Environmental Pollution xxx (2016) 1–9

Contents lists available at ScienceDirect

Environmental Pollution

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

Bioaccumulation of organochlorine pesticides and polychlorinated biphenyls by loaches living in rice paddy fields of Northeast China ☆

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ARTICLE INFO

Article history:
Received 18 April 2016
Received in revised form
7 June 2016
Accepted 27 June 2016
Available online xxx

Keywords:
Bioaccumulation
Loach
Persistent organic pollutants
Rice field

ABSTRACT

The concentrations of 21 organochlorine pesticide (OCP) residues and 18 polychlorinated biphenyl (PCB) congeners were measured in two loach species (*Misgurnus mohoity* and *Paramisgurnus dabryanus*) and the soils of their inhabiting rice paddies from three typical rice production bases of Northeast China to explore the main factors influencing the bioaccumulation. The concentrations of $\sum_{18}$PCBs and $\sum_{21}$OCPs in loaches were determined to be in the ranges of 0.14–0.76 ng g^{-1} wet weight (ww) and 1.19–78.53 ng g^{-1} ww, respectively. Most of loaches showed the considerably high contamination levels of dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), which accounted for over 97% of the total OCPs. The much lower maximum allowable loach consumption rates (<15 g d^{-1}) indicated a high carcinogenic risk that results from the consumption of rice-field loaches. The field biota-soil accumulation factor (BSAF) was calculated as a main measure of bioaccumulation potential. The comparisons of BSAF values and the results of multivariate analysis indicated that habitat-specific environmental conditions, mainly the paddy soil contamination levels and average temperature, decisively affected the bioaccumulation of organochlorine contaminants. When the influence of lipid contents was offset, *M. mohoity* loaches were found to have a higher potential to accumulation PCBs and OCPs than *P. dabryanus* loaches, while the bioaccumulation potentials did not exhibit significant differences between juvenile and adult loaches and between male and female loaches. The octanol-water partition coefficient (K_{OW}) was the main chemical factor influencing bioaccumulation potentials. The BSAF values presented an increasing tendency with increasing log K_{OW} values from 6.0 to approximately 7.0, followed by a decreasing tendency with a continuous increase in log K_{OW} values. Moreover, loaches exhibited an isomeric-selective bioaccumulation for *p,p′*-chlorinated DDTs, α-HCH, β-HCH, δ-HCH and *cis*-chlordane.

1. Introduction

Rice (*Oryza sativa L.*) is a staple crop that is widely cultivated in East Asia. Its production requires a broad range of pesticides to combat pests, weeds and pathogens. Organochlorine pesticides (OCPs), which are a category of persistent organic pollutants (POPs), have been heavily used as pesticides and fungicides in rice paddy fields for several decades (Kim and Smith, 2001; Wang et al., 2005). A large quantity of OCPs still remains in paddy soils (Fu et al., 2003; Wang et al., 2007; Yu et al., 2013). The long-term irrigation of polluted river water also inevitably induces the paddy field contamination by other POPs, such as polychlorinated biphenyls (PCBs), often dominating the non-agricultural POPs in paddy soils (Zhang et al., 2010; Teng et al., 2013). Due to their high lipophilicity and resistance to biodegradation, OCPs and PCBs in paddy soil could accumulate in rice-field organisms in considerable amounts.

Loach is a widespread freshwater fish that inhabits rice paddy fields in East Asia. It has a bottom-dwelling habit, higher lipid content and the ability to migrate freely in a rice field pool. As an

☆ This paper has been recommended for acceptance by Chen Da.

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http://dx.doi.org/10.1016/j.envpol.2016.06.064
0269-7491/

edible fish with high nutritional value, the wild loaches in paddy fields are often caught and eaten by the rice farmers and local residents. Meanwhile, rice-loach farming technology has been widely adopted in China to produce sufficient numbers of loaches (approximately 200 kt per year) to meet commercial demand (Wang et al., 2008). Rice-field loaches have been found to have a high capacity to accumulate POPs from paddy fields (van der Oost et al., 2003; Teng et al., 2013). Therefore, a serious attention should be paid to the human health risks that result from the consumption of rice-field loaches.

The fish bioaccumulation behaviors of POPs and their influencing factors have been well documented (van der Oost et al., 2003; Arnot and Gobas, 2006; Gobas et al., 2009; Ael et al., 2013; Baptista et al., 2013), and some mechanistic or kinetic bioaccumulation models have been successfully developed to understand and predict how POPs accumulate in fish (Gobas, 1993; Mackay and Fraser, 2000; Nfon and Cousins, 2007; Barber, 2008; de Laender et al., 2010; Eichinger et al., 2010; Selck et al., 2011). Many environmental, ecological, biological and chemical factors have been demonstrated to influence POPs concentrations and bioaccumulation in fishes, and the relative importance of each factor often varies according to chemical properties and fish species. The bioaccumulation models can identify the relative importance of the different factors influencing POPs bioaccumulation. However, these models developed from laboratory studies might deviate substantially from what is measured in the field due to the conceptual flaw and inappropriate model parameterization (Selck et al., 2011). Most of studies on POPs bioaccumulation in fish were conducted in marine and lake ecosystems (van der Oost et al., 2003; Arnot and Gobas, 2006; Grung et al., 2015). The monitoring field data on POPs levels in rice-field loach are scarce, and the bioaccumulation behaviors of POPs in loach are also less mentioned.

