Water Research 95 (2016) 330–339

Contents lists available at ScienceDirect

Water Research

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

Environmental relevance of laboratory-derived kinetic models to predict trace metal bioaccumulation in gammarids: Field experimentation at a large spatial scale (France)

N. Urien [a, b, *], J.D. Lebrun [a, b], L.C. Fechner [a, b, c], E. Uher [a], A. François [d], H. Quéau [d], M. Coquery [d], A. Chaumot [d], O. Geffard [d]

[a] Irstea, UR HBAN Hydrosystems and Bioprocesses, 1 rue Pierre-Gilles de Gennes, F-92761 Antony Cedex, France
[b] FIRE FR-3020, 4 place Jussieu, 75005 Paris, France
[c] AgroParisTech, 19 Avenue du Maine, F-75732 Paris Cedex 15, France
[d] Irstea, UR MAEP Freshwater Systems, Ecology and Pollution, F-69626 Villeurbanne Cedex, France

ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form
3 March 2016
Accepted 9 March 2016
Available online 14 March 2016

Keywords:
Metal uptake
Amphipods
Biomonitoring
Biokinetic model
Field validation
Water chemistry

ABSTRACT

Kinetic models have become established tools for describing trace metal bioaccumulation in aquatic organisms and offer a promising approach for linking water contamination to trace metal bioaccumulation in biota. Nevertheless, models are based on laboratory-derived kinetic parameters, and the question of their relevance to predict trace metal bioaccumulation in the field is poorly addressed. In the present study, we propose to assess the capacity of kinetic models to predict trace metal bioaccumulation in gammarids in the field at a wide spatial scale. The field validation consisted of measuring dissolved Cd, Cu, Ni and Pb concentrations in the water column at 141 sites in France, running the models with laboratory-derived kinetic parameters, and comparing model predictions and measurements of trace metal concentrations in gammarids caged for 7 days to the same sites. We observed that gammarids poorly accumulated Cu showing the limited relevance of that species to monitor Cu contamination. Therefore, Cu was not considered for model predictions. In contrast, gammarids significantly accumulated Pb, Cd, and Ni over a wide range of exposure concentrations. These results highlight the relevance of using gammarids for active biomonitoring to detect spatial trends of bioavailable Pb, Cd, and Ni contamination in freshwaters. The best agreements between model predictions and field measurements were observed for Cd with 71% of good estimations (i.e. field measurements were predicted within a factor of two), which highlighted the potential for kinetic models to link Cd contamination to bioaccumulation in the field. The poorest agreements were observed for Ni and Pb (39% and 48% of good estimations, respectively). However, models developed for Ni, Pb, and to a lesser extent for Cd, globally underestimated bioaccumulation in caged gammarids. These results showed that the link between trace metal concentration in water and in biota remains complex, and underlined the limits of these models, in their present form, to assess trace metal bioavailability in the field. We suggest that to improve model predictions, kinetic models need to be complemented, particularly by further assessing the influence of abiotic factors on trace metal uptake, and the relative contribution of the trophic route in the contamination of gammarids.

1. Introduction

In freshwaters, metal contamination is often determined by measuring dissolved trace metal concentrations in the water column (European directive 2013/39/EC). However, these measurements do not give information about the bioavailable metallic fraction, which can be defined as the fraction that is potentially toxic for biota (Rainbow, 1995). Alternatively, determination of bioaccumulated trace metal concentrations in aquatic organisms offers a promising approach to monitor metallic contamination as it provides time-integrated trace metal measurements over the

---

* Corresponding author. Irstea, UR HBAN Hydrosystems and Bioprocesses, 1 rue Pierre-Gilles de Gennes, CS 10030, F-92761 Antony Cedex, France.
E-mail address: nastassia.urien@gmail.com (N. Urien).

http://dx.doi.org/10.1016/j.watres.2016.03.023
0043-1354/

exposure period, and is considered as directly linked to the bioavailable metallic fraction (Baudrimont et al., 1999; Besse et al., 2013; Rainbow, 2007). The link between trace metal concentrations in the water column and in the exposed organisms is not straightforward because it depends on the organisms considered, the trace metal under study, and the physico-chemical water characteristics (Luoma and Rainbow, 2005). For example, calcium has often been pointed out as an inhibitor of Cd and Pb uptake in aquatic organisms. Indeed, Cd and Pb have been shown to be preferentially accumulated via calcium channels and, as a consequence, are in competition with calcium ions for binding to biological sites (Bourgeault et al., 2010; Grosell et al., 2006; Macdonald et al., 2002; Urien et al., 2015; Verbost et al., 1989).

To link trace metal contamination in water and in biota, kinetic models of trace metal bioaccumulation have been proposed for several trace metals. The biodynamic model is the most commonly used to describe bioaccumulation in aquatic organisms (Luoma and Rainbow, 2005). This model considers net trace metal bioaccumulation as the result of a balance between trace metal uptake (from both the dissolved and diet routes) and trace metal loss (due to excretion and/or growth). During waterborne exposures, trace metal uptake and loss rates depend on kinetic parameters, i.e., the uptake and elimination rate constants, which are usually determined in the laboratory through simple and controlled exposures. For essential trace metals, such as Cu, saturation may occur, because of the limited number of biological binding sites. Thus, several studies have reported that Cu bioaccumulation was better described by a saturation model than a biodynamic model, as observed for the amphipod, *Hyalella azteca*, or for the freshwater snail, *Lymnaea stagnalis* (Borgmann and Norwood, 1995a; Croteau and Luoma, 2007). Besides, recent studies quantified the effects of major ions found in freshwaters (i.e., calcium, sodium and magnesium) on trace metal uptake and consequently improved the bioaccumulation models when the competitive effects of cations were taken into account (Bourgeault et al., 2010; Urien et al., 2015).

