Which Organism is More Suitable As A Toxic Metal Accumulation Bioindicator – Fishes Or Diatoms: A Case Study Of An A Class Wetland In Northwest Türkiye Under Effect Of An Intensive Paddy Cultivation Stress?

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Abstract

In this research, “diatoms” as the first step and “fishes” as the last step of the food chain were compared as the toxic metal accumulation bioindicator in an A Class wetland in Turkey. Toxicant bioaccumulations were determined in liver, gill and muscle tissues of 2 commercially consumed fish species "*Carassius gibelio*" and "*Cyyprinus carpio*" and in frustules of epiphytic diatom communities living on submerged macrophytes. Samples were collected from the Gala Lake, which is among the best stopover habitats of birds migrating between Europe and Africa, seasonally considering the paddy harvest period, which is a major stress factor for the ecosystem. Also potential human health risks associated with the consumption of fishes and consumption – dermal contact of diatoms were evaluated both for summer – before paddy harvest (BPH) and autumn – after paddy harvest (APH) periods. As a result of this research, the investigated toxic metal bioaccumulation levels were increased significantly in diatoms in the APH period, while less significant exchanges were recorded in fish tissues, in general. The data showed that the diatoms are much more sensitive to changes in the environmental conditions than fishes and they are more effective biological tools as toxic metal accumulation bioindicators than fishes.

Keywords: Diatoms, Fishes, Gala Lake, Health risk assessment, Toxic metal accumulation bioindicator

Introduction

Environmental pollution and especially toxic metal contamination in water ecosystems have been the top of attention in scientific community and especially in recent years, when each of us has felt the impact of global climate change closely, the protection and sustainability of freshwater habitats have become the first priority of almost the whole world (İslam et al. 2015, Mutlu and Uncumusaoğlu 2018, Varol 2020, Ustaoğlu et al. 2020, Tokatlı et al. 2021, İslam 2021, Tokatlı and Varol 2021). Toxic metals are significant threats to the aquatic habitats, because they may easily bioaccumulate in aquatic biota and may transported to the higher trophic steps through the food chain (Wei et al. 2016, Hu et al. 2018, Köse et al. 2020). Bioindicators may provide valuable information on the bio – available fractions of the toxic metals. Bioaccumulation levels of toxicants in organisms, especially in the first steps of the aquatic food chain may be an early – warning of the hazards of the toxicants for the other organisms located at the higher levels of the food chain by means of many trophic interactions (Farias et al. 2018). Numbers of previous researches show that some aquatic organisms living at different stages of the food chain, such as algae, invertebrates and fishes may be used as effective and suitable bioindicators of toxic metal contamination (Caçador et al. 2012, Chakraborty et al. 2014, Chiarelli and Roccheri 2014, Billah et al. 2017, Chua et al. 2018).

Meriç River Delta is an A Class Wetland and the most significant natural stagnant freshwater ecosystem located in the south – western of Thrace Region of Turkey. The delta has a great agricultural potential because of its fertile lands and fresh water resources. Therefore, the most important paddy fields of Turkey are located on this basin and the region, where supplies about 25% of the total rise production in Turkey, is deservedly known as the "Rice Land" (Tokatlı and Baştatlı 2016, Tokatlı 2018, 2021, Tokatlı and Ustaoğlu 2020, 2021). Gala Lake, which is a Ramsar Area, has a very special importance for not only for Turkey but also for the Europe in terms of its natural beauty and biological diversity. The lake is located in the Meriç River Delta and paddy cultivation is known as a significant stress factor for the system. Especially in the fall season before the paddy harvest, the direct drainage waters of the paddy fields into the Gala Lake through the drainage canals adversely affects the water quality and the biota. Paddy production has been conducted uninterruptedly about 60 years in the region and therefore, the use of pesticides and chemical fertilizers, which are being caused many toxic metals to pass into the soils and waters of the region, have been reached to an alarming rate. It was clearly documented in numbers of studies that the Gala lake is getting shallower and eutrophic character day by day. The concentrations of toxic metals in both abiotic and biotic components of the lake have reached very critical levels (Elipek et al. 2010, Tokatlı 2017, Öterler 2018, Aydın and Çamur 2021, Varol and Tokatlı 2021, Tokatlı and İslam 2022).

In the present study, temporal variations of toxic metal bioaccumulations in frustules (permeable, 3-dimensional, silica cell wall of diatoms) of epiphytic diatom communities (living on submerged macrophyte species) and in liver, gill and muscle tissues of selected 2 significant fish species (*Carassius gibelio* and *Cyyprinus carpio*) living in the Gala Lake were investigated and the data were assessed using some potential human health risk evaluation indices. Thus, the diatoms as the first step of the food chain and the fishes as the last step of the food chain were compared in terms of their effectiveness and usefulness as the best toxic metal accumulation bioindicator in this significant wetland habitat. The flowchart that shows the steps of the present investigation is given in Fig. 1.

