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Mass balance modelling of contaminants in river basins: Application of the flexible matrix approach

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Abstract

It is useful to have available a variety of catchment-scale water quality models that range in complexity, spatial resolution and data requirements. In a previous paper [Warren, C., Mackay, D., Whelan, M., Fox, K., 2005. Mass balance modelling of contaminants in river basins: a flexible matrix approach. Chemosphere 61, 1458–1467] a series of simple to intermediately complex mass balance models was presented which can be used for tiered exposure assessments in river basins. The connectivity of the segments is expressed using a matrix that permits flexibility in application, enabling the model to be re-segmented and applied to different catchments as required. In this paper, the intermediate models, QWASI matrix-rate constant (QMX-R) and QWASI matrix-fugacity (QMX-F) are used to estimate concentrations of linear alkylbenzene sulfonates (LAS) in the rivers Aire and Calder, UK, and of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in the Fraser River basin, Canada. The results compare satisfactorily with monitoring data, suggesting that these QWASI-based models for exposure and risk assessment may be applicable under data-limited conditions. The use of QWASI-based models for regulatory purposes in an evaluative river system is also discussed with reference to assessments of *para*-dichlorobenzene (*p*DCB), trichloroethylene (TCE), bis(2-ethylhexyl) phthalate (DEHP) and toluene. It is shown that multi-media QWASI model predictions can be usefully depicted graphically on chemical space diagrams and used to highlight regions in which advection, partitioning to sediments and volatilization may be important determinants of chemical fate in river systems.

Keywords: Mass balance model; River basin; Screening level; Evaluative

1. Introduction

A knowledge of contaminant fate and effects is important for managing ecosystem health, especially in heavily populated, industrial and/or agricultural regions where anthropogenic sources can be large and numerous. In principle, monitoring programs provide the most reliable means of quantifying contaminant concentrations. However, because of cost constraints for sampling and analysis, combined with temporal and spatial variability in large systems such as river networks, monitoring data may not always provide a reliable picture of exposure (e.g., Hazelton, 1998; Whelan et al., 1999; Facchi et al., 2007). This may be particularly relevant in less affluent regions of the world or large countries such as Canada, where resources are limited.

As an alternative to relying only on monitoring data, mass balance models have been successfully applied to predict contaminant fate in aquatic systems and thus provide complementary information on environmental exposure and the risk of adverse effects. Provided that they have been properly evaluated, models can be used to estimate concentrations across a wide range of spatial and temporal scales and can also be used to explore "what if?" scenarios, such as the potential impacts resulting from the release of new chemicals or from changes in quantity used. Although

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data on chemical properties, chemical emission rates and the hydrology of receiving waters are usually required (Fox et al., 2000b; Gandolfi et al., 2000, 2001; Schulze and Matthies, 2001; Schroder et al., 2002), these chemical-specific and system-specific data may be easier to obtain or estimate (e.g., from permanent in-stream flow gauges and per capita chemical usage estimates) than representative monitoring data.

In recent years the Government of Canada has initiated a program to evaluate some 24 000 chemicals on its domestic substances list (DSL), of which approximately 3000 have been identified as potential priority organics. Consequently, relatively fast and simple tools are needed to screen the likely fate of these chemicals in rivers systems. Combined with limited data availability for most Canadian rivers, relatively simple models with moderate spatial resolution are valuable when seeking screening level assessments of various chemicals.

In a recent paper, Warren et al. (2005) presented a series of models of varying complexity for modelling chemical fate in river systems. These models can be used in a tiered assessment approach, depending on data availability and regulatory needs. As well as estimating chemical concentrations *per se*, such models can also be used to plan targeted monitoring programs and to help identify those chemicals for which more complex models may be required. Furthermore, these models can be used to rank chemicals under evaluative conditions, similarly to approaches using EQC (Mackay et al., 1996) or SimpleBox (van de Meent, 1993) but with the advantage of giving spatially explicit predictions which may be useful in targeting monitoring.

Given this context, the objectives of this paper are twofold. The first is to evaluate the performance of two moderate-spatial-resolution river water quality models (QMX-R and QMX-F; Warren et al., 2005) by comparing predictions with monitoring data for two very different chemicals and river systems, namely, linear alkylbenzene sulfonates (LAS) in the Aire-Calder basin, UK and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in the Fraser River catchment, Canada. The second is to explore how these models can be used at a screening level to simulate the fate of chemicals with a range of physical–chemical properties in an evaluative river system. Specifically, we assess the fate of two volatile organic chemicals, trichloroethylene (TCE) and toluene, a hydrophobic chemical, DEHP (bis-2-ethylhexylphthalate) and an intermediate hydrophobic and volatile chemical, *p*DCB (*para*-dichlorobenzene). The goal here is to highlight the applicability of these models as assessment tools for a range of chemicals and river basins under data-limited conditions.

2. Simple models of varying complexity: QWASI, QMX-R and QMX-F

The simplest model described by Warren et al. (2005), QWASI (quantitative water air sediment interaction – Mackay et al., 1983), assumes single well-mixed compartments of water and sediment, a total water flow rate, bulk chemical discharge and loss processes, including volatilization, water and suspended particle advection, degradation in water and sediment and sediment burial. QMX-R and QMX-F are both multi-segment models in which the river network is conceptualised as a series of linked QWASI segments representing river reaches with a given set of volumes, effluent loads, tributary loads and average river flow conditions. The simpler of the two, QMX-R (QWASI matrix-rate constant), uses a lumped chemical loss rate constant (calculated from QWASI results or measured experimentally) to calculate chemical concentrations in the water column. Sediment–water partitioning coefficients can be used to calculate concentrations in sediment by assuming equilibrium between the water and sediment compartments. Sediment–water fugacity ratios, calculated using QWASI, can be used to assess the state of equilibrium in a system and these ratios can be further applied as correction factors to the QMX-R sediment concentration calculations. In the second model, QMX-F (QWASI matrix-fugacity), individual river reaches are simulated as multi-media compartments, each with an explicit description of chemical exchanges between different media and are connected by water and suspended particle advection. Fig. 1 depicts these models and their data requirements.

Segmentation within the QMX models is influenced by three criteria: (i) large point-source emissions; (ii) tributary nodes resulting in large changes in water flow; and (iii) the location of chemical monitoring sites, if present. The primary goal is to capture spatial variability in chemical concentrations due to chemical emission and dilution and secondly to be able to evaluate predictions using monitoring data. Both models use a simple matrix to represent this segmentation. This allows for changes in river basin connectivity without altering model equations; hence, multiple river basin structures can be simulated relatively rapidly.

A major aim for these simple mass balance models is to reduce the amount of input data required to simulate chemical fate in a river system. While this approach provides obvious advantages, a consequence is that a number of assumptions have to be made, including: (i) steady-state conditions and (ii) loading only from point-sources (e.g., sewage treatment plant (STP) discharges and mill or factory effluents), tributaries (no runoff or groundwater sources) and atmospheric input resulting from a constant atmospheric concentration (no atmospheric degradation of chemical). Depending upon the users' needs and data availability, it is possible to build more complexity into these models (e.g., linkages to the terrestrial compartments of the watershed or episodic events).

3. Model evaluation

The QWASI-based models are first evaluated using two very different chemicals (an ionic involatile organic versus a highly hydrophobic involatile organic) in two very different river systems (a relatively small, slow flowing river versus a