Advances in Engineering Software 41 (2010) 84–91

Contents lists available at ScienceDirect

Advances in Engineering Software

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

Transport of lead in the Mersey Estuary: The development of a novel approach to deriving partition coefficients

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ARTICLE INFO

Article history:
Received 26 August 2008
Accepted 27 November 2008
Available online 1 January 2009

Keywords:
Partition coefficient
Heavy metal modelling
Lead modelling
Sediment modelling
Mersey Estuary

ABSTRACT

Modelling heavy metals in estuarine environments is extremely complex for various reasons; one of the primary complicating factors is that metals exist in two phases, dissolved and particulate bound. Dynamic changes in water chemistry, and in particular salinity, affect the partitioning of metals between the two phases and hence make it difficult to determine the fractions of each phase. A relatively simple approach was developed to relate variations in partition coefficient for Pb to salinity fluctuations in the Mersey Estuary. The functional relationship developed between partition coefficient and salinity departs from the traditional exponential type curve, providing a more realistic relationship.

A numerical model was then developed for predicting the transport and distribution of Pb about the Mersey Estuary. The model couples transport of metals throughout the water along with incorporating the chemical processes controlling how lead is fractioned between dissolved and particulate phases through the newly developed partition coefficient relationship. Model predictions of dissolved Pb along the longitudinal axis of the estuary were compared with measurements of Pb for two events; very good correlation was obtained between the model results and the data. The approach is compared with approaches adopted by other researchers. Also results are presented for the determination of partition coefficients for a second metal, Ni, using the Author's approach. These results are used to support the approach developed by the Authors.

1. Introduction

Heavy metals such as lead, zinc, cadmium and nickel are toxic to many fish species when present in water in quite low concentrations and also very dangerous in drinking water sources. The EC Dangerous Substances Directive [1] is implemented to control the release of dangerous substances into water. In this directive Pb has been assigned an environmental quality standard (EQS) of 25 μg/l for coastal and estuarine waters. In implementing EU Directives such as the Dangerous Substances Directive [1], the Shellfish Directive [2] and the Habitats Directive [3] numerical models are used to make predictions of various water quality parameters, including heavy metals. The development of a numerical model to accurately predict the transport of heavy metals in water is a complex task including dynamically coupling between hydrodynamics, sediments and the metals. The task becomes more complex when modelling the distribution of heavy metals in large estuaries due to salinity fluctuations.

One of the legacies bequeathed by the Industrial Revolution to the Mersey Estuary is a that a large build up of industrial discharges has left considerable deposits of heavy metals bound to the fine sediments of the estuary. As a result of poor waste management, the estuary earned itself the ignominious title of the most polluted estuary in Europe. During the period 1850–1950, increased industrial output resulted in many industries requiring large volumes of water for cooling and processes such as bleaching, tanning and metalworking. It is likely that during the 1960's the water quality status of the Mersey Estuary was at its lowest being severely contaminated by toxic organic and inorganic compounds from the local industries. At the beginning of the 1970's pollution effects from heavy metals caused serious concerns. UK Government laboratories reported that fish caught in Liverpool Bay contained elevated levels of many heavy metals. These raised levels were attributed to the contaminated waters of the Mersey Estuary due to the wanton discharging of industrial wastes, Jones [4].

Because of the serious nature of metal contamination of the Mersey Estuary, many other studies have been undertaken to define and better understand the nature of the problem and, in particular, lead (Pb) reactivity in the Mersey Estuary. Others have studied the fate of different metals in the Mersey Estuary; Campbell et al. [5] present and discuss the distribution and behaviour of both dissolved and particulate bound nickel (Ni) in the Mersey Estuary. One of the main conclusions from their work is that the

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doi:10.1016/j.advengsoft.2008.11.007

distribution of Ni throughout the Mersey Estuary is complex and clearly deviates from simple end-member mixing behaviour.

Turner et al. [6] undertook a detailed study of seven trace metals distributed throughout the Mersey Estuary including Pb. In their paper they describe the estuary as a highly contaminated, organic-rich estuary and they observed an increase in the sediment-water partition coefficient, K_D, with increasing salinity for all metals considered except Cd. These observations were inconsistent with inorganic speciation calculations and empirical modelling studies in other estuaries, predicting an inverse relationship between K_D and salinity. The primary focus of their paper was to investigate the factors controlling the salinity distributions of metal data based on defining the chemical processes that control the K_D salinity relationship. They developed an empirical model based on salting out of neutral organic chemicals which reflected the salinity distribution of the data. This is a different approach to the one adopted in this paper; however, the model developed by Turner et al. has promise for incorporation into numerical model simulations also.

