Journal of Marine Systems 126 (2013) 82–93

Contents lists available at ScienceDirect

Journal of Marine Systems

journal homepage: www.elsevier.com/locate/jmarsys

The geochemical behavior of natural radionuclides in coastal waters: A modeling study for the Huelva estuary

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ARTICLE INFO

Article history:
Received 6 September 2011
Received in revised form 21 May 2012
Accepted 2 August 2012
Available online 14 August 2012

Keywords:
Numerical modeling
Dispersion
Natural radionuclides
Odiel–Tinto estuary
Acid mine drainage
Phosphogypsum

ABSTRACT

A numerical model to study the behavior and distribution of natural radionuclides in sediments of an estuary (Odiel and Tinto rivers, SW Spain) affected by acid mine drainage and industrial activities has been developed. The model solves water circulation due to tides and river stream flows. The dispersion model includes uptake/release reactions of radionuclides between the dissolved phase and bed sediments in a dynamic way, using kinetic transfer coefficients. Seasonal pH and chlorinity distributions are simulated, and a formulation has been developed to consider these seasonal variations on kinetic coefficients. Calculated concentrations of ^{226}Ra and ^{238}U in sediments have been compared with measurements from four seasonal sampling campaigns. Numerical experiments have been carried out to study the relative significance of the different radionuclides sources into the estuary as well as the effect of the two components of water circulation (tides are river flows) on radionuclide dispersion patterns.

1. Introduction

Acid mine drainage (AMD) is caused by the weathering of sulfide rich mining materials, and may persist for centuries after closing the mine. AMD is polluted water which normally contains high levels of sulfates, metals and metalloids and is characterized by a low pH (de la Torre et al., 2011).

The Odiel–Tinto rivers, in the southern Iberian Peninsula, are affected by AMD since they drain the Iberian Pyrite Belt (Sainz and Ruiz, 2006), one of the most important mining areas in the south of Europe. Mineral resources have been extracted in the last 5000 years during two main periods: the Roman age and the last two centuries. During the last period, intensive exploitation has led to a relevant environmental impact caused by AMD. Both rivers form a fully mixed tidal estuary which surrounds the town of Huelva. Rivers join at the south of this town and then flow together to the Atlantic Ocean (see Fig. 1).

Additionally, a fertilizer processing complex is located near Huelva town, by the Odiel River estuary. These factories generate a by-product called phosphogypsum, which contains enhanced levels of natural radionuclides and heavy metals (Rajkovic et al., 1999; Van der Heijde et al., 1988). Phosphogypsum has been stored in open air piles located in the salt marsh of the Tinto River until the end of 2010. These piles cover 1600 ha, of which 600 ha have been restored. There is a total amount of 80 Mt of stored phosphogypsum. Water leached from the phosphogypsum piles into the Tinto River contains significant levels of the pollutants mentioned above (Bolívar et al., 2009); in particular, some 50–100 Bq/l of ^{238}U and some 1–5 Bq/l of ^{226}Ra.

Several works have been published in the recent past concerning the contamination of the Odiel-Tinto estuary by metals (de la Torre et al., 2011; Martín et al., 2002; Respaldiza et al., 1993) and radionuclides (Absi et al., 2004; Bolívar et al., 2000, 2002; Martínez-Aguirre et al., 1996). Indeed, the Odiel–Tinto estuary constitutes one the most metal and radionuclide polluted estuaries in the world (Ruiz, 2001).

Even more recently (Hierro, 2009; Hierro et al., 2012), the presence of natural radionuclides in sediments of the Odiel and Tinto rivers and estuary has been investigated in detail. Four sampling campaigns (one per season) have been carried out to study the behavior of different natural radionuclides under the variable pH and salinity conditions which occur in the estuary. Interpretation of results is not an easy task due to the many factors in play; the mains are tidal mixing, pH and salinity gradients and uptake/release reactions of radionuclides between water and sediments. The solid phase may act as a sink or as a source of radionuclides to the water column, depending on the concentration of radionuclides in each phase and on the rates governing the adsorption and release reactions, which also depend on environmental conditions (pH, temperature, and salinity).

