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EMERGING CONTAMINANTS: ZN AND CU. EFFECTS AND IMPORTANCE IN MICROCRUSTACEANS, FISH, AND MICROALGAE

(Contaminantes emergentes: Zn e Cu. Efeitos e importância em microcrustáceos, peixes e microalgas)

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ABSTRACT

The study of emerging contaminants in aquatic ecosystems is of great importance to understand the functioning of the multiple physical-chemical interactions that occur at the various trophic levels. In water systems, for instance, increasing the flow of elements, such as Zn and Cu, can generate alterations in algae, microcrustaceans, and fish. To identify these alterations, there are various methodologies along with their results that show the level of affectation or adaptation of these organisms concerning these metals, and how they can contribute to knowing the quality of water bodies, being already used as bioindicators, either due to their high susceptibility or adaptability to changes in the concentration of these substances. Thus, this paper compiles popular science articles published by various authors about the effects of Cu and Zn on algae (Chlorella vulgaris), fish, and zooplankton.

Keywords: Chlorella vulgaris, bioindicators, heavy metals, fish, microcrustaceans.

RESUMO

O estudo de contaminantes emergentes em ecossistemas aquáticos é de grande importância para compreender o funcionamento das múltiplas interações físico-químicas que ocorrem nos diversos níveis tróficos. Em sistemas aquáticos, por exemplo, o aumento do fluxo de elementos como Zn e Cu pode gerar alterações em algas, microcrustáceos e peixes. Para identificar essas alterações, existem diversas metodologias juntamente com seus resultados que mostram o nível de afetação ou adaptação desses organismos em relação a esses metais, e como eles podem contribuir para o conhecimento da qualidade dos corpos hídricos, sendo já utilizados como bioindicadores, seja por sua alta suscetibilidade ou adaptabilidade a mudanças na concentração dessas substâncias. Desta forma, este artigo compila artigos científicos populares publicados por vários autores sobre os efeitos de Cu e Zn em algas (*Clorella vulgaris*), peixes e zooplâncton.

Palavras-chave: Chlorella vulgaris, bioindicadores, metais pesados, peixe, microcrustáceos.

INTRODUCTION

In a global context of scarcity and climate change, aquatic systems are vulnerable. Humanity faces a problem of sustainability and distribution of water resources. Rivers, lakes, reservoirs and other freshwater bodies are exposed to point and diffuse contamination as a result of human activities (RAYMS-KELLER *et al*., 1998; AGUDELO, 2005; ALVAREZ-LEGORRETA, 2009; ALVAREZ DALINGER *et al.,* 2022). In addition to affecting the quality of the resource and its possible uses, the contamination of the resource affects the flora, fauna, human beings and the ecosystems in general. Although there are self-purification processes, mainly in rivers, the effects can be severe and long-term (ARIAS *et al*., 2022).

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Pollutants such as heavy metals can be transported through soil, water or air. The lethality of these depends on the bioavailability of each metal, that is, the ability to transfer it to living organisms, which is directly related to some physicochemical characteristics of the environment, such as pH, redox potential, organic matter index, solubility, bioaccumulation, among others (ZATTA *et al*., 1992; VOIGT *et al.,* 2015; SOUZA, 2018).

In natural aquatic ecosystems, the concentration of metals depends on processes such as weathering and leaching, although increases can be generated through various anthropic activities such as mining, untreated domestic waste disposal and the excessive use of fertilizers, algaecides and fungicides (TULONEN *et al*., 2006). These increases represent an environmental and health threat, which can affect water ecosystems and their components.

Some toxic effects of the accumulation of heavy metals are known, such as the ability to interfere with the basal respiration of microorganisms, the fixation of carbon and nutrients by plants, the growth and development of planktonic organisms, the permeability of plasma membranes, in the structure of DNA and proteins, in the production of hormones, among others (VALKO *et al*., 2015).

The present study compiles published information from scientific works on the effects of zinc (Zn) and copper (Cu) NPs on a microalgae, microcrustaceans and fish. Likewise, it exposes the methods to determine the concentration of metallic NPs of Zn and Cu in water or organisms, for their use as environmental monitoring tools. Although there are several studies on the effects of Copper and Zinc, the information is not condensed, which makes it difficult to access. These metals are important in freshwater ecosystems, especially due to bioaccumulation processes, and compiling studies of their effects in a single article can greatly facilitate their understanding.

