RISK ASSESSMENT OF TRACE METAL CONCENTRATIONS IN SEDIMENTS OF THE MAIPO RIVER BASIN AND ITS RELATIONHIP WITH BIOACCUMULATION IN BENTHIC ORGANIMS

SYLVIA V. COPAJA [a], GIGLIOLA MUÑOZ [a], DAVID VÉLIZ [b,c] AND CAREN VEGA-RETTER [b]*

[a]*Departamento de Química.*
[b]*Departamento de Ciencias Ecológicas, Facultad de Ciencias. Universidad de Chile.*
[c]*Centro Milenio de Ecología y Manejo Sustentable de Islas Oceánicas (ESMOI), Coquimbo Chile.*

Trace elements in aquatic ecosystems are considered as major pollutants due to their environmental persistence, toxicity and ability to be incorporated into food webs. Contaminated sediments represent a threat to benthic macroinvertebrates which in turn expose high trophic organisms to hazardous trace elements, therefore metals accumulated in benthic organisms can also be bio concentrated in food webs. Direct toxic effects of metals include changes in diversity and abundance of benthic invertebrates while, indirect effects include modifications of species interactions and reductions in food quality. In this work, we study the potentially toxic metal concentrations in both sediments and benthic macroinvertebrates in the Maipo River basin (central Chile) evaluating the risk assessment of sediment, toxicity to the biota and bioaccumulation in the organisms.

Sediments and benthic organisms were sampled in spring (October-December) 2016 from four sites of the Maipo River basin. Twelve trace elements (As, Al, Cd, Cu, Cr, Hg, Fe, Mn, Mo, Ni, Pb and Zn) were determined by AAE. The Geo accumulation index showed that Zn was moderate to strong pollute in all sites and the enrichment factor showed that there were no important anthropic impacts in the river. High level of contamination was found for Cu in PEL and the pollution index showed that PEL was extremely polluted. Three (Cu, Mn and Zn) out of the five metals analyzed were the elements which presented the largest toxicity to organisms in these aquatic systems based on the Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) analysis. Most of the metals analyzed did not show bioaccumulation; however, Ni and Pb were the metals with the highest bioaccumulation factor in all the studied sites.

Keywords: Trace metals; benthic organisms; sediments, Maipo River Basins; bioaccumulation.

1. INTRODUCTION

Metal pollution is of widespread concern for aquatic ecosystems management [1][2]. Both anthropogenic pressures (e.g. industrial activities, mining, and urban runoff) and natural processes (e.g. weathering) account for trace metals in aquatic ecosystems [3][1][2]. The release of metals into aquatic ecosystems through natural processes like weathering is highly dependent on geology [4] and mining is regarded as a significant source of mercury, lead and others metals contamination in the environment [5][6][7]. Trace elements in aquatic ecosystems are considered as serious pollutants due to their environmental persistence, toxicity and ability to be incorporated into food webs [8]. However, metals in natural waters can play an important role in the biological function of the aquatic organisms. Some metals are considered essential, such as Fe, Al, Zn, while others, such as Cr and Ni, can present a high toxicity level to living organisms. Overall, even essential metals can be toxic in high concentrations [9].

Pollutants introduced into an aquatic system, can be greatly modified by interaction with natural variables of water, and they can be toxic just by their presence or by degradation processes [10]. Sediment samples have proved to be useful in studying trace elements levels accumulation because they act as sinks and usually contain historical evidence of natural and anthropogenic fluxes of metals [11][12][13][14]. Attached to or intimately linked with the sediments inhabit the benthic macroinvertebrates, which are the primary material exchangers across the sediment-water interface [15][16]. Then, contaminated sediments represents a threat to benthic macroinvertebrates which in turn expose high trophic organisms to hazardous trace elements [17][2], therefore metals accumulated in benthic organisms can also be bioconcentrated in food webs [18].