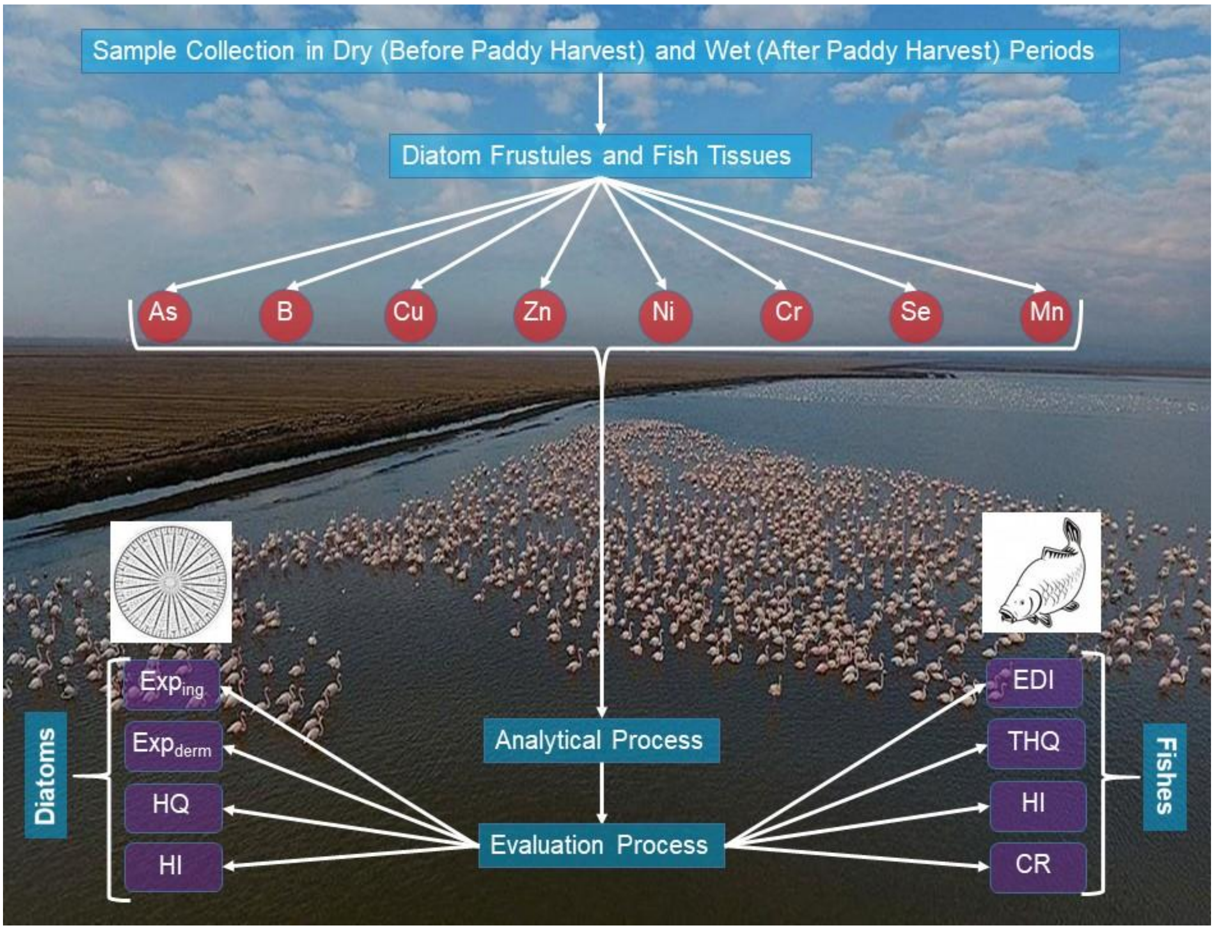

Fig. 1. The flowchart of this research and a view from the Gala Lake

Materials and Methods

Study area

Gala Lake, which is located in the north – western part of Turkey at about 2 m above sea level, is a significant stopover wetland habitat for many migratory birds (Fig. 2). The lake, which has a depth varies of about 0.4 m (in dry – summer season) – 2.2 m (in wet – winter season), has a surface area of about 5.6 km^2. The lake is surrounded by numbers of rice cultivation lands, which are sown at the early May and harvested at the middle October in the region (Fig. 2). The Gala Lake that has an alluvial set lake characteristic is connected to the Aegean Sea by means of Meriç River. The lake is fed by rain water as well as drainage water coming from the paddy fields (Tokatlı et al. 2014, Interreg-IPA CBC 2018, Batur and Maktav 2019, Varol and Tokatlı 2021).

Collection of biotic samples

In this research, diatoms and fishes were taken from the Gala Lake in summer (July – before paddy harvest – BPH) and autumn (October – after paddy harvest – APH) seasons of 2019. The main reasons for sampling in July and October are; (1) pesticides and fertilizers are being applied to the rice cultivation lands in June and July, and (2) paddy is being harvested in September and October.

Fish samples

The fish samples were collected by the nets of fishermen. Than they were transported to the laboratory as soon as possible in a cooler (4 °C). After recording some metric and meristic characters of fish species liver, gill and muscle tissues of each fish sample were dissected in the laboratory. 3 fish samples of each fish species (*Carassius gibelio* and *Cyprinus carpio*) approximately the same length and weight were caught in each seasons (summer – BPH and autumn – APH). The determined metric – meristic characteristics of analysed fishes are given in Table 1.

Epiphytic diatom samples

Epiphytic diatom samples were taken from the dominant submerged macrophyte species (*Potamogeton crispus, Ceratophyllum demersum* and *Myriophyllum spicatum*) from 5 stations (G1 – G5) selected on the lake (Fig. 2), where thought to represent the whole lake best. The macrophytes were collected by removing from the ground. Than the taken macrophyte samples were washed with distilled water. Thus, the transition of the epiphytic diatoms from submerged macrophytes to distilled water was provided. Then 3 composite samples were obtained by mixing the diatoms collected from 5 stations. After this, the diatom samples were cleaned with a concentrated acid mixture (98% H_2SO_4 and 35% HNO_3) in order to the elimination of organic contents and non-diatom epiphytic algae. Then the frustules obtained (kieselguhr soil) were washed with distilled water for 5 days to remove the acid mixture from the samples. The same process was also performed on an empty container and element contents were read and then these results were deduced from the kieselguhr soil reads obtained.