MATERIAL AND METHODS

Resources and database

This study carried out an analysis based on original publications (scientific articles, theses, scientific congresses and technical reports) from 1976 to 2022 (n=31). The bibliometric analysis was carried out with the Scopus database from Editorial Elsevier. This database is multidisciplinary and considered one of the most complete in terms of scientific publications, covering practically all areas of knowledge (ELSEVIER, 2019). In addition, the Google Scholar and SciELO databases were considered. Data collection was carried out during the month of May 2022. The selected scientific articles were obtained by using keywords in the search, such as "Zinc", "Copper", "Chlorella vulgaris", "Zooplankton", " Fish", "Nanoparticles".

Statistical Analysis

Of the total of studies analyzed, 45% corresponded to studies of metal effects on C. vulgaris, 35.5% on microcrustaceans, and 19.5% of studies corresponded to the effect of metals on fish. In the case of the effects on *Chorella sp*, some works analyzed the effects of contaminants on other microalgae besides *C. vulgaris*, however, this review only considers the results of *C. vulgaris*. Besides, of the total papers analysed, 29% correspond to studies carried out by laboratories on the Asian continent, 25% to laboratories in Latin America, 19% to North America and 19% to the European continent.

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RESULTS AND DISCUSSION

Chorella vulgaris

Chlorella vulgaris is a predominantly autotrophic, unicellular microalgae (ORTIZ MONTOYA *et al.*2014), with a high growth rate (YAMAMOTO *et al*., 2004; ILLMAN *et al.,* 2000) and resistant to unfavorable factors, which is why its cultivation is simple and used for various applications in the food industry, aquaculture, cosmetics, pharmaceuticals, wastewater treatment and biofuel production (HULTBERG *et al*., 2014).

Effect of heavy metal contamination on *Chlorella vulgaris*

Chlorella vulgaris has been used in a large number of works as a type species to evaluate the effects of various contaminants, among these heavy metals, for example Zinc and Copper. Results obtained by authors are compiled below:

Lam *et al*. (1999) examined the effect of the combined and individual presence of Cu and Cd on the growth of *Chlorella vulgaris*. As Cu and Cd concentrations increased, *Chlorella* decreased, with EC50 values of 1.02 and 4.01mg/L, respectively. The impact of acidifying the medium with HCL was also evaluated, observing that in a pH range between 2 and 7, the inhibitory effect of copper was greater than that of acidification. On the other hand, the effects of both metals combined at low concentrations had stronger growth inhibitions than the effect of a single metal. On the contrary, at higher concentrations, the individual effect of a single metal was greater than the combined effect.

Franklin *et al*. (2000) analyzed the effects of copper and uranium on *Chlorella sp*, at two pH values (5.7 and 6.5), with an exposure of 72 h. It was observed that *Chlorella sp*, was 20 times more sensitive to Cu (0.7 and 1.4µg/L at pH 6.5 and 5.7, respectively) than to U (13 and 34µg/L at pH 6.5 and 5.7, respectively). The copper concentrations required to inhibit the growth rate (cell division) by 50% increased from 1.5 to 35µg/L as the pH decreased from 6.5 to 5.7.

Wilde *et al*. (2006) evaluated the toxicity of copper and zinc on *Chlorella vulgaris* for a range of pH (5.5 and 8) and water hardness (between 40 and 48mg $CaCO_3$/L). The tests lasted 48 hours and the effects of metals on the rate of cell division were evaluated. As the pH decreased, the concentration of Cu to inhibit growth by 50% increased from 1.0 to 19µg/L, while for zinc it increased from 52 to 2700µg/L in the same pH range. Extra and intracellular copper was directly related to growth inhibition in *Chlorella* sp., while zinc toxicity was related only to cell-bound zinc.

Franklin *et al*. (2009) evaluated the toxicity of copper *Chlorella* sp. It worked with flow cytometry considering the inhibition of cell division rate, chlorophyll *a*, cell size, and enzyme activity. Acute (1-24h) and chronic (48-72h) toxicity tests were considered. 50% inhibition of cell division was observed at a concentration of 10µg/L or less of Cu after exposures of 48 and 72h for *Chlorella* sp.