Thus, the objective of this work consists of developing a numerical model of the estuary, including all processes mentioned above. It solves the hydrodynamics of the estuary and the dispersion of natural radionuclides, including the interactions between the dissolved and solid (bottom sediments) phases. An earlier and simplified modelling

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http://dx.doi.org/10.1016/j.jmarsys.2012.08.001

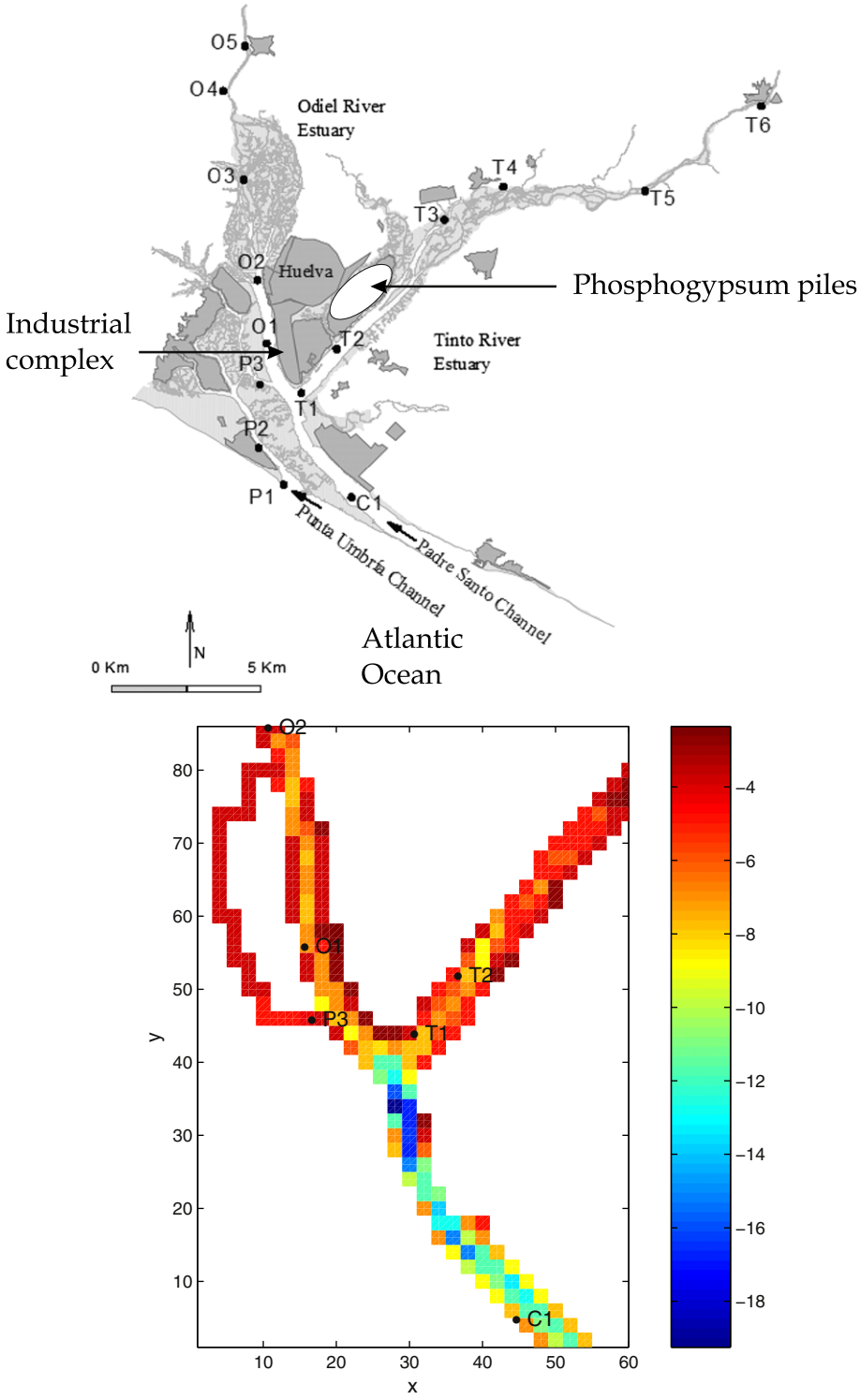

Fig. 1. Map of the estuary (up) and model domain (down) with location of sampling points. The colorbar gives water depths in m. Each number in the *x* and *y* axis gives the grid cell number (thus each unit corresponds to 125 m).

study of the estuary has already been carried out by the authors (Periáñez et al., 2005). This model was developed and applied to the study of the redissolution of ^{226}Ra from previously contaminated estuarine sediments.

Essentially, the model solves the water circulation in the estuary, caused by tidal motions and river stream flows. This circulation is used to calculate seasonal pH and chlorinity distributions. Uptake/release reactions for radionuclides between water and sediments are described in a dynamic way, using kinetic transfer coefficients. In particular, a two-step model consisting of two consecutive reversible reactions has been applied. A new formulation has been developed to consider how pH and chlorinity variations affect kinetic rates. Calculated currents, pH and chlorinity distributions are then used to simulate the dispersion of radionuclides. The model has been applied to ^{226}Ra and ^{238}U. Calculated radionuclide concentrations in sediments have been compared with measurements for the four seasonal sampling