Chemical analysis

For determination of As, B, Cu, Zn, Ni, Cr, Se and Mn concentrations in liver, gill and muscle tissues of fishes and prepared epiphytic diatom frustules (kieselguhr soil), each biotic sample was dried for 3 hours at 105 ºC. 0.25 g of each oven dried (Isolab) biotic samples were placed in a microwave device (CEM Mars Xpress) for the digestion process. Than an acid mixture (1/3 rates of $HClO_4$ and HNO_3) were inserted into the reactors. Then the biotic samples were mineralized by heating at 200 ºC for 30 minutes. After the step of mineralization, the samples were filtered by a Whatman® nitrocellulose membrane filters with pore size of 0.45 µm. After the step of filtration, volumes of the samples were completed 100 ml by ultrapure water. Toxic metal accumulations in fish tissues and diatom frustules were measured by using an ICP – MS device (Agilent 7700) as means of triple reads in the central laboratory of Thrace University (Edirne/Turkey) (accreditation certificated) (TS EN / ISO IEC 17025) (EPA 1998, 2001). The accuracy of analytical method was controlled by measuring a CPAchem (Ref Num: 110580.L1) branded certified reference material (CRM).

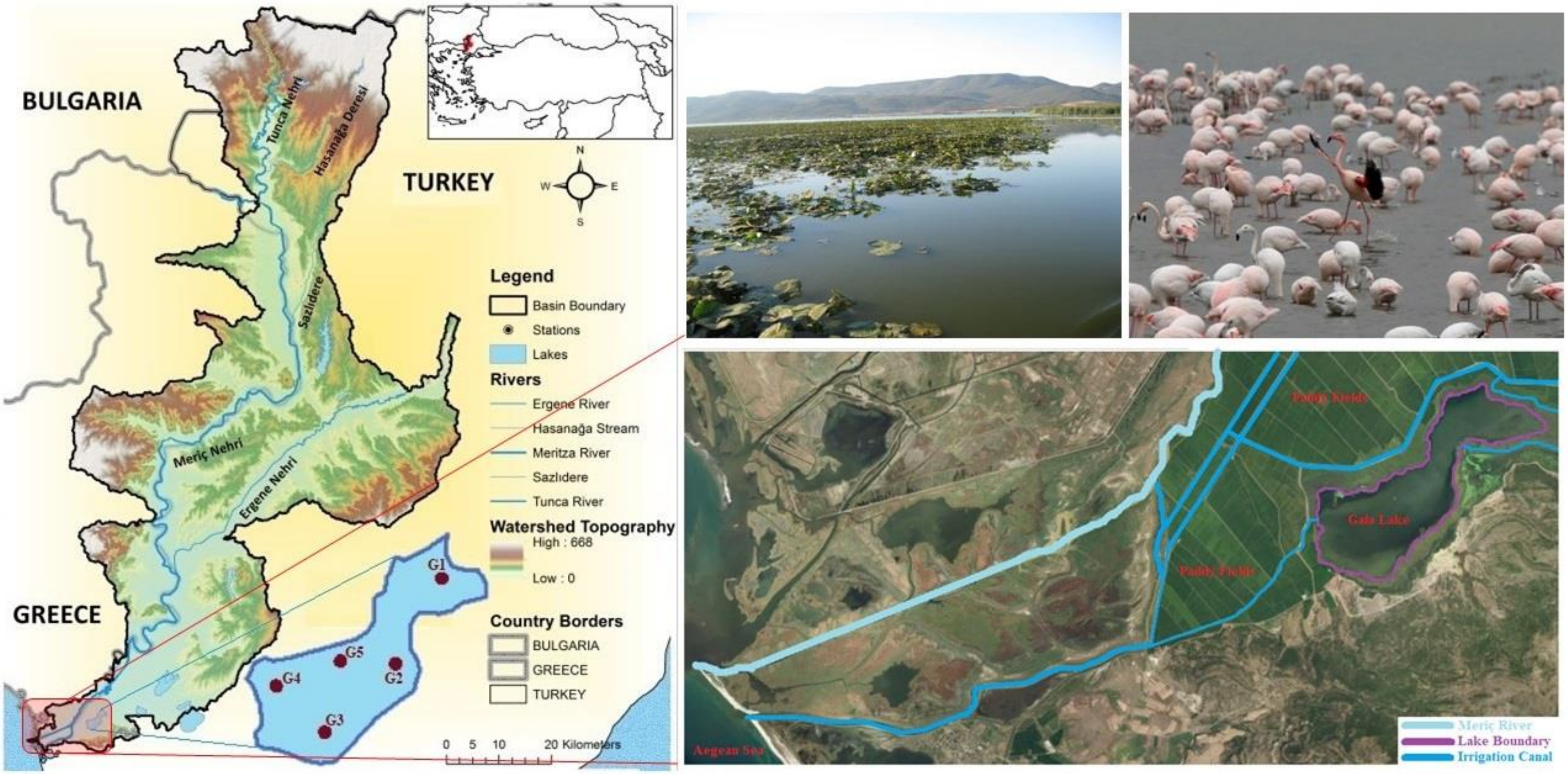

Fig. 2. Meriç River Basin, selected diatom stations on the lake, the system of drainage canal and paddy fields around the Gala Lake