Chen *et al*. (2012) studied the effects of zinc in the form of nanoparticles and zinc oxide. The authors showed that the presence of nanoparticles and zinc ions affected the morphology, viability and integrity of *Chlorella vulgaris*. They also observed a possible mechanical cell damage, however, the alga showed a defense mechanism by minimizing its

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surface contact area and suppressing the release of zinc ions from the nanoparticles through exudation.

Ouyang *et al*. (2012) analyzed the impact of concentrations of Cu, Cr, Zn, Cd and Pb at sublethal concentrations (0.05, 0.5, 5µmol/ L) on the rate of photosynthesis and growth of *Chlorella vulgaris*, in 96-h exposure trials. It was observed that the effects depended on the concentration of the 5 metals as well as the exposure time. At a concentration of 5µmol/L of Cu, Cr, Zn, Cd and Pb, an inhibition of microalgae growth was observed, the effect being an increase in the duration of exposure.

Wan-Loy *et al*. (2018), analyzed the effect of copper in the form of CuO nanoparticles and copper sulfate CuSO4 on *Chlorella vulgaris*. 96-hour toxicity tests were performed. The medium was enriched with $CuSO_4$ in a concentration between 0 and 200µM and other assays with CuO nanoparticles in a range of 0 to 2mM. Effects on pigmentation, response to oxidative stress and cell morphology of *Chlorella* sp. The tests showed that the microalgae were more sensitive to copper in the form of sulfate than in the form of nanoparticles. After 96 hours of testing, a considerable increase in reactive oxygen species was observed. On the other hand, clumps of *Chlorella* in those cultures that were added with CuSO4, while CuO nanoparticles had the ability to penetrate the cell wall of the algae.

Djearamane *et al*. (2019) analyzed the short-term cytotoxicity of zinc oxide nanoparticles in *Chlorella vulgaris*. Various concentrations of ZnO nanoparticles (10, 50, 100, 150 and 200mg/L) were considered for 12 h. Changes in chlorophyll fluorescence emission, algal biomass, and viable cell count were considered to assess toxicity. Results showed a decrease in chlorophyll content, algal biomass, and cell viability after ZnO treatment compared to control.

Ajitha *et al*. (2019) analyzed the effect of metals on *Chlorella vulgaris*, Cr, Hg and Zn were considered to exceed the permissible limits. In the acute exposure test of *Chlorella* to the effluent, an increase in the production of reactive oxygen species was observed, while total proteins and chlorophyll gradually decreased in relation to the concentration of the effluent. The lower concentrations of the effluent stimulated the antioxidant enzyme systems.

Wang *et al*. (2020) evaluated the response of *Chlorella vulgaris* to nanoparticles and copper ions (Cu). After 5 days of exposure to CuO (at concentrations between 1 and 10mg/L and dissolved Cu ions (at concentrations between 0.08 and 0.8mg/L), growth without significant changes and production of reactive oxygen species and significant membrane damage (at 10mg/L CuO particles). A total of 75 differentiated metabolites were identified. Altered metabolic pathways were observed after exposure to nanoparticles and copper ions.

Saxena *et al*. (2021) evaluated the effect of zinc (ZnO) and iron oxide (Fe_2O_3) nanoparticles on *Chlorella vulgaris*. A lower growth was observed that depended on the administered dose of the contaminants. The EC50 value for ZnO was 0.258mg/L and 12.99mg/L. The results showed significant decrease in chlorophyll content and increase in proline content. On the other hand, the results suggested a disintegration of the cell membrane due to the effect of the nanoparticles, as an increase in the level of lactate dehydrogenase was observed.

Again in 2021, Ajitha *et al*. considered the effects of zinc and mercury (Hg) on *Chlorella vulgaris*, in acute (48h) and chronic (7 days) trials. To evaluate the effect of these metals, the content of photosynthetic pigments, morphological changes, total proteins, reactive

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oxygen species present and antioxidant enzymatic activities were considered. A reduction between 32 and 100% of photosynthetic pigments was observed, depending on the applied dose of metals. Proteins, on the other hand, increased during acute and chronic exposure, although as the concentration of both metals increased, they decreased up to 80%. The combined presence of Hg and Zn generated a 5- to 7-fold increase in reactive oxygen species, indicating oxidative stress. Toxicity was significantly higher for the combined exposure than for the metals alone.

