requirements with the environmental sustainability of these zones (Adger et al., 2005; Barbier et al., 2011; Jackson, 2001; Lotze et al., 2006; Monte et al., 2006; Yassuda et al., 2000). These management strategies must take into consideration the heavy metal mobilization (Du Laing et al., 2009; Zoumis et al., 2001). Some efforts have been made about the evaluation of the mobilization capacity focusing on management aspects (Fernández-Ortiz de Vallejuelo et al., 2014) with the objective to determine specific management parameters through indexes utilization (Palma et al., 2015) or the heavy metal behavior modeling regarding its distributions in water and sediments (Periáñez, 2009), for example. In this context, a numerical model could facilitate such management tasks, but as could be expected, every numerical model must be given the appropriate information if adequate results are desired. A critical aspect of the numerical modeling of heavy metal fate and transport is the required input information to quantify this mobilization. In this context, the diffusion rate of the system has a significant influence on the obtained outputs. To deepen the knowledge regarding how the diffusive processes of pollutants are carried out at the sediment–water interface

of an estuary, specific batch experiments could be applied. The experimental results can then be used as input values, which will improve the performance of the numerical model. Very often, transport models neglect the effects of suspended matter (James, 2002); however, processes such as sedimentation and erosion can significantly alter the predictions of contaminant substances evolution (Ji, 2008). Sediment plays an important role in regulating dissolved concentrations in natural waters. Heavy metals are often present largely in non-bioavailable forms and are adsorbed onto sediment particles. Then, the selection of the numerical model is also crucial and must guarantee the capacity to simulate not only the pollutants transport, but also the effects of suspended matter. In addition, environmental conditions (such as pH and salinity) must be taken into consideration, as they significantly affect the solubility of metal (Irwin et al., 1997). In general, the solubility of different metals are lower near a neutral pH than in acidic or highly alkaline waters. However, the influence of salinity is mainly reflected in variations of the density, chemical reactivity, the partition coefficient and flocculation processes within the system (Ji, 2008). Thus, varying salinities are expected to affect metal mobility (Du Laing et al., 2008). Furthermore, the results of both laboratory (Paalman et al., 1994) and field experiments (Hatje et al., 2003) have demonstrated an increasing metal mobilization with increasing salinities.

Moreover, sediment is an essential, integral and dynamic part of the aquatic environment. They can reflect both human-induced processes and natural phenomena. Therefore, the assessment of their current status is a vital first step for planning the sustainable management of these areas, especially if we consider that sediment can act not only as a sink

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for a wide variety of environmental chemicals but also as a potential long-term secondary source of pollutants (Irabien et al., 2008).

The physical mechanisms of mass transfer at the sediment–water interface are of paramount importance because they control the fluxes of dissolved organic molecules, inorganic ions and gases between the surface of the sediment and the overlying water (Steinberger and Hondzo, 1999). Near this interface, interdependent physical, chemical and biological processes form vertical geochemical gradients that can induce a benthic flux out of the sediment or can be consumed by it (Boudreau and Jorgensen, 2001). In this context, the diffusion process (movement of material from an area of high to an area of low concentration due to concentration gradients), which takes place at the microscopic level, must be highlighted and is driven by the scattering of particles through random molecular motions (Ji, 2008). In the sediment bed, metal ions in pore waters of the sediment can diffuse to the overlying water column and vice versa, depending on the concentration gradient, the porosity and the molecular weight of the pollutant (Chapra, 1997; Carrer et al., 2005). Furthermore, the dissolved fraction of the pollutant in the sediment has a significant impact on the diffusion process because it determines the available concentration in the interstitial water between solid particles of sediment (Sámano, 2011). This process across the sediment–water interface is likely to cause an increasing concentration of the contaminant in the overlying water column even after sources of externally supplied contaminants have been removed or heavily reduced (Jing-Yu et al., 2013).

To carry out this study, the Suances Estuary (northern Spain) was selected for the application of the proposed methodologies because, historically, it has suffered an increasing mixture of industrial pressures, which have been leaving a pollution record in its sediment for decades. As a consequence, high concentrations of many heavy metals and some organic compounds are found in the surface sediment of this estuary (Coz et al., 2007). The zinc concentration in this zone must be highlighted because it far exceeds the recorded concentration of other heavy metals in this estuary (Irabien et al., 2008). Zinc is an important element in many economic sectors, such as metallurgical operation units, the electroplating industry, mining industry and mine drainage operations. Additionally, it is widely distributed in nature as one of the most abundant elements in the Earth's crust (Irwin et al., 1997). Either natural or anthropogenic, most of the zinc in water bodies settles to the bottom. However, a small amount may remain either dissolved in water or as fine suspended particles. According to Table 1, the Suances Estuary could be considered a heavily polluted area, as it exhibits a mean sediment concentration of zinc of approximately 13,500 mg·kg^{-1} (Sámano et al., 2014). Therefore, this severely polluted sediment acts as an internal source or provider of zinc to the water column due to diffusive processes derived from the concentration gradient between the interstitial water between the solid particles of sediment and the base of the water column.