Aquatic biota can assimilate metals from ingestion of contaminated food [19], the water column or sediment through direct uptake across the gill surfaces and other external body parts [20][21]. Macroinvertebrates are key components of aquatic food webs that link organic matter and nutrient resources (e.g. leaf litter, algae and detritus) with higher trophic levels, for example fish [22] and they are also a major component of stream biodiversity [23]. The distribution of aquatic macroinvertebrate communities is controlled by factors such as habitat characteristics, water and sediment quality, pollution and biological factors such as competition and predation [24]. Because of this, many indices based on macroinvertebrate communities have been used to assess the pollution status of freshwater ecosystems [25]. *Ephemeroptera*, *Plecoptera* and *Trichoptera* species have been pointed out as sensitive species, while Oligochaeta and Chironomidae has been indicated as tolerant taxa [26]. Guilpart et al. (2012)[27] detected an increase in the total abundance of macroinvertebrates immediately downstream a fish farm with an increase of the *Oligochaetes* and Chironomids proportions, while the proportions of *Ephemeropterans*, *Plecopterans* and *Trichopterans* decreased. Another study detected important changes in the macroinvertebrate community structure in the waterways contaminated by active and abandoned mining and industrial activities, indicating an ecological impairment [28]. However, most studies focus on the impact of organic pollution and eutrophication [29][30][31].

Benthic organisms can be directly and/or indirectly impacted by metals in water [32], substratum [33], and food resources [34][35][36]. Direct toxic effects of metals include changes in diversity and abundance of benthic invertebrates [37] while, indirect effects include modifications of species interactions [38] and reductions in food quality (Carlisle, 2000)[39]. Thus, benthic organisms, beyond their abundance and diversity, could be used as sentinels in biomonitoring programs in freshwater indicating the environmental implications of these pollutants [40] and to determine the transfer process of metals to higher trophic levels.

Maipo River basin is the main hydrographic basin of the Metropolitan Region, Chile; its waters come from both winter precipitation and mountain snowmelt. This hydrographic basin covers practically the entire territory of the Metropolitan Region and part of Regions V and VI, Chile, draining an area of 15,304 Km^2 and with a length of 250 km, being the main source of water in the Metropolitan Region, serving around 70% of the current demand for potable water and about 90% of irrigation demands, in addition to other uses of the basin, such as the use of its flows for hydroelectric power plants [41]. In the surroundings, there is a high concentration of inhabitants (practically 40% of the national population lives in the vicinity of this basin) and industries, with a total of 12 highly populated localities. Most of the lands of the basin are used for crops, vineyards, livestock, etc. This basin also contains the largest number of factories in the country, in addition to the presence of mining in the Andes, which adds heavy metals to the Maipo River basin [41]. Studies of fish diversity over the last 30 years have shown a significant reduction in species richness and abundance in this basin. Moreover, recent studies showed effects of the pollution on the biota, for example on the silverside fish *Basilichthys microlepidotus* [42] studied 5 five populations of the silverside, two inhabiting polluted areas and three non-polluted areas, identifying evidence of selection on loci related to pollution [43] and upregulation of genes related to cell proliferation, suppression and progression of tumors and to apoptotic processes in the populations inhabiting the polluted areas [44]. An study show that the macroinvertebrate community inhabiting a non-polluted site of the basin presents higher taxa richness, caloric and lipid content than the macroinvertebrate communities inhabiting polluted sites [45].

**Corresponding author email: svcopaja@gmail.com*

Under this context, the goals of this study were to determine: i) the risk assessment and toxicity of sediment to aquatic ecosystem, ii) potentially toxics metals concentrations in sediments to benthic macroinvertebrates in the Maipo River basin and, iii) bio magnification effect of trace elements in macroinvertebrates.