Table 1. Some metric and meristic characteristics of investigated fish species

Season	Species	Descriptive statistics	Weigh (gr)	Linea lateral stamps	**Length** (mm)						**Height** (mm)	
					Head	**Predorsal**	**Preanal**	**Standart**	**Fork**	**Total**	**Tail stalk**	**Total**
Summer – Dry (Before Paddy Harvest)	*C. carpio* (n=3)	min	510	35	70	142	200	262	285	320	38	110
		max	654	37	80	160	230	305	330	365	43	120
		mean	**604**	**36**	**76**	**151**	**218**	**287**	**312**	**348**	**40**	**114**
		SD	81.19	1.00	5.29	9.02	16.07	22.50	24.01	24.21	2.52	5.13
	C. gibelio (n=3)	min	354	27	58	118	182	235	267	282	38	100
		max	444	31	69	125	198	255	285	305	40	105
		mean	**406**	**29**	**64**	**121**	**190**	**245**	**277**	**294**	**39**	**103**
		SD	46.46	2.08	5.69	3.61	8.00	10.00	9.29	11.53	1.15	2.52
Autumn – Wet (After Paddy Harvest)	*C. carpio* (n=3)	min	615	36	80	150	225	290	315	340	40	115
		max	733	37	83	160	230	310	337	370	47	118
		mean	**677**	**36**	**81**	**155**	**227**	**301**	**329**	**356**	**44**	**117**
		SD	59.23	0.58	1.53	5.00	2.52	10.41	12.16	15.28	3.61	1.73
	C. gibelio (n=3)	min	333	30	50	110	160	215	245	27	33	100
		max	410	31	60	125	180	235	270	29	38	108
		mean	**375**	**30**	**55**	**118**	**170**	**225**	**255**	**28**	**35**	**104**
		SD	39.17	0.58	5.00	7.64	10.00	10.00	13.23	1.00	2.52	4.04

Health risk assessment in fishes

Edible Daily Intake (EDI)

EDI values for adults (EDI= mg/kg body weight/day) were calculated according to the following formula:

$$EDI = \frac{C_{element} \times D_{food\ intake}}{BW} \quad (1)$$

$C_{element}$: Toxic metal content in muscle tissues of fishes (mg/kg),
$D_{food\ intake}$: Average daily fish consumption (g / person / day) (in Turkey 15.069 gr / person / day) (GDFA 2018),
BW: Mean body weight (70 kg for adults).

In this study, the EDI coefficients were compared with the values of oral reference doses (RfD_o) recommended by the USEPA (2019).

Target Hazard Quotient (THQ)

THQ is an effective estimation technique of the potential health risks (non-carcinogenic) based on pollutant exposure. THQ of each toxic metal was calculated with the following formula (Chien et al. 2002):

$$THQ = \frac{EF \times ED \times FIR \times C}{RfD_o \times BW \times AT} \times 10^{-3} \quad (2)$$

EF: Exposure frequency (365 days / year),
ED: Exposure duration (average life expectancy: 70 years),
FIR: Food intake rate (20 g/day),
C: Toxic metal content in muscle tissues of fishes (mg/kg),
RfDo: Reference dose – oral (mg / kg / day),
BW: Mean body weight (70 kg for adults),
AT: Average time of exposure for toxicant (365 days / year x number of years of exposure)

If the THQ coefficients would higher than 1, that means potential non-carcinogenic health effects may be seen. If the THQ coefficient would lower than 1, that means no potential non-carcinogenic health effects may be seen (Çulha et al. 2016, Mehmood et al. 2020, Töre et al. 2021).

Hazard Index (HI)

HI enables to assess the cumulative effects of toxicants and it is the sum of the THQ's for all the calculated toxic metals (equation 3) and it means safe if HI < 1 and dangerous if HI > 1 (Varol et al. 2019, Tokatlı and Varol 2021).

$$HI = \sum_{i=1}^{n} THQ_i \quad (3)$$

Cancer Risk (CR)

The Cancer Risk (CR) that may occur as a result of lifetime exposure to Cr, Ni, Pb and As may be determined according to the following formula (Javed and Usmani 2016):

$$CR = \frac{EF \times ED \times FIR \times C \times CSF}{BW \times AT} \times 10^{-3} \quad (4)$$

CSF: It is the slope factor of carcinogenic from the IRIS (Integrated Risk Information System) (Cr: 0.5; Ni: 1.7; Pb: 0.0085; As: 1.5 mg/kg/day).

Evaluation of the calculated CR coefficients are being done as follows (USEPA 2019);

$CR < 10^{-6}$: negligible,
$10^{-4} > CR > 10^{-6}$: acceptable,
$CR > 10^{-4}$: unacceptable.

Health risk assessment in diatoms

Exposure – Ingestion (Exp_{ing}) and Dermal (Exp_{derm})

The following formulas are applied to determine the exposure through two significant pathways of ingestion and dermal contact (EPA 2004, Rovira et al. 2011):

$$Exp_{ing} = \frac{C_{frustule} \times IR \times CF \times EF \times ED}{BW \times AT} \quad (5)$$

$$Exp_{derm} = \frac{C_{frustule} \times CF \times SA \times AF \times ABS \times EF\ ED}{BW \times AT} \quad (6)$$

Exp_{ing}: Ingestion exposure from the diatoms (mg/kg),
$C_{frustule}$: Measured toxic metal content in the diatoms,
IR: Ingestion rate (114 mg / day),
CF: Unit conversion factor (10^{-6} kg / mg),
EF: Exposure frequency (350 days / year),
ED: Exposure duration (30 years),
BW: Mean body weight (70 kg for adults),
AT: Average time (10,950 days),
Exp_{derm}: Dermal contact exposure from the diatoms,
SA: Skin surface area (5700 cm^2),
AF: Adherence factor from diatoms to skin (0.07 mg / cm^2),
ABS: Dermal absorption slope from diatoms (0.001).

Hazard Quotient (HQ)

HQ is being used to evaluate the potential human health risks (non-carcinogenic) from the exposure of toxicants by means of diatoms according to the health risk assessment guidelines of EPA (2004). HQ values of each toxic metal for the two exposure pathways were calculated with the following formula:

$$HQ_{ing-derm} = \frac{Exp_{ing}-derm}{RfD_0} \quad (7)$$

Hazard Index (HI)

HI enables to assess the cumulative effects of toxicants via ingestion or dermal contact and it may be calculated by summing the HQ's for all determined toxic metals as given in the following formula:

$$HI = \sum_{i=1}^{n} HQ_{ing-derm} \quad (8)$$

Results

Temporal bioaccumulation data of investigated toxic elements in three significant tissues (liver, gill and muscle) of *C. gibelio* and *C. carpio* and epiphytic diatom frustules are given in Fig. 3 and the variation rates of bioaccumulation levels in *C. gibelio* and *C. carpio* and epiphytic diatom frustules from summer (dry) – before parry harvest (BPH) to autumn (wet) – after paddy harvest (APH) periods in Gala Lake are given in Table 2.