More recently, attention has been focused on modeling waterborne trace metal bioaccumulation in the freshwater amphipods of gammarid species, which are abundantly present in temperate European freshwaters and are known to significantly accumulate trace metals (Lebrun et al., 2012, 2011; Pellet et al., 2009; Urien et al., 2015). In addition, gammarids have been shown to be promising candidates for biomonitoring freshwater trace metal contamination (e.g. in transplanted gammarids by Besse et al. (2013), or in resident gammarids by Fialkowski et al. (2003a,b), Lebrun et al., 2014 and Urien et al., 2015). However, although kinetic models of trace metal bioaccumulation have been successfully developed in various aquatic species including gammarids, the question of their environmental relevance to predict trace metal bioaccumulation in the field is rarely assessed. In a previous study, we field-tested a laboratory-derived kinetic model of Pb in *Gammarus pulex*, and showed that model predictions were in good agreement with field measurements in resident gammarids, and particularly when calcium concentrations were considered (Urien et al., 2015). More generally, in all the studies that tested kinetic models in the field (Luoma and Rainbow, 2005; Ponton and Hare, 2010; Roditi et al., 2000), the observed bioaccumulation used resident organisms. However, collecting resident organisms for bioaccumulation measurements may limit the number of sampling sites insofar as the acquisition of bioaccumulation data depends on the effective presence of resident individuals at the sites of interest. Yet, to strengthen the significance of model validation with field data, it is necessary to increase the number of observations and to work in contrasting environments in terms of water chemistry and contamination. An active approach, based on transplanted organisms, will *a contrario* allow water quality monitoring at sites devoid of resident organisms and offer more flexibility to choose sampling sites even at a wide spatial scale. In addition, because this approach limits the influence of confounding factors on trace metal bioaccumulation by controlling exposure time and the collection site for all the transplanted organisms, a robust inter-site comparison can be achieved (Besse et al., 2012).

The aim of the present study was to assess the environmental relevance of kinetic models of trace metal bioaccumulation, developed in the laboratory for Cd, Cu, Ni and Pb, to predict trace metal bioaccumulation in gammarids in the field, at a wide spatial scale (national scale, France). In the case of Cd and Pb, the half-saturation constant of calcium for biological binding sites, expressing the competitive effect of calcium on Cd and Pb uptake, was also included. To confront model predictions with field measurements, we selected 141 sites, homogeneously spread out in France, where size-calibrated male gammarids were transplanted in cages for 7 days, before analysis of Cu, Cd, Ni and Pb concentrations. To our knowledge, this study is the first to undertake model validation in the field with such numerous bioaccumulation data and at such a wide spatial scale.

2. Materials and methods

2.1. Field data

2.1.1. Collection of test organisms and transplantation procedure

Adult males of the species *Gammarus fossarum* (average body length of 9 ± 1 mm) were collected using a hand-held net at “La Tour du pin” (Bourbre River, France, Fig. 1), referred to site 0 in the present study. This site was chosen because data recorded by the RNB (Réseau National de Bassin, French Watershed Biomonitoring Network; contamination levels assessment in water and sediment, http://sierm.eaurmc.fr/eaux-superficielles/index.php) showed low metal levels. Gammarids were then similarly acclimated in the laboratory for 15 days to groundwater (containing very low trace metal concentrations: Cu < 0.3 μg L^{-1}, Cd < LoQ, Ni < 0.12 μg L^{-1} and Pb < LoQ) mixed with osmosis water at two different final hardness levels: 112 or 223 mg L^{-1} of $CaCO_3$, depending on the hardness level at the subsequent transplantation site. During acclimation, a 10/14 h light/dark photoperiod was maintained and the temperature was kept at 12 ± 1 °C; organisms were fed *ad libitum* with alder leaves (*Alnus glutinosa*) collected at a site with negligible anthropic pressure and previously conditioned by immersion in groundwater for 6 days (Besse et al., 2013; Geffard et al., 2014). Freeze-dried Tubifex® worms, were added twice a week as a dietary supplement.

The transplantation procedure, based on the methodology proposed by Besse et al. (2013) consisted of introducing 20 gammarids in openwork polypropylene cylinders (one cylinder per site, length, 10 cm; diameter, 5.5 cm) closed in their extremities by nylon nets (1-mm mesh). Each cylinder was stored in a rigid plastic case for protection and placed in the streambed for 7 days, parallel to the direction of the water flow and immobilized with natural rocks. During the transplantation period, each cylinder was supplied with 20 alder leaves (*Alnus glutinosa,* the same leaves as used in the laboratory and previously conditioned in groundwater) discs (20 mm in diameter), so as to limit mortality by cannibalism. After 7 days of transplantation, either one or three replicates of five gammarids were collected (depending on the need of other outcomes not presented in this study) and stored frozen at −80 °C. A 7d-transplantation period was chosen to be consistent with the exposure-period applied to calibrate the kinetic models of bioaccumulation in gammarids in the literature.