Oliveira *et al*. (2021) evaluated the effects and interferences of Cu and Zn using pig wastewater as a culture medium for microalgae, among which *Chlorella vulgaris*. We worked with a pond with a high rate of algae that were fed with different concentrations of Cu (0.5 to 3mg/L) and Zn (5 to 25mg/L). The effects of these metals on the microalgae's ability to remove nutrients from the medium used were analyzed. In the case of *Chlorella* at concentrations of 1.8mg Cu/L and 15mg Zn/L an increase in growth was observed, while at higher concentrations inhibition was observed. Of both metals, only Cu decreased ammonium removal rates, while in the case of Zn the effects were not significant.

Ratnayake *et al*. (2021) analyzed the effects of 3 metals, copper, zinc, and cadmium on 4 species of microalgae (*Desmodesmus* sp 1*, Desmodesmus* sp 2*, Coelastrella* sp, and *Chlorella vulgaris*). Three different culture media and one modified culture medium were used to compare the effects of the added metals, with an exposure time of 72h. It was observed that the composition of the different media has implications for the availability of metals, so the results obtained are highly correlated with the culture medium used. The EC50 of each species was evaluated, and it was different in each medium used. The results show that *Chlorella vulgaris* was the most resistant microalgae of the 4 strains considered.

In relation to the compilation of works on the toxic effects generated by exposure to Cu and Zn in *Chlorella vulgaris*, it was observed that metals tend to affect the photosynthetic rate and growth (OUYANG *et al.,* 2012; WAN *et al.,* 2018; DJEARAMANE *et al.,* 2019). On the other hand, some authors have verified morphological changes, accumulation of substances and damage to the cell membrane (CHEN *et al*., 2012; OUYANG *et al.,* 2012; WAN-LOY *et al.,* 2018). The activity of some enzymes was highly affected at higher concentrations, as well as an increase in the amount of reactive oxygen species. In general, Cu would seem to have more decisive effects on the algae than Zn, it is observed that at much lower concentrations, the effects are much more harmful and serious morphological changes and photosynthetic rate occur, as reported by the researchers. Authors of analyzed papers (AL-RUB e ASHOUR, 2006; FRIAR *et al*., 2005; RATNAYAKE *et al*., 2021).

Effect of heavy metal contamination on microcrustaceans

Winner and Farrel (1976) analyzed the response of 4 species of the genus *Daphnia* to acute and chronic exposure to copper under experimental conditions (*Daphnia magna, D. pulex, D. parvula* and *D. ambigua*.) They considered the EC50 values of a 72 houres exposure, with the 2 larger species being less sensitive to acute stress than the 2 smaller ones. In the 4 species, a lower survival was observed with Cu concentrations higher than 40µg/L. The highest concentrations that showed no reduction in survival and 72h EC values ranged from 0.47 to 0.59 and showed no significant differences between the 4 species *Daphnia* have no differences in their sensitivity to chronic copper stress.

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Publicado: mar./2024.

Belanger *et al*. (1989) worked with the species *Ceriodaphnia dubia*, and considered the effects of diet, water hardness, and population source, on water and chronic copper toxicity. Two diets were considered, a diet of 3 green algae added with vitamins and synthetic diets composed of yeasts and trout chow. It was observed that those newborn individuals of mothers raised on diets with algae were more resistant to copper exposure. The 48h EC50 increased from 34 to 79µg/L with increasing hardness (94 to 170mg/L $CaCO_3$). Three different populations of *Ceriodaphnia dubia* and showed no differences in sensitivity to Cu.

Untersteiner *et al*. (2003) analyzed the changes in the locomotion of *Daphnia magna* when exposed to copper. A series of real-time images were analyzed to assess response. The criteria considered were the average swimming speed and the duration of the swim itself or of immobility. A control test (without Cu) and a Cu application test at sublethal levels (1.5, 10, 20 and 30ug/L of Cu) were considered. The tests lasted 24h under static conditions. After 9 h, a significant decrease in the swimming average was observed for the individuals exposed to the highest concentration. The group exposed to 20ug/L of Cu, showed a decrease in swimming at 13h of exposure. Only the group exposed to 1 and 5ug/L Cu did not show a significant reduction in swimming speed.