The estimated average EDI values, non-carcinogenic THQ and HI values and carcinogenic CR values of the 2 commercially consumed fish species living in Gala Lake in dry – before paddy harvest (BPH) and wet – after paddy harvest (APH) periods are given in Table 3. The estimated average exposure and non-carcinogenic HQ values for ingestion and dermal contact and HI values of the diatoms of Gala Lake contaminated by toxic metals in dry – BPH and wet – APH periods are given in Table 4. Also the percentage exchange rates of estimated potential human health risks from dry to wet seasons both for fishes and diatoms are given in Table 3 and 4.

The Edible Daily Intake (EDI) coefficients of all the investigated toxic elements in all the investigated fish species were quite higher than the reported reference doses. The EDI coefficients detected in the muscle tissues of *C. gibelio* and *C. carpio* were 97 – 60 times higher for Cr, 7 – 3 times higher for Mn, 4 – 3 times higher for Ni, 5 – 5 times higher for Cu, 24 – 16 times higher for Zn, 192 – 182 times higher for As, 3 – 3 times higher for Cd and 5 – 2 times higher for Pb respectively, than the reference doses.

The THQ values of Cr, Zn and As were higher than 1 (an average of 5.52, 1.39 and 13.11 respectively), while Mn, Ni, Cu, Cd and Pb were lower than 1 (an average of 0.32, 0.27, 0.34, 0.19 and 0.24 respectively). The HI coefficients of fishes were quite higher than 1 and the average HI values of *C. gibelio* and *C. carpio* were recorded as 23.59 and 19.18 respectively. The detected results reflect the potential non-carcinogenic concern of especially Cr, Zn and As via consumption of these fishes and also adverse effects on health of human may be seen in the region. It was also determined that the values of HIs in *C. gibelio* and *C. carpio* in the APH period were approximately 33% and 3% higher than the values detected in the BPH period respectively.

CR coefficients of Pb were in the range of 10^{-4} – 10^{-6} (acceptable) in all the investigated fish species, while CR coefficients of Cr, Ni and As were considerably higher than the reported limit of value 10^{-4} (unacceptable). Therefore, there may be a significant carcinogenic risk for consumers in case of exposure to Cr, Ni, and As from the consumption of *C. gibelio* and *C. carpio* species caught from the Gala Lake.

The recorded exposure coefficients of diatom frustules both for ingestion and dermal contact were below the reported reference doses. Although, all the HQs and HIs of non-carcinogenic toxic metals in the diatom frustules in terms of both ingestion and dermal contact were less than 1, the values of HQs and HIs detected in the APH period were approximately 1000 times higher than the values detected in the BPH period.

