ASSESSMENT OF TOXIC AND TRACE ELEMENTS (As, Cd, Cu, Cr, Hg, Ni, Pb, Sr, Zn) IN ZOOPLANKTON FROM CARP FISH PONDS

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ANALIZA KONCENTRACIJE TOKSIČNIH I ESENCIJALNIH ELEMENTA (As, Cd, Cu, Cr, Hg, Ni, Pb, Sr, Zn) U ZOOPLANKTONU SA ŠARANSKOG RIBNJAKA

Apstrakt

U poslednjih 20 godina zagađivanje slatkovodnih ekosistema toksičnim elementima je u porastu širom sveta. Zagađenjem su pogođeni pre svega izvori za vodosnabdevanje stanovništva i životno okruženje, ali i industrija kao i privreda uopšte. Međutim zbog perzistentnosti i transfera kroz lance ishrane i potencijalnog akumuliranja u ribama i drugim vodenim organizmima koji se koriste u ishrani, toksični elementi predstavljaju stalnu pretnju ljudskom zdravlju. Zagađivanje naših reka teškim metalima nameće pitanje ne samo zdravstvene ispravnosti riba iz reka već i riba iz ribnjaka obzirom da se većina šaranskih ribnjaka napaja vodom iz sistema kanala DTD.

Cilj ove studije je bio da se analizira koncentracija 9 elemenata u zooplanktonu koji predstavlja značajnu prirodnu hranu šarana u poluintenzivnom sistemu gajenja. Istraživanje je obavljeno na 4 ribnjačka objekta, tokom dva ciklusa gajenja šarana, od juna do oktobra, na ribnjaku „Despotovo". Uzorci zooplanktona za analizu elemenata su uzimani sa tri tačke u svakom jezeru pomoću planktonske mrežice veličine 250 μm jednom mesečno. Na ovaj način su sakupljene samo krupnije veličinske klase zooplanktona (Cladocera i Copepoda), koje šaranska mlađ najviše konzumira. Sa svakog jezera je uziman po još jedan uzorak zooplanktona za kvantitativnu i taksonomsku analizu. Koncentracija elemenata je analizirana induktivno spregnutom plazma masenom (ICP-MS) i optičkom emisionom spektrometrijom (ICP-OES).

Rezultati su obrađeni jednofaktorijalnom analizom varijanse (ANOVA) u statističkom programu PAST 3.06. Značajnost razlika testirana je primenom Tukey's post hoc testa. Podaci su klasifikovani na prolećni, letnji i jesenji aspekt tokom jednog proizvodnog ciklusa.

Cladocera su dominirale u populaciji zooplanktona, osim u junu kada su Copepoda bile zastupljenije. Iako nije bilo značajnih razlika u koncentraciji elemenata između godina, osim za Cu i Sr, uočen je karakterističan sezonski obrazac kretanja koncentracija elemenata tokom celog istraživanja. Prolećni i jesenji aspekti u 2012 su bili veći nego u 2013, dok je letnji aspekt u 2013 bio viši nego u 2012. godini. Izuzetak je bila koncentracija Zn u zooplanktonu gde je situacija bila obrnuta.

Povišene vrednosti većine toksičnih metala u zooplanktonu na ribnjaku Despotovo se mogu objasniti relativno velikim afinitetom egzoskeleta Cladocera za većinu dvovalentih jona. Nakon adsorbcije elementi na površini ljuštura ovih životinja, tokom vremena bivaju absorbovani kroz telesni zid u unutrašnje organe. Neke studije čak navode da površinski akumulirani kontaminanti na plenu mogu biti dostupniji predatorima od onih akumuliranih u tkivima, zbog niskog pH i visokog nivoa jonske kompleksacije koji vladaju na mestu abstorpcije, u digestivnom traktu većine životinja,

Ovi rezultati nameću zaključak da je u budućim istraživanjima kontaminacije vodenih ekosistema i riba poželjno uključiti analize ne samo vode kao izvora toksičnih elemenata, već i odgovarajućih izvora hrane (plena) koji, kako je pokazano, sadrži potencijal ne samo za značajnu akumulaciju elemenata već i njihovu potencijalnu veću biodostupnost konzumentima.

Ključne reči: Cladocera, toksični elementi, egzoskelet, ribnjačka jezera, šaran
Key words: Cladocerans, toxic elements, exoskeleton, fish ponds, common carp

INTRODUCTION

Pollution of freshwater ecosystems with toxic elements is increasing over the past few decades worldwide, and accordingly a lot of attention is raised. The threats are posed primarily on the water supply and environment, but also towards industry and economy in general. However, due to persistence and transfer of toxic elements through food webs, and potential accumulation in fish and other aquatic animals used as food, it presents a constant danger to human health. In recent years, a considerable number of papers dealing with the pollution of fish, water and sediments of the Serbian part of River Danube with toxic elements have been published concluding that the situation needs urgent action and regular monitoring. One of the main issues is the low level of wastewater treatment of municipal and industrial waters, where rivers in Serbia usually serve as collectors of a range of pollutants. One of the concerns that these situations bring is not only the safety of fish from rivers for human consumption but also the level of contamination present at fish farms. The majority of fish farms in Serbia are located in the north of the country and are fed by Danube-Tisza-Danube Canal (DTD) hydro system. The present study is a part of a series of studies investigating element transfer through food webs and sediments at the carp fish farm "Despotovo" during 2012 and 2013. The aim of this research was to analyze the concentration of nine toxic elements (As, Cd, Cr, Hg, Ni, Pb, Sr, Zn and Cu) in zooplankton, a major part of the diet of common carp (*Cyprinus carpio* L.) in semi-intensive fish production.