In this context, the general objective of this paper is to assess, both experimentally and numerically, the amount of zinc annually transferred to the water column from each square meter of sediment (diffusion rate) in a heavily polluted estuarine zone. The experimental data will provide useful information for the validation of the numerical tool. The validated numerical tool could then be used to support water quality and decision making regarding the management of estuarine zones because it will be capable of realistically representing the

transport processes that occur in these zones. It must be highlighted that both methodological approaches could be used for an assessment of the diffusion rate of any substance at any polluted estuary if the required information, samples and materials are available.

2. Study zone

The Suances Estuary is a shallow mesotidal estuary located in the north of Spain (Bárcena et al., 2012; Sámano et al., 2014). As previously mentioned, this estuary has experienced an increasing mixture of pressures due to mineral extraction and industrial activities. Currently, the industrial activity is carried out mainly in the innermost area (Fig. 1). Some industries are currently permitted to discharge wastewater that may contain zinc, among other heavy metals. However, it must be highlighted that the discharge limits are clearly established by the competent authority through the corresponding authorizations.

Information on the environmental quality of this zone from 2007 to the present was obtained from the Quality Monitoring Program established along the entire Cantabrian coast by the Environmental Regional Administration. This program comprises 20 sampling stations distributed in the study area for which physicochemical parameters are regularly determined. Occasionally this program includes additional sampling stations to carry out specific field surveys, such as P1 and P2, which were established for the preliminary detection of priority substances (regarding the Water Framework Directive list, 2000) in this zone (Fig. 1).

As expected, a clear variation in salinity is observed among the sampling stations that were established along the transitional waters of this estuary. Consequently, the innermost sampling stations (A-SB04, A-SB09 and A-SB10) exhibit salinity values below 1 psu (1969 μS/cm at 25 °C), whereas at the outermost stations (AB-SB01S and AM-SB01), these values are greater than 25 psu (39,270 μS/cm at 25 °C). However, the sampling stations established in coastal waters (AB-AC05 and AB-AC22) show typical values of approximately 35 psu (53,075 μS/cm at 25 °C).

No significant gradients are observed for the pH values. The sampling stations established in transitional waters exhibit a neutral pH, which means the value oscillates between 7.43 and 7.99. Only sampling station A-SB09 shows a slightly lower pH value (6.49) as a consequence of one of the most significant discharges in the area, which has a pH of approximately 3.8. In any event, the recorded values along the estuary are in agreement with the authorized pH interval (6.5–9.2) according to the corresponding discharge authorizations.

Zinc concentrations of 0.184 mg·l^{-1} and 0.05 mg·l^{-1} were obtained for the water column at sampling points P1 and P2, respectively, from a specific field survey carried out in June 2008 (Fig. 1). In the sediment, the concentration of zinc varied from 4600 mg·kg^{-1} (in the outermost zone) to almost 16,000 mg·kg^{-1} (in the innermost zone with high industrial pressure). For the entire estuary, a mean concentration of approximately 13,500 mg·kg^{-1} was determined.

3. Materials and methods

With the aim of enhancing the analysis of the diffusive processes that occur at a historically polluted estuary, this paper presents a two-pronged approach for the assessment of the zinc diffusion rate: experimental practice and numerical simulation. For both approaches, the fact that a single metal can have many different chemical forms must be considered. Owing to the tremendous number of interactions of a metal in water, the metal concentration should include all of these forms. Therefore, the total concentration of a metal, rather than one or a few particular chemical forms of the metal, should be considered in the sampling and modeling of heavy metals (Ji, 2008). The developed methodologies are presented next.

Table 1
Zinc background concentrations in surface water and sediment for non-polluted, typical and heavily polluted areas (Irwin et al., 1997).

	Zn background concentrations in surface waters	Zn background concentrations in sediment
Non-polluted areas	0.0001 mg·l^{-1} – 0.020 mg·l^{-1}	<10 mg·kg^{-1}
Typical areas	0.020 mg·l^{-1} – 0.050 mg·l^{-1}	<120 mg·kg^{-1}
Heavily polluted areas	0.100 mg·l^{-1} – 0.050 mg·l^{-1}	≥120 mg·kg^{-1}