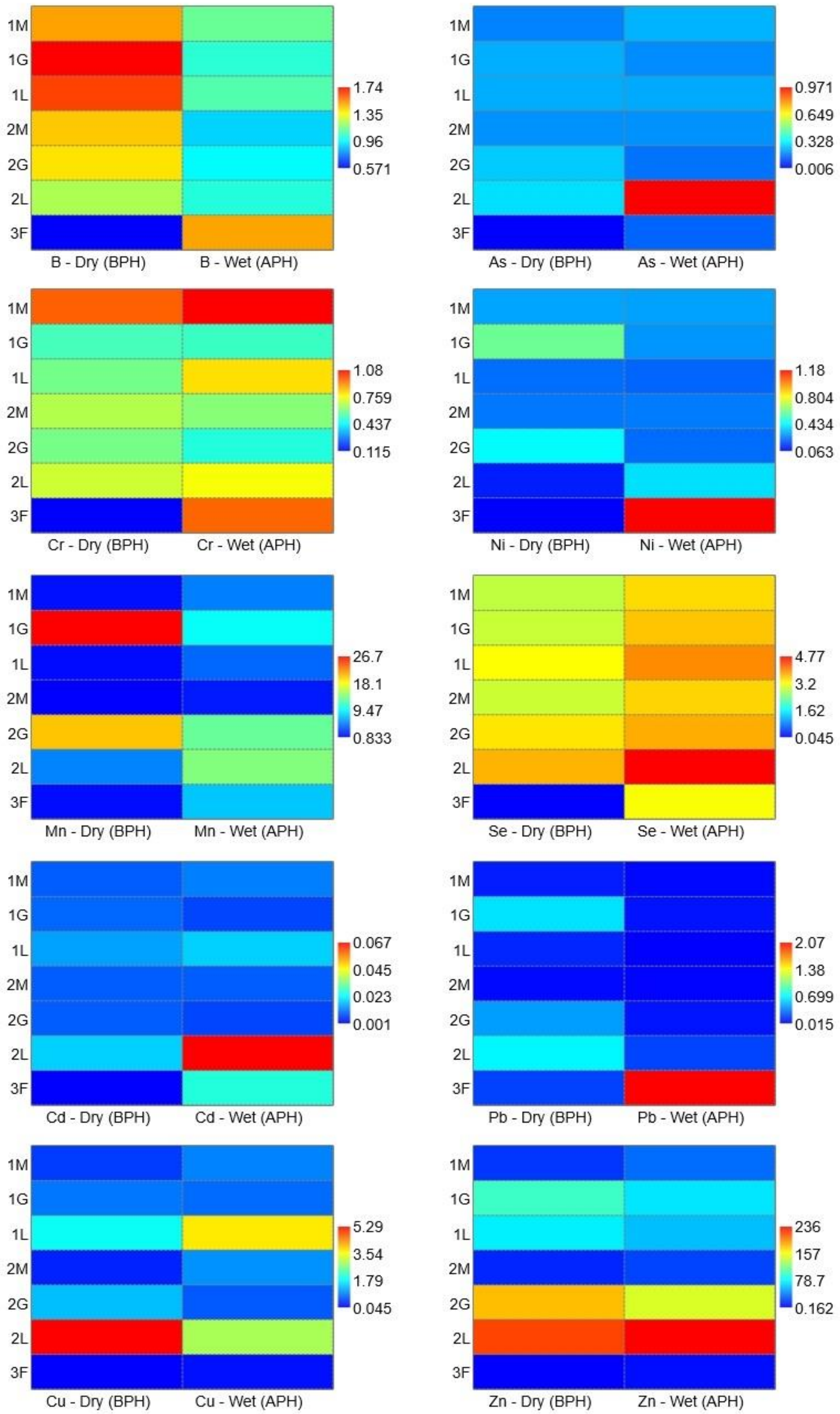

Fig. 3. Trace and toxic element bioaccumulations in muscle (M), gill (G) and liver (L) tissues of fish species (1: *C. gibelio*; 2: *C. carpio*) and frustules (F) of EPF diatom communities (3) in dry – before paddy harvest (BPH) and wet – after paddy harvest (APH) periods (ppm)

Table 2. Percentage variation rates of toxicants in investigated fish species and diatoms from dry – before paddy harvest (BPH) to wet – after paddy harvest (APH) periods (%)

Toxicant	***C. gibelio***	***C. carpio***	**Diatoms**
	Average of all tissues		Frustules
B	-33.273	-28.670	+160.19
As	+5.4841	+64.558	+1997.5
Cr	+15.756	-6.3090	+724.92
Ni	-19.996	+73.056	+1761.3
Mn	+163.02	+78.149	+524.37
Se	+22.820	+20.271	+6962.1
Cd	+8.8011	+81.103	+2489.6
Pb	-78.985	-62.340	+974.46
Cu	+64.946	+59.882	+227.63
Zn	+18.089	+23.806	+2292.6
Overall	**+16.666**	**+30.350**	**+1811.4**

Table 3. EDI, THQ, HI, and CR scores of fishes and percentage exchange rates from dry to wet seasons

Toxicant	Summer – Dry (Before Paddy Harvest)						Autumn – Wet (After Paddy Harvest)						% Exchange	
	EDI		Non-carcinogenic risk THQ		Carcinogenic risk CR		EDI		Non-carcinogenic risk THQ		Carcinogenic risk CR			
	C. gibelio	*C. carpio*	*C. gibelio*	*C. carpio*	*C. gibelio*	*C. carpio*	*C. gibelio*	*C. carpio*	*C. gibelio*	*C. carpio*	*C. gibelio*	*C. carpio*	*C. gibelio*	*C. carpio*
Cr	2.738E-01	1.897E-01	6.389E+00	4.427E+00	9.584E-03	6.641E-03	3.088E-01	1.736E-01	7.204E+00	4.051E+00	1.081E-02	6.077E-03	+12.7	-8.49
Mn	3.849E-01	2.379E-01	1.924E-01	1.190E-01			1.476E+00	4.979E-01	7.381E-01	2.489E-01			+283	+109
Ni	8.630E-02	6.803E-02	3.020E-01	2.381E-01	1.027E-02	8.096E-03	8.511E-02	6.986E-02	2.979E-01	2.445E-01	1.013E-02	8.314E-03	-1.37	+2.69
Cu	1.306E-01	7.989E-02	2.285E-01	1.398E-01			2.697E-01	2.993E-01	4.720E-01	5.238E-01			+106	+274
Zn	4.783E+00	3.364E+00	1.116E+00	7.850E-01			9.646E+00	6.047E+00	2.251E+00	1.411E+00			+101	+79.7
As	4.879E-02	5.482E-02	1.139E+01	1.279E+01	5.123E-03	5.756E-03	6.668E-02	5.451E-02	1.556E+01	1.272E+01	7.001E-03	5.724E-03	+36.6	-0.56
Cd	2.641E-03	2.452E-03	1.849E-01	1.716E-01			3.365E-03	2.639E-03	2.355E-01	1.847E-01			+27.3	+7.65
Pb	2.592E-02	1.065E-02	4.537E-01	1.864E-01	1.542E-05	6.336E-06	1.031E-02	7.246E-03	1.804E-01	1.268E-01	6.134E-06	4.311E-06	-60.2	-31.9
HI			2.025E+01	1.886E+01					2.694E+01	1.951E+01			33.01	3.46

Table 4. Exposure, HQ and HI scores of diatoms and percentage exchange rates from dry to wet seasons