MATERIAL AND METHODS

The study was carried out at the fish farm Despotovo, located in Vojvodina Province during two production cycles of common carp (in 2012 and 2013), from June to October. For the experiment 4 fish ponds were used. Zooplankton samples were taken monthly from three sites in every pond using a 250 μm mesh plankton net. Samples from each lake were rinsed with distilled water, placed in plastic bottles and frozen prior to analysis of elements. One extra sample of zooplankton per lake was taken and preserved with 4% formaldehyde for taxonomic and quantitative analysis. The content of As, Cd, Cr, Cu, Hg, Ni, Pb, Sr, and Zn in zooplankton samples was determined by inductively coupled plasma mass spectrometry and optical emission spectrometry respectively.

The results of the concentration of toxic elements in zooplankton were tested using analysis of variances (one-way ANOVA). Differences between treatments were tested using Tukey's post hoc test. The analyses were performed using PAST 3.06. The results were classified into three seasons during one year, spring, summer and autumn aspect.

RESULTS AND DISCUSSION

Overall there are not many field studies that investigated the concentration of toxic elements in freshwater zooplankton, and even less those done in fish ponds. There is one dealing with methyl mercury (Schultz et al., 2012) and another investigating introduction of heavy metals to fish and zooplankton via sediment resuspension (Cheng et al., 2013). Additionally, there are problems in comparing the results from different studies due to different methodologies for element analysis and measures used for expressing element concentration (e.g. μg/L wet weight and μg/g dry weight).

In both years, Cladocerans were dominating (80%) in the Crustacean population, except in June, when the Copepods were more abundant. Except for Cu and Sr, no significant differences were found in the investigated elements between two production cycles. However, there was a pattern that was consistent for most of the elements throughout the study: spring and autumn aspects in 2012 were higher than in 2013, while summer aspect in 2013 was higher than in 2012. Conversely, the level of Zn in zooplankton was higher in spring and summer in 2013 while lower in autumn compared to 2012.

The concentration of elements found in zooplankton of the investigated fish ponds were generally in the range reported for a number of natural uncontaminated lakes (Chen et al., 2000, Farkas et al., 2003). However, mean values of some elements (Cu, Ni, Pb and Zn) in our zooplankton samples (12.1 μg/g dw 3.1 μg/g dw, 2.8 μg/g dw and 75.3 μg/g dw, respectively) were higher than reported by Nguyen et al. (2005) for Lake Balaton during the calm weather period (4.8 μg/g dw, 1.65 μg/g dw, 0.95 μg/g dw and 71 μg/g dw, respectively) and especially higher than those found at Halali reservoir lake (0.022 μg/g dw, 0.009 μg/g dw, 0.048, 0.117 μg/g dw, respectively) (Malik et al., 2013).

Strontium was the most variable heavy metal during the investigation period with the highest values observed especially during spring and summer aspects of subsequent years (115.81 μg/g dw and 142.4 μg/g dw, respectively). The increased level of Sr found in our samples could be due to the high affinity of Cladoceran exoskeleton for this metal. This is also the case with lead that binds to the carapax possibly by the exchange with calcium,

cadmium, nickel, zinc, copper and other positively charged contaminants (Robinson et al., 2003). This mechanism seems to be the result of high affinity of chitin, the main constituent of cladoceran carapaces, for heavy metals. However, the adsorbed toxic elements on the surface of animal shells are sooner or later absorbed up to a certain level into the organisms through the integument and distributed to different internal organs (Robinson et al., 2003). Munger et al. (1999) reported that internal accumulation of cadmium in *Ceriodaphnia dubia* is primarily located at the gut diverticula, the main place where nutrients and Ca are uptaken in Cladocerans. Both, external and internal deposition of toxic elements in these organisms raises risk for dietary exposure of consumers/predators (Robinson, 1999). Some studies even suggest that the surface-associated contaminants of prey may be even more bioavailable to predators than the those accumulated in tissues due to the suitable conditions found in the gut of most animals as low pH and high ion complexation (Robinson et al., 2003). Additionally, several recent studies have stressed the relative importance of dietaryborne vs. waterborne exposure route for contamination of predators e. g. fish (Filipović Marijić and Raspor, 2012). This is observed also on lower trophic levels as phytoplankton/zooplankton and zooplankton/invertebrate predators (Taylor et al. 1998).

In conclusion, based on these findings, we propose that future studies on the pollution of aquatic ecosystems and contamination in fish should not only take into account the potential of waterborne routes, but also the significance of element accumulation in prey and additionally their potentially higher bioavailability to consumers.

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