Ng et al. [7] carried out a detailed contaminant modelling study of the Humber Estuary. They outline the difficulties of making accurate predictions of heavy metals in the Humber due to many controlling variables including: salinity, pH and availability of complexing species. Within the model, the partition coefficient was allowed vary as a function of salinity in either of two ways: using a relationship developed by Millward and Turner [8] or using explicit tabulations of measured values of K_D as a function of salinity. Millward and Turner's relationship is discussed in more detail in a later section of this paper. The paper by Ng et al. illustrates how a geochemical module based on empirically-derived partition coefficients, coupled to a two-dimensional hydrodynamic model, was developed to form the basis of a geochemical contaminant transport model. This basic approach of Ng et al. is the one followed in the research undertaken by the author; however, the authors have extended the above approach with regards to the formulation of the partition coefficient for Pb.

Martino et al. [9] reported upon high resolution, seasonal distributions of six dissolved trace metals in the Mersey Estuary. The purpose of this study was to obtain a more detailed comprehension of the mechanisms controlling metal reactivity in the estuary. An empirical sorption was used and reproduced, with reasonable success, axial distributions of the metals that exhibited the largest peaks, namely Co and Pb. One of the drawbacks of this research is that the partition coefficients used were single-valued, unrelated to salinity.

Comber et al. [10] undertook research into the partitioning of trace metals between the dissolved phase and suspended solids on both the Humber Estuary and the Mersey Estuary. One of the aims of this research was to develop partition coefficients for a number of metals. A single-valued partition coefficient for Ni in the Mersey Estuary was estimated at c.1×10^4 and the corresponding value in the Humber Estuary was estimated c.5×10^3. The reason for the higher value of K_D in the Mersey was attributed to higher loadings of sewage into the Mersey along with differences in suspended particulate composition. The partition coefficient for Pb in the Mersey was shown to vary between 1×10^5 and 3×10^5, generally increasing with increasing salinity. This shows an opposite trend to that postulated by Millward and Turner. One interesting feature of the work of Comber et al. is that at very low salinity the partition coefficient shows a high spike that is at variance with other low salinity data.

In this paper the authors describe a model that was developed to predict distributions of Pb throughout the Mersey Estuary. An extensive water quality monitoring programme was developed for the Mersey Estuary from the mid 1970's. Water samples are collected from up to 23 mid-stream locations and analysed for various constituents including sanitary parameters and trace contaminants. This programme has continued to date providing an extensive data set for use in many aspects of water quality management and planning of the Mersey Estuary. It is noted that this monitoring programme is relatively expensive, in particular the determinations of trace metals requires more sophisticated instrumentation and skilled personnel than is required for the determination of sanitary parameters. Because of the high costs of trace contaminant analyses the development of accurate numerical models to aid in the development of monitoring programmes and in predicting distributions of trace metals is desirable.

The development of the Mersey Estuary transport model for Pb is detailed below; particular emphasis is placed on how the model computes the partition coefficient for the metal. Advantage is taken of the extensive database developed by the Environment Agency in model development and model calibration and validation.

2. Methodology and results

2.1. Overview of approach adopted

When metals are introduced into water containing suspended particulate matter, SPM, a portion of the metal is dissolved in the water and the remainder is absorbed onto surface of the SPM. The distribution of the metal fractions between these two phases is described by a partition coefficient, K_D, defined as:

$$K_D = \frac{P}{C} \tag{1}$$

where P is the concentration of metal absorbed on suspended sediments (μg/g) and C is the concentration of metal dissolved in the water column (μg/l).

The coefficient K_D is a function of spatially varied water chemistry and is notoriously difficult to quantify in marine waters. It is well-documented and generally accepted that there is a strong functional relationship between K_D and salinity. In many studies only the influence of salinity are considered and other direct water chemistry effects are ignored; this approach is adopted in this research also. In order to model, hindcast and predict heavy metals, with a reasonable degree of accuracy, the following staged approach was adopted.

A hydrodynamic model of the Mersey Estuary was developed, calibrated and validated. This model allowed current speeds and directions be predicted; these parameters were necessary for subsequent modelling of transport processes. A solute transport model was developed, calibrated and validated and used to predict salinity distributions throughout the estuary at various stages of the tide using the results from the hydrodynamic model. From field data an expression was developed relating partition coefficient to salinity; this is a novel component of this research. Combining the model salinity predictions and the K_D *–salinity* relationship, the model has the capability of computing spatially varied and temporally varied partition coefficients as the model calculations progress forward in time. A sediment transport model of the Mersey Estuary was then developed, calibrated and validated and used to predict estimates of cohesive sediments. Finally, having predicted cohesive sediment concentrations and values of K_D at each grid point of the model for each computational timestep, the model computes the fraction of the heavy metal which is dissolved and that fraction which is absorbed onto the cohesive sediments.

2.2. Hydrodynamic model of Mersey Estuary

The Mersey Estuary is one of the largest estuaries in the UK, having a catchment of some 5000 km^2 that includes the major