Toxicant	RfD	Summer – Dry (Before Paddy Harvest)				Autumn – Wet (After Paddy Harvest)				% Exchange
		Exposure assessment		Non-carcinogenic risk		Exposure assessment		Non-carcinogenic risk		
		Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	
Cr	3,000E-03	1,802E-07	6,307E-10	6,006E-05	2,102E-07	1,486E-06	5,203E-09	4,955E-04	1,734E-06	+725
Mn	1,400E-01	1,904E-06	6,664E-09	1,360E-05	4,760E-08	1,189E-05	4,161E-08	8,492E-05	2,972E-07	+524
Ni	2,000E-02	9,860E-08	3,451E-10	4,930E-06	1,725E-08	1,835E-06	6,423E-09	9,176E-05	3,212E-07	+1761
Cu	4,000E-02	7,034E-08	2,462E-10	1,759E-06	6,155E-09	2,305E-07	8,066E-10	5,761E-06	2,016E-08	+228
Zn	3,000E-01	2,535E-07	8,873E-10	8,451E-07	2,958E-09	6,066E-06	2,123E-08	2,022E-05	7,077E-08	+2293
As	3,000E-04	9,952E-09	3,483E-11	3,317E-05	1,161E-07	2,087E-07	7,306E-10	6,958E-04	2,435E-06	+1997
Cd	1,000E-03	1,583E-09	5,541E-12	1,583E-06	5,541E-09	4,099E-08	1,435E-10	4,099E-05	1,435E-07	+2490
Pb	4,000E-03	3,005E-07	1,052E-09	7,513E-05	2,630E-07	3,229E-06	1,130E-08	8,072E-04	2,825E-06	+974
$HI_{ing/derm}$				1,911E-04	6,688E-07			2,242E-03	7,848E-06	1073

Discussion

In the current research, temporal variations of toxic elements in diatoms and fishes of a worldwide significant migratory bird stopover habitat were evaluated by using some potential human health risk assessment indices and the most effective bioindicator organism group has been revealed by comparing the bioaccumulation levels of toxicants in tissues of fishes and in frustules of epiphytic diatom (kieselguhr soil) before and after paddy harvest periods, which is known to be the most significant stress factor for the lake.

There are three major pathways including ingestion, dermal contact and respiration considered in potential human health risk assessment in general. This research focused on the ingestion pathways in terms of fish muscles and ingestion and dermal contact pathways in terms of diatom frustules. As a result of applied health risk evaluation techniques, consumption of fishes living in the Gala Lake was found as quite risky in terms of both non-carcinogenic and carcinogenic effects, while the non-carcinogenic health risks of toxic metals bioaccumulated in the diatoms were found to be as lower in terms of both ingestion and dermal contact. In addition, significant increases in toxic element bioaccumulation levels both in fishes and diatoms after the paddy harvest period (APH) were recorded and As was determined as the riskiest toxicant for the lake (Fig. 4).

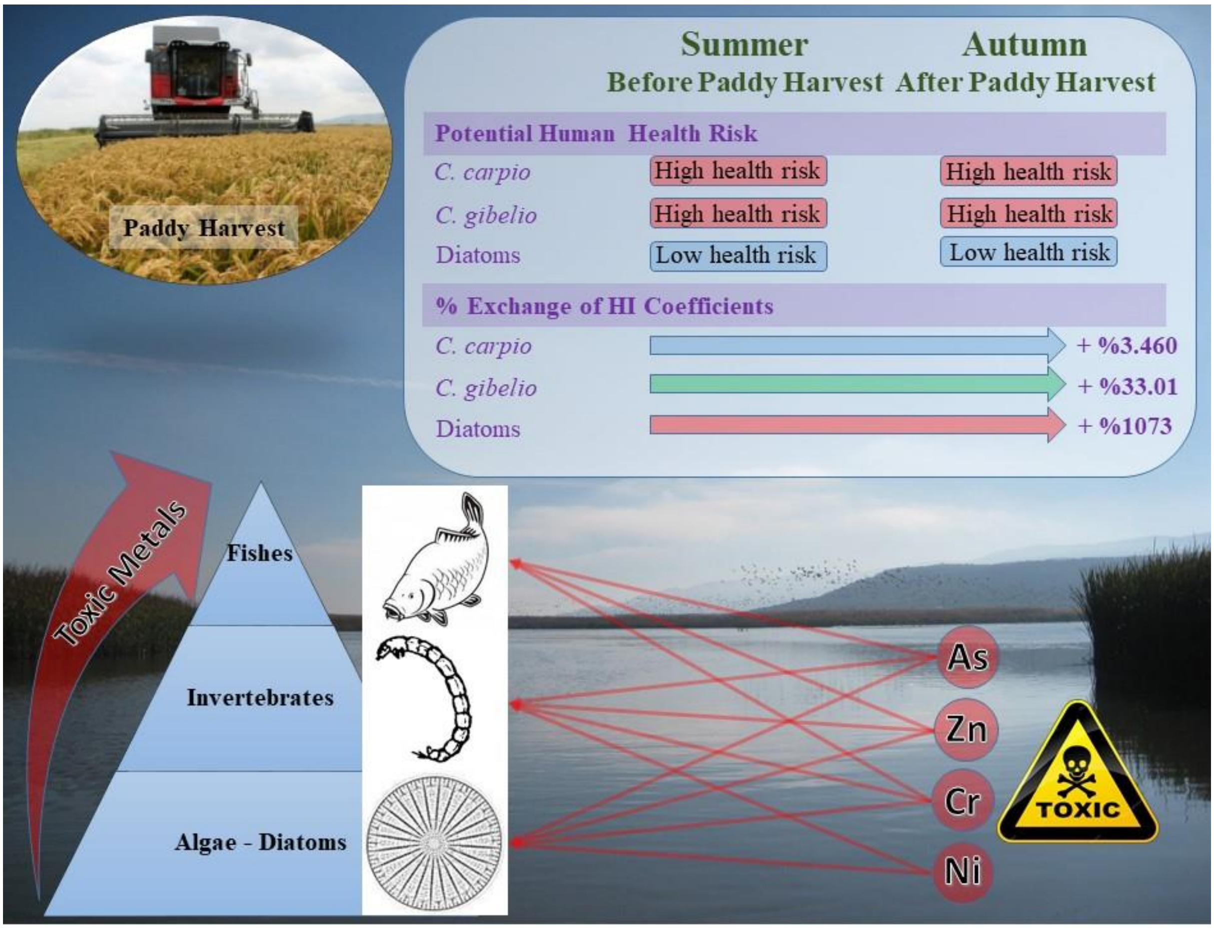

Fig. 4. A visual summary of the research data and an image from the Gala Lake

Arsenic is known as a carcinogenic and toxic element and many industrial processes and especially use of pesticides with high arsenic content contribute to arsenic contamination of air, water and soil. Exposure of arsenic may cause many significant health problems including immunological disorders, cardiovascular disorders, dermal lesions, reproductive failure and skin cancer (Liu et al. 2013, Çiçek et al. 2014, Bhowmick et al. 2018). In the present research, arsenic was recorded as the most dangerous toxicant for fishes of the Gala Lake, and calculated THQ and CR coefficients for arsenic were found significantly higher than the limit values.

Gala Lake, which is located in the north – west part of Turkey, is known as one of the most significant wetlands of Turkey in terms of especially biodiversity. It is covering about 750 ha area of Meriç Delta, where contains many productive farmlands. Gala Lake, which was declared as "National Park" in 2005, allows dwelling many birds migrating between Europe and Africa. But unfortunately, this internationally important wetland is under effect of an intensive pressure of agriculture. Cultivation of paddy is a quite an intense around the Gala Lake and it is known that about 25% of total rice production of Turkey is being supplied from Meriç Plain. Paddy harvest of the region starts in autumn season and gradually continues until the end of this season and drainage waters from these rice cultivation lands are being discharged to the Gala Lake through numbers of irrigation canal systems (Erkmen and Kolankaya 2006, Güher et al. 2011, Öterler 2017, Tokatlı 2015, 2017, 2018, Batur and Maktav 2019, Tokatlı and Ustaoğlu 2020, Varol and Tokatlı 2021).

Efficient bioindicators are required to evaluate the contamination status of freshwater ecosystems subjected to toxic metals. Many researches have considered the suitability of algae and fishes as bioindicators of toxic metal contamination (Caçador et al. 2012, Chakraborty et al. 2014, Billah et al. 2017, Plessl et al. 2017, Chua et al. 2018). It is known that suitable and effective toxic metal bioindicators may accumulate quite high levels of toxicants without death (Zhou et al. 2008). But additionally, best bioindicators have to show quite high sensitive to changes in the water environment. and bioindicators should also show a significant relation between the levels of toxic metals in the surrounding habitats and in their tissues (Bonanno and Orlando-Bonaca 2018, Hu et al. 2019). Varol and Tokatlı (2021) reported that paddy fields are being adversely effected the water quality of Gala Lake. According to the results of this research, which was conducted at the same time with the present research, As levels increased about 3 times; Ni and Cu levels increased about 15 times; Cr, Cd and Pb levels increased about 50 times; and Zn levels increased about 200 times in water of Gala Lake after the paddy harvest period. Similarly, to the data of this research, significant increases were recorded in the toxic metal levels in the epiphytic diatom frustules in the after paddy harvest period and also the health risk coefficients recorded in diatoms were much higher than those recorded in fishes in this season.

Diatoms are highly diverse and can reach higher productivity than other algae species. Some diatoms may survive even in very contaminated waters, because they are well adapted to use their efficient cellular systems in combating toxicants. Their 3-dimensional frustule nano-architecture that composed almost purely of silica provide quite large contact area facilitating in toxic metal binding (Atıcı et al. 2016, 2018, Lin et al. 2020, Tokatlı et al. 2020, Marella et al. 2020, Solak et al. 2020). As a result of this research, it has been determined that the potential human health risk coefficients calculated in diatoms increase much more than those detected in fishes during the APH period, when rapid pollution discharges occur in the Gala Lake. Also the non-carcinogenic health risks of toxic metal contaminated diatoms were found to be as quite low, while the non-carcinogenic and carcinogenic health risks of toxic metal contaminated fishes were found to be as quite high.

Conclusions

This research was conducted to identify the best toxic metal accumulation bioindicator organism for an A Class Wetland under effect of an intensive paddy cultivation stress. In this investigation, some trace and toxic element bioaccumulation levels including As, B, Cu, Zn, Ni, Cr, Se and Mn were investigated in diatoms and fishes living in Gala Lake, which are located at the bottom and at the top of the food chain in the freshwater ecosystems. Also potential human health risks (1) associated with the consumption of fishes were evaluated by calculating “Estimated Daily Intake (EDI)", "Target Hazard Quotient (THQ)", "Hazard Index (HI)" and "Cancer Risk (CR)" and (2) associated with the consumption and dermal contact of diatoms were evaluated by calculating "Exposure-Ingestion (Exp_{ing})", “Exposure-Dermal (Exp_{derm})”, "Hazard Quotient (HQ)" and "Hazard Index (HI)". In order to detect the most sensitive bioindicator organism to toxic element changes in water environment, care was taken to collect the biotic samples in dry – before paddy harvest (BPH) and wet – after paddy harvest (APH) periods, which are known to affect the toxic metal accumulation levels in water of the lake at a maximum level.

According to detected data, toxic metal concentrations were increased significantly in the frustules of diatom communities in the APH period, while less significant exchanges were determined in muscle, gill and liver tissues of *C. gibelio* and *C. carpio*, in general. The total toxic element accumulation levels increased an average of 23 times in fishes and 1800 times in diatoms, while the HI scores increased an average of 20 times in fishes and 1000 times in diatoms, in the APH period. The data clearly reflects that the diatoms are much more sensitive to instant changes in the environmental conditions than fishes. Therefore, diatoms are recommended as effective and useful bioindicators in toxic metal bioaccumulation researches and may be used as a biological tool for the elimination of toxic metal pollution in freshwater ecosystems.

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Author contribution

Cem TOKATLI established the idea of the research, obtained all the data, assessed the obtained data and prepared the manuscript.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication All authors have given their consent to publish this research article.

Competing interests The authors declare no competing interests.

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