Loach can accumulate POPs through two main routes. One is membrane absorption of freely dissolved POPs through the gill and skin; the other is intestinal wall absorption through the gastrointestinal tract as a result of predation and soil ingestion (van der Oost et al., 2003). Several studies have reported relatively high levels of OCPs, PCBs and polybrominated dipenyl ethers (PBDEs) in loaches collected from rice fields, polluted rivers and lakes (Qin et al., 2009; Zhang et al., 2009; Hu et al., 2010a, 2010b; Teng et al., 2013). In addition, Ma et al. (2013) reported the toxicokinetics of α-hexachlorocyclohexane (α-HCH) in loach. It was found that α-HCH was rapidly accumulated in loach and the uptake was enantioselective for (+)-α-HCH. The elimination process of α-HCH fitted the first-order kinetics with a half-life of approximately 5 d.

In rice fields, environmental and ecological conditions (mainly temperature, soil composition and feeding ecology) and biological factors (e.g., species, age, body size, sex, metabolism) may vary both spatially and temporally. These factors may directly or indirectly influence the net bioaccumulation of POPs in rice-field loaches. In this work, loaches and the soils of their inhabiting rice paddies were simultaneously sampled; and the sampled loaches were distinguished according to the different species, age and sex. The field biota-soil accumulation factors (BSAF) of OCPs and PCBs were derived as measures of bioaccumulation. The primary objective of this study was to identify the relative importance of different environmental, biological and chemical factors influencing the bioaccumulation of POPs in loaches living in rice fields. Examining a large number of OCPs and PCBs also allowed us to explore the effects of chemical properties on the bioaccumulation of POPs and to evaluate the human health risk associated with loach consumption.

2. Materials and methods

2.1. Study area and sample collection

Loach and paddy soil samples were collected from three typical rice production areas of Northeast China, located in the lower reach of the Daliao River Basin (LDRB), the middle reach of the Shonghua River Basin (MSRB) and the middle reach of the Wusuli River Basin (MWRB), respectively (Fig. 1). The detailed information on sampling sites is shown in Fig. S1 (see Supplementary Material). The sampling areas have monsoon climates of medium latitudes, with the average annual temperatures of 8–11 °C in the LDRB area, 5–7 °C in the MSRB area and 3–6 °C in the MWRB area, respectively. The sampled rice fields were all irrigated by river water, and most of them had a history of rice cultivation that exceeded 40 years. In the 1970s and 1980s, organochlorine pesticides, mainly dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), hexachlorobenzene (HCB) and chlorodane, were widely used in these three rice production bases.

Sample collection was carried out at 41 sampling sites during September 2013. Each paddy was comprised of top soil (0–15 cm) from a central point of a paddy field pool and top soils from four additional points located 5–15 m in the four primary directions from the central point. The composite loach samples were collected with the help of local farmers using fishing net. The collected samples were placed in cleaned aluminum/polyethylene bags with zippers, and subsequently transported to the laboratory on ice.

2.2. Chemicals and reagents

Five kinds of ^{13}C-labeled stock solutions were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA) and Wellington Laboratories Inc. (Ontario, Canada) for the quantification of OCPs and PCBs; detailed information on the ^{13}C-labeled stock solutions can be found in Table S1. Hexane (Honey Well, USA) and dichloromethane (Honey Well, USA) used for sample pretreatment were of all pesticide analysis grade. Florisil (LGC, UK; 60–100 mesh) was extracted with dichloromethane, and then activated in an oven at 250 °C for 12 h. Reagent grade anhydrous sodium sulfate was obtained from Aldrich.

2.3. Sample preparation

In the laboratory, the paddy soil samples were air-dried, freeze-dried, ground to pass through a 60-mesh stainless steel sieve, and then homogenized. Loaches of different species, age and sex were distinguished according to their morphological characteristics. Two loach species, *Misgurnus mohoity* (*M. mohoity*) and *Paramisgurnus dabryanus* (*P. dabryanus*), were identified. The loaches of the same species were further classified into four groups according to their age and sex. Two age groups, age-1^- and age-1^+, were determined using standard age-body size relationships. The age-1^- group consisted of juvenile loaches that were born in the current year, and the age-1^+ group contained adult loaches that were more than one year old. The loach larvae that were born for less than 20 days were not obtained because the loach reproduction occurs in summer. Male and female groups were further identified according to the shapes and sizes of the pectoral fins, and were confirmed by their anatomy. A total of 106 loach groups were obtained, and their biological parameters are listed in Table S2. Whole loach samples were homogenized using a stainless steel commercial meat grinder and then freeze-dried. The lyophilized samples of paddy soils and loaches were stored in pre-cleaned brown glass bottles at −20 °C until analysis. The total organic carbon (TOC) contents in the paddy soils were measured using the high-temperature combustion

Please cite this article in press as: Zhang, H., et al., Bioaccumulation of organochlorine pesticides and polychlorinated biphenyls by loaches living in rice paddy fields of Northeast China, Environmental Pollution (2016), http://dx.doi.org/10.1016/j.envpol.2016.06.064