2. MATERIALS AND METHODS

2.1 Study area and sampling

Sediments and benthos organisms were sampled in spring (October-December) 2016 from four sites of the Maipo River basin (central Chile), namely Isla de Maipo (IM), San Francisco de Mostazal (SFM), Melipilla (Mel) and Pelvin (PEL), with the geographic coordinates of sites recorded using a GPS system (Figure 1). San Francisco de Mostazal (SFM; 33º58'19.97" S, 70º42'56.49" O), Isla de Maipo (IM; 33º44'58" S, 70º53'26" O), Melipilla (MEL; 33º42'49,988" S, 71º12'39,13" O), Pelvin (PEL; 33º36'21" S, 70º54'33" O). For each site three samples of sediment were taken, while five samples of macroinvertebrates were collected in each site. Samples were transported in cool until the laboratory. The macroinvertebrates were collected at each site using a 30x30 cm Surber network, removing all the bento attached to the rocks and stored in plastic bottles [46]. While, sediment samples (1kg) were collected in a polyethylene bag, according to the protocol sediment collection [47]. Sediment samples were collected from the top 10 cm of the surface using a plastic shovel. Samples were stored at 4 °C in the laboratory. Sediments were dried in polyethylene trays at room temperature, and were sieved into of a particle size less 0.063 mm.

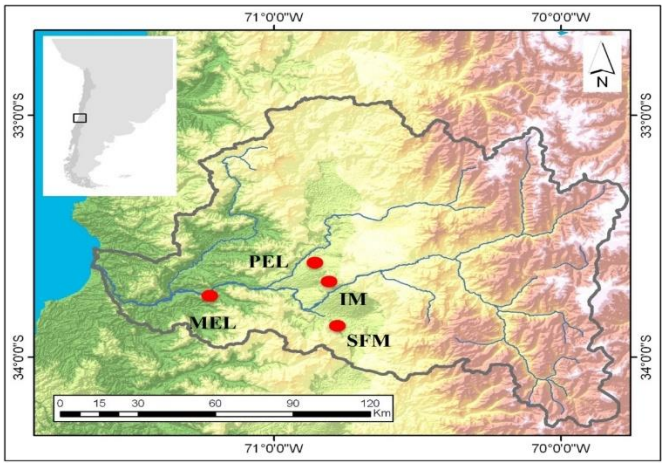

Figure 1. Sampling sites in Maipo River basin. IM: Isla de Maipo, MEL: Melipilla, PEL: puente Pelvin, Peñaflor, SFM: San Francisco de Mostazal.

2.2 Material preparation.

The material used for the sampling and the analysis of the samples in laboratory, was pre-treated, to avoid and rule out possible contamination. This was made for both polyethylene plastic materials and glassware. It was washed with potable water and Extran® detergent (Merck), then rinsed with plenty of potable water and distilled water. A 2% solution of nitric acid (HNO_3) Suprapur® (Merck) was added, allowing it to stand for 48 hours. It was subsequently rinsed with distilled water and then with Milli-Q grade deionized water. It was left to dry until later use.

2.3 Trace elements analysis

The trace elements analyzed in this study were: As, Al, Cd, Cu, Cr, Hg, Fe, Mn, Mo, Ni, Pb and Zn. To perform the digestions of the total fraction of the metals in sediment, microwave oven MarsXpress 5 was used, equipped with tubes of Teflon PFA of 55 mL, protective sleeves of kevlar and an Xpress temperature sensor. This digestion allows greater control over the sample temperature and the heating rate than that of the heating plates. This digestion facilitated in closed containers ensuring that the trace analyses are accurate and precise. The total fraction was obtained by digesting 0.25 g of sediment with 10 mL of nitric acid (suprapur Merck) in a microwave oven (MarsX press) using the following conditions power 800 W; tower 100-5; time 11 min.; temperature 175 ºC, maintenance 15 min.; cooling 15 min. This was based on EPA method 3015, finally, the samples were kept cold (4 ºC) for posterior analysis.

For the trace elements concentration in benthos, 0.25 g were digested in the high-resolution microwave (Marsx Press) (EPA Method 3015) with 10 mL 65 % Suprapur HNO_3 (Merck); digested samples were diluted 10 times with MilliQ (Table 1). The digested sample was taken to a final volume of 50 mL with miliQ grade deionized water.

Table 1. Digestion conditions of samples for quantification of trace elements.

Matriz	Stage	Power (W)	Power (%)	Time (min)	Temperature (°C)	Time (min)
Sediments	2	400 800	80 80	5:50 5:50	175 180	4:00 10:00
Benthic organisms	1	1600	65	15:00	200	15:00

2.4 Chemical analysis

Only analytical grade chemicals were used in the study. Aqueous solutions of the metals were prepared from Titrisol standards (Merck). Deionized water was used throughout the study (Millipore, milliQ grade,). All glassware and other containers were thoroughly cleaned by soaking in detergent, followed by soaking in 10% nitric acid (Suprapur 65% Merck) for 48 h, and finally rinsed with deionized water several times prior to use.

Trace elements concentrations were determined by flame atomic absorption spectrometry using a Shimadzu atomic absorption spectrometer (model AA-6800) with an air-acetylene flame. Operational conditions were adjusted to yield optimal determination. Quantification of the metals was based upon calibration curves standard solutions for the respective metals. To verify the accuracy of the data obtained, recovery experiments were performed using standard reference material for sediments (BCR-320R) and for biological tissue, (DOLT-4).

2.5. Experimental conditions

A sample of sediment or benthos, then samples were homogenized, diluted to 10 mL and measured immediately. Shimadzu atomic absorption spectrophotometer A- 6800 model with hydride generator HVG -1 was used As: λ = 193.7 nm and Hg: λ = 250.7 nm.

2.6 Assessment of sediment quality

Index	Equation	References
Geoacumulation index (I_{geo})	$\frac{geo = \log 2Cn}{1.5}$ Bn (eq. 1) C_n is the measured concentration of metal *"n"* in soil, B_n is the geochemical background value for the metal "*n*" in soil, while the 1.5 factor accounts for the possible variation in background data caused by lithology effects.	[48][49][50][51[[52][53]
Enrichment factor, *EF*	$EF = \frac{[Metal/Fe]_{Sample}}{[Metal/Fe]_{UCC}}$ (eq. 2) $[Metal]_{sample}$ is the amount of metal in soil and $[Metal]_{UCC}$ refers to the concentration of the same metal in the upper continental crust (UCC).	[53][54][55][49][51]
Contamination factor, CF	$CF = \frac{M_c}{B_c}$ (eq. 3) M_c and B_c are the metals' measured concentration and background values, respectively. The contamination factor is categorized into four lasses	
Pollution load index, PLI	$PLI_{site} = \sqrt[n]{CF_1 \times CF_2, \ldots, \times CF_n}$	[56][57][58][59][60][49][53][51][61[[62]

2.7 Toxicity index, PEC and TEC

TEC (threshold effect concentration) and PEC (probable effect concentration. Then, the TEC value indicates the concentration below which adverse effects are expected to occur rarely and PEC value indicates the concentration above which adverse effects are expected to occur frequently [63] (Table 2).

Table 2. Toxicity values of sediment.

Metal	TEC (mg·Kg^{-1})	PEC (mg·Kg^{-1})
Cooper	32	150
Lead	36	130
Zinc	120	460
Iron	20000	40000
Manganese	460	1100

2.8 Bioaccumulation Factor (BAF).

The concept of bioaccumulation refers to the accumulation of contaminants in aquatic organisms. The Bioaccumulation Factor (BAF) is expressed in terms of the ratio between the amount of a pollutant in a living organism and the concentration of the pollutant in the habitat [18]. This index is obtained by the following equation:

BAF = Trace elements (concentration in the benthos, mgkg^{-1}) / Trace elements (concentration in the sediment, total fraction (mgkg^{-1}).

3. RESULTS AND DISCUSSIONS

A total of twelve trace elements were quantified in both sediments and benthic organisms.

3.1. Trace elements concentration in sediments.

Trace elements were quantified in sediments total fraction; however, of the 12 metals analyzed, Cd, Hg and Mo were not detected. The concentrations of the detected elements are shown in Table 3.

Table 3. Metals concentrations in sediment of Maipo River basin (mgKg^{-1}). Each value is the average of three samples ± SD.

SITES	Al	As	Cu	Cr	Fe	Pb	Mn	Ni	Zn
SFM	24184± 30.1	0.2 0 ±0.011	125 ±1.8	41± 5.0	16196 ±29.0	45 ± 2	824 ± 6.6	10 ±0.2	109 ± 0.4
IM	18387± 11.9	0.182 ±0.003	65± 6.1	59± 6.1	10291 ±11.4	28 ± 5	537 ± 6.0	18 ± 1.3	126 ± 1.6
PEL	21057± 13.0	0.265 ±0.004	220 ±1.8	20 ± 5.2	10220± 12.4	38 ± 0.8	680 ± 5.2	5 ± 0.1	164 ± 9.1
MEL	22357± 14.5	0.318 ±0.003	66 ± 1.2	48± 3.9	9938 ± 1296	14 ± 1.0	781 ± 8.9	21± 2.3	111 ± 13

The results obtained for the total fraction show a similar trend in the 4 sites: Al> Fe> Mn; are the major metals whose concentrations fluctuate between Al: 24184 mgKg^{-1} in SFM and Mn 537 mgKg^{-1} in IM. Arsenic showed the lowest concentrations (0.318 - 0.182 mgKg^{-1}). The SFM site presented the highest concentrations in 4 of the 9 quantified metals.

3.1.2 Trace elements in benthic organisms

Nine out of twelve metal analyzed were quantified in macroinvertebrates. As, Hg and Cr were not detected. Due to the variability detected among samples, the concentrations found in the five replicates differed considerably, for this reason a range of the concentrations of the detected metals were considered. The highest concentrations correspond to Al and Fe, especially in SFM. The lowest concentrations correspond to Zn for all sites (Table 4).

Table 4. Range of concentration (µgg^{-1}) of metals detected quantified in macroinvertebrates.

METAL	SFM	IM	PEL	MEL
Al	4201 – 14519	2317 - 5981	2045 - 7841	84 – 40519
Cd	2.5 – 28.6	1.2 – 15.4	0.2 – 0.6	0.9 – 1.9
Cu	16 – 98	75 - 123	95 - 167	37 – 143
Fe	14298 – 27086	2764 - 6758	1971 - 6399	14298 – 27086
Mn	41 – 886	116 - 1052	186 - 401	633 – 1189
Mo	558 – 3433	2.8 - 600	12 - 89	93 – 702
Ni	16 – 351	5.9 - 130	13 - 15	16 – 59
Pb	261 – 5091	97 - 1156	27 - 166	134 – 931
Zn	7 – 12	0.6 - 727	2.3 – 4.5	0.8 – 427

3.2 Sediment toxicity

On the global scale, sediment of aquatic ecosystems serves as a sink for both organic and inorganic pollutants [64][65]. These pollutants can be released back into the water column through several pathways such as resuspension of sediment particles. Dredging, bioturbation, or via diffusive flux from sediment to water [66][67] [68]. Therefore, contaminated sediment often act as a secondary source of pollutants to aquatic ecosystem [69][70][71]. In the current context of the concern about water quality it is necessary to explore the potential ecological risk of trace metals in sediment of Maipo River basin.

3.2.1 Geo accumulation index

Considering our results shown that As, Al, Cu, Cr, Fe, Ni, Pb were unpolluted in all the sites, Mn is moderately polluted in MEL and, Zn is moderate to strong polluted in all the sites (Table 5).

Table 5. Geoaccumulation index calculated. Ranges and meaning of the index: $0 \leq$ Igeo unpolluted; $0 \leq$ Igeo ≤ 1 unpolluted to moderately polluted; $1 \leq$ Igeo ≤ 2 moderately polluted; $2 \leq$ Igeo ≤ 3 moderately to strongly polluted; $3 \leq$ Igeo ≤ 4 strongly polluted; $4 \leq$ Igeo ≤ 5 strongly to extremely polluted; Igeo ≥ 5 extremely polluted.

Sites	Metals								
	Al	As	Cu	Cr	Fe	Mn	Ni	Pb	Zn
SFM	0.06	0.003	0.56	0.09	0.07	0.19	0.29	0.45	**2.29**
IM	0.05	0.003	0.29	0.13	0.04	0.13	0.53	0.28	**2.65**
PEL	0.05	0.004	0.98	0.04	0.04	1.76	0.15	0.38	**3.45**
MEL	0.06	0.005	0.29	0.11	0.04	**2.22**	0.62	0.14	**2.33**

3.2.2 Enrichment Factor

Table 6. Enrichment factor (EF) calculated from eq 2. Ranges and meaning of the index: EF < 1 = Natural, Litogenic; 1<EF<10 = Natural and antropic; EF>10 = Important entropic contribution.

Sites	Metals							
	Al	As	Cr	Cu	Mn	Ni	Pb	Zn
SFM	**3.31**	1.03	0.47	1.45	1.42	0.19	0.35	2.32
IM	**3.97**	1.45	1.08	1.29	1.44	0.55	0.35	**4.22**
PEL	**4.57**	2.20	0.51	**4.39**	1.83	0.16	0.47	**5.53**
MEL	**5.00**	2.77	0.91	1.31	2.19	0.68	0.18	**3.85**

Cr in SFM, PEL and MEL and Ni, Pb in all of sites are in natural, litogenic conditions, while Al, As, Cu, Mn and Zn presents natural and anthropic conditions in all the studied sites and, Cr only in IM (Table 6). These values suggest that there is no important anthropic impact in the river. Other Chilean basins have shown high EF values for Cu and Zn. For example, in the Choapa River Basin an EF value of 31.9 and 22 was detected for Cu and Zn, respectively, which is in accordance with the assumption that Cu and Zn are carried into the river by mining activities. Further, large enrichment factor of 17.6 for Cu was observed in the Cachapoal basin, which could be associated with Cu-enriched from a treatment plant [72].

3.3 Contamination factor, CF

Al, As, Cr, Fe, Mn, Ni and Pb in MEL showed low contamination factor; Cu in SFM, IM, and MEL; Pb in SFM, PEL and IM showed a moderate contamination and considerable contamination factor was detected for Cu in PEL (Table 7).

Table 7. Contamination factor (CF) calculated from eq 3. CF < 1: low contamination; 1 ≤ CF < 3: moderate contamination; 3 ≤ CF < 6: considerable contamination; CF ≥ 6: high contamination.

Sites	Metals								
	Al	**As**	**Cu**	**Cr**	**Fe**	**Pb**	**Mn**	**Ni**	**Zn**
SFM	0.30	0.015	2,77	0.46	0.34	2.25	0.97	0.15	1.15
IM	0.23	0.014	1.44	0.66	0.22	1.40	0.63	0.26	1.33
PEL	0.26	0.020	**4.88**	0.22	0.22	1.90	0.80	0.07	1.72
MEL	0.28	0.024	1.46	0.53	0.21	0.70	0.92	0.31	1.67

3.4 Pollution load index, PLI

Values of Pollution index show that the three sites SFM, IM and Mel are strongly polluted while PEL is extremely polluted (Table 8).

Table 8. Pollution load index (PLI), calculated from eq.4. PLI < 1 indicate a no-pollution status of the assessed soil; PLI > 1: indicates pollution; 1 < PLI < 2: indicates a moderate pollution; 2 < PLI < 10: indicates strong pollution; PLI > 10: indicates an extreme pollution.

Sites			
SFM	**IM**	**PEL**	**MEL**
8.43	6.18	10.09	6.09

3.3.1 Toxicity index

TEC and PEC values are shown for five of the nine heavy metals found in sediments, because there are not values for Al, Cr, Ni, Cd. TEC value indicates the concentration below which adverse effects are expected to occur rarely and PEC value indicates the concentration above which adverse effects are expected to occur frequently [63].

Table 9. Toxicity of sediments to biota from TEC and PEC values (Table 2) related with metal concentration (Table 3).

Cu	Fe	Mn	Pb	Zn
Above TEC in all of sites and below PEC in all of sites except PEL	Below TEC and PEC in all sites	Above TEC and below PEC in all sites	Above TEC in SFM and PEL sites, and below PEC in all the sites	Above TEC in IM and PEL sites and below PEC in all of sites

Overall, of the five metals considered, Cu, Mn, Pb and Zn were the elements which present the greatest toxicity to the organism of these aquatic systems based on the TEC and PEC analysis. Similar results were found in Lluta River basin [73].

3.5. 1 Bioaccumulation factor in Benthic organisms (BASF).

Bentos or zoobentos is the invertebrate community that inhabits the solid-liquid interface of aquatic systems. The solid phase is fundamentally the sediment, which is why the concentration of metals in the total fraction has been considered. The BASF factor indicates the bioconcentration that these organisms present with respect to the trace elements present in the habitat of these organisms.

As, Cr and Hg were below the limit of detection in macroinvertebrates, whereas Cd and Mo were not detected in the sediments. Then, it was not possible to establish the BASF factor for these metals, most of the analyzed metals did not show bioaccumulation; however, Ni and Pb showed bioaccumulation in all the sites. In addition, Cu and Mn shows bioaccumulation in IM and Fe in SFM (Table 10).

Table 10. Range of bio concentration factor calculated in Benthos. Range was calculated using the concentrations detected from the 5 samples of each site. Values >1.0 in bold.

METAL	SFM	IM	PEL	MEL
Al	0.17-0.60	0.13-0.30	0.10-0.37	0.004-0.05
Cu	0.13-0.79	0.64-**1.89**	0.43-0.76	0.55-**2.17**
Fe	0.88-**1.76**	0.27-0.66	0.39-0.63	0.29-0.52
Mn	0.05-0.10	0.22-**1.96**	0.27-0.59	0.81-15.22
Ni	**1.59-35.13**	0.33-**2.20**	**2.60-2.30**	0.76-**2.80**
Pb	0.0-**113.10**	**3.40-55.90**	0.71-**4.37**	**9.50-66.50**
Zn	0.007-0.020	0.005-0.060	0.020-0.030	0.0008-0.040

CONCLUSIONS

Trace elements were found in sediments and benthos in the four sites studied from Maipo River basin.

Geo accumulation index shown that Zn is moderate to strong pollute in all the sites, while enrichment factor shown that there is no important anthropic impact in the river.

Values of Pollution index shown that PEL was extremely polluted.

Based on the TEC and PEC analysis, from the five metals considered, Cu, Mn and Zn were the elements which present the greatest toxicity to the macroinvertebrates of the basin.

Finally, Ni and Pb show bioaccumulation in all the sites.

ACKNOWLEDGMENT

The authors are grateful to the Fondecyt Project 11150213 and Proyecto Enlace Universidad de Chile 2013.

CONFLICT OF INTEREST.

The authors declare that they have no conflict of interest.

REFERENCES

1. Y. Iwasaki, T. Kagaya, K-I. Miyamoto, H. Matsuda, *Environm. Toxicol. Chem.* **28**, 354 (2009).
2. J. K. Bentum, M. Anang, K. O. Boadu, E.J. koranteng-Addo, E.O. Antwi, *Bull. Chem. Soc. Ethiop*, **25,** 191, (2011).
3. K.E. Carpenter, *Ann. Appl. Biol.* **12,** 1, (1925).
4. S. Gupta, U.S.Banerjee, *Int. J. Geomat. Geosci.*, **2** , 853, (2012).
5. R. Hanson, D.K. Dodoo, D.K. Essumang, J. BlaY