Bossuyt *et al*. (2004) analyzed the acute sensitivity to copper for *cladoceran* obtained under natural conditions, using surface waters and one as a test or control medium. We worked with 43 species from different sites that presented differences in the composition of the water. The genera considered *were Daphnia, Ctenodaphnia, Ceriodaphnia, Simocephalus, Scapholeberis, Alona, Acroperus, Chydorus, Eurycercus, Disparalona, Pleuroxo.* Acute experiments showed that EC%= at 48 h for cladocerans ranged from 5.30 to 70.6µg Cu L-1 in standard test water and from 9.60 to 853µg Cu L-1 in natural waters. On the other hand, the average sensitivity of the sites ranged between 10.1 and 27.4µg Cu L - 1 in standard water and between 16.4 and 281µg Cu L - 1 in natural water. The authors conclude that bioavailability is more relevant than species composition per site, if the objective is to determine the toxicity of copper and its variability in aquatic ecosystems.

Brown *et al*. (2005) analyzed the effect of Zn on the species *Bryocamptus zschokkei*. Food availability was considered as a response variable, observing that, in the absence of food, larval stages were more sensitive to zinc than adult females, with a lethal concentration of 0.62mg Zn/L at 96h. In the case of tests with the presence of food, toxicity was significantly reduced in adult females. At a concentration of 0.48mg/L of Zn, a reduction in the number of pups per pup was observed.

A study carried out in the lower basin of the Salado River in Argentina, by Gagneten and Paggi (2007), showed a greater tolerance of *Copepod* in the presence of water contaminated with heavy metals such as copper and lead. As with previous studies, the research by Drira *et al.* (2018), showed that *Copepods* can be used as a bioindicator of anthropogenic contamination. Another study carried out by Zebral and partners in the coastal region of southern Brazil, showed that metallothioneins (MT) and lipid peroxidation (LPO) are present in large quantities in zooplankton from regions affected by agriculture and industrial activity, these regions contain high levels of pollutants. As a pesticide and heavy metals from agricultural and industrial activities, the authors concluded from the results that MT and LPO present in zooplankton in polluted areas can be used as biomarkers of environmental contamination by

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heavy metals such as copper, zinc and lead. as well as markers of contamination by organic substances.

Shaw *et al*. (2006) investigated the acute effects of Zn and Cd with 48h exposure on *Ceriodaphnia dubia, Daphnia magna, Daphnia ambigua and Daphnia pulex*, individually and in combination. Lethal concentrations for these species were determined and EC15, EC50 and EC85 calculated. The 48 hour LC50 values ranged from 0.09 to 0.9 micromol/L and 4 to 12.54 micromol/L for cadmium and zinc, respectively. It was also observed that, in exposures to a single metal, *D. magna* was more tolerant, while, in the combined treatments, all species showed a similar response to EC15. No differences were observed in the mixture tests *for D. magna*, suggesting that this species may not be representative of other cladocerans.

Vasela and Vijverberg (2007) studied the sensitivity to Zn of 4 species of the *Daphnia*, considering their average body size. The authors observed a possessive relationship between Ec50 values at 24 and 48h and the size of the newborns. As the individual was smaller, it was also more sensitive to exposure. The species that showed the most marked decrease was *D. magna*, while *D. galeata* was more resistant. In relation to its body size, the EC50 values for *D. magna*were higher than expected by the authors.

Cooper *et al*. (2009) performed acute bioassays with Cu, Zn and Pb on *Ceriodaphnia dubia* and *Daphnia carinata*. The 3 combined metals at doses up to 5.2, 4.5, and 51.8ug/L, respectively, were found to have no significant mortality in acute exposures. However, an exposure to 10.6, 9 and 101.8ug/L did show a mortality of 65 and 100%. It was observed that, in the case of acute tests, exposure to the mixture Cu^{+} and Pb was more toxic than the Cu^{+} and Zn mixture.

A study by Elmoor-Loureiro *et al*. (2016) demonstrated an opportunistic enrichment of zooplankton species near the mouth of the Doce River, shortly after mining sludge from Samarco reached the Atlantic Ocean. The Copepod species*, Parvocalanus sp*. and *Oithona nana*, made up 61% of the total zooplanktonic species, and their abundance was related to the presence of iron, lead, copper and zinc. There was also a momentary increase in the species *Calanoides carinatus*. These species are considered opportunistic predators and feed mainly on nanoplankton present in large quantities due to iron enrichment in the water.

Copepod species have also been found in abundance in other studies at sites with high mineral content, such as the study by Acary *et al*. (2020) off the coast of Kalpakkam, southwestern Bay of Bengal, India. The presence of Copepods was also associated with the presence of excessively dissolved copper, iron and zinc in the water. Sobrino-Figueroa *et al*. (2020) analyzed the effect of heavy metals such as copper and lead on Acanthocyclops americana copepods, and the presence of copper caused a large oxidative effect on lipids and a 79% inhibition of Acetylcholinesterase in these organisms.

In the same way, Carrion and De la Cruz (2015) state that the presence of heavy metals manages to influence the functioning of water systems, to the point of altering life cycles as in the case of cladocerans, which as a measure of containment against the changes presented in the environment, they alter their type of reproduction from asexual to sexual, where resistance eggs are generated that have developed as one of the adaptive responses to guarantee their survival in bodies of water. Therefore, the permanence of these species will depend on the ability of their eggs to hatch and recolonize aquatic systems once the environmental pressure disappears.

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Despite the importance of the elements zinc and copper for the survival of organisms, their high concentration can cause cell toxicity. In the environment, especially in aquatic environments, the excessive presence of these metals is mostly the result of anthropogenic activities.

Studies such as those mentioned above have shown that aquatic contamination by zinc and copper can affect the entire food chain. Its ability to bioaccumulate is one of the most worrying factors. Toxicity in relation to zooplankton is one of the most explored areas of study, since these heterotrophic organisms play a fundamental role in the balance of the ecosystem.

Microcrustaceans are one of the main groups that make up zooplankton, with Cladocera and Copepoda species being the most abundant. Studies carried out in areas with high concentrations of zinc and copper have shown that these species represent the largest class of individuals, and are capable of adapting to conditions of excess of these minerals, becoming an opportunistic species, especially when the presence of these metals stimulates the multiplication of nanoplankton that serves as food for these species.

Although Cladocera and Copepoda species are found in large numbers in environments contaminated with copper and/or zinc, studies have shown that copper and zinc contamination is capable of causing negative damage to the cells of these animals, especially the oxidation of the membrane lipids. Most studies indicate that the Copopedes class is an efficient biomarker of aqueous contamination by heavy metals, including zinc and copper, and can be used for environmental and water quality monitoring purposes.

The impact of zinc and copper contamination depends on many factors such as the availability of these metals, the pH of the water, the temperature, the presence of other contaminants, the leaching and resuspension capacity, the diversity of microorganisms, etc. However, studies indicate that despite these factors, these metals can bioaccumulate and be transferred to higher trophic levels. The long-term and short-term damage that this bioaccumulation of heavy metals such as zinc and copper can cause is still unknown. And it has been exploited over the years, especially due to the increase in the world population and, consequently, the increase in pollution of fresh and salt water. Although more studies are needed, it is possible to say that we must look for strategies to minimize environmental contamination by these heavy metals, since they are active and capable of bioaccumulating in the organisms that form the base of the food chain.

Effects and bioaccumulation in fish

Márquez *et al*. (2008) analyzed the content of metals in muscle tissues of fish from the Unare lagoon, Anzoátegui state, Venezuela. The measurement of metals in the water was carried out in order to compare with the concentration of muscle tissue. Low mean concentrations of Zn (0.004-0.012μmol/L) were observed, while no copper was detected in the water. Elevated zinc levels exceeding 17μg/g were detected in muscle samples in most species. The authors found evidence of bioaccumulation, as the concentrations of metals were higher in the individuals inside the lagoon.

Cai *et al*. (2017) analyzed the concentrations of metals, including copper and zinc, in the muscle of ten species of fish that were collected from the Chishui River, China. The mean concentration of copper and zinc was 0.363±0.106, 8.538±3.877mg/kg, respectively. The authors found no correlations between metal accumulation and fish length.

Recebido: fev./2023.
Publicado: mar./2024.

Vasconcelos *et al.* (2011) studied the presence of metals in commercial fish (*Solea solea, Solea senegalensis, Platichthys flesus, Diplodus vulgaris and Dicentrarchus labrax*) that were collected from various points subjected to intense human activity. It was observed that the concentration of metals varied depending on the species considered. Cu and Zn concentrations ranged from 1.0 to 2.1 and from 14 to 59µg/g of muscle dry weight, respectively.

In the work of Ortega *et al*. (2020), benthic fish from Amazonian rivers were collected and copper accumulation was evaluated. Three species of boquichico (*Prochilodus nigricans*), carachama (*Chaetostoma* sp) and julilla (*Parodon buckleyi*) were selected. Twelve specimens per species were sampled at three sampling points of the Monzón River. Muscle, liver, and water and sediment samples were considered. It was observed that the greatest accumulation occurred in the liver. The average copper concentrations of 2.78ppm in julilla; 2.44ppm in Boquichico and 2.41ppm in Carachama. The authors conclude that the greatest bioaccumulation in these species occurs in the liver.

Aveiga Ortiz, 2020 studied the bioaccumulation of metals in fish organs in the Carrizal sub-basin. The sediment and the species (*Hoplias microlepis, Aequidens rivulatus and Oreochromis niloticus*) were considered. The highest values of Zn found were 0.371mg/Kg of Zn in gills *of Oreochromis niloticus*, 1.243mg/Kg of Zn in liver of *Hoplias microlepis* and 0.415mg/Kg of Zn in gills of *Aequidens rivulatus.* Mesa Pérez *et al*. (2021) monitored the bioaccumulation of heavy metals in water samples collected from the Pedroso reservoir (Mayabeque province, Cuba) and its main tributaries, considering the concentration of metals per kilogram of wet weight in fish fillets (*Oreochromis spp., Tinca and Clarias gariepinus*). The results showed that the copper content in fish muscle was in the range of 0.01 and 0.58mg/L, while the Zn content varied between 4.9 and 29.9mg/L.

The presence of heavy metals in bodies of water intended for consumption and recreation constitute a major environmental and health threat, due to the bioaccumulation capacity of these metals by some edible species, for example, fish.

In the case of chromium and zinc, their effects are largely related to water pH and temperature, as well as gender and tissue specificity. The pH affects the solubility, for example, in rainbow trout, acute chromium toxicity can cause morphological changes in gills, kidney and digestive tube when the water has a pH of 7.8, while these changes are only caused in gills. when the water has a pH of 6.5 (VAN DER PUTTE *et al*., 1981).

Depending on the pH of the sites analyzed by the authors, it is possible that the metals tend to settle, causing even greater toxicity in the ecosystem and fauna. Bioaccumulation in fish can occur by diet, by their presence in the water or through contact with sediments.

The results observed in the analyzed studies indicate that there is a relationship between the composition of the water and the accumulation of substances in the fish, so these are excellent bioindicators.

CONCLUSIONS

Through the results presented above, it can be concluded that microalgae, microcrustaceans and fish respond differently to changes in the concentration of Zn and Cu as emerging contaminants, which denotes their applicability as bioindicators in water quality. In the same way it is pertinent to clarify that, although many elements are found naturally and are

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essential for the development of life, the rise of anthropic activities (especially the exploitation of mining resources); they increase the amount of elements in movement through the different transfer processes, which generates an imbalance in the optimal functioning of ecosystems, to the point of overcoming resilience barriers. This, although it can be seen as a problem of purely biological interest, can have repercussions on the social side, even in populations far from the affected water bodies, by increasing the concentrations of these elements due to bioaccumulation phenomena in species of biological-fishing interest, that therefore end up being consumed by the human being.

The works carried out by various authors in different ecosystems have determined the level of affectation of emerging contaminants such as Zn and Cu and the possible causes of said contamination, generating indications of which individuals may be capable of generating and/or accelerating the processes of contamination. bioremediation of the environment, due to its high adaptability and that can then be useful in the remediation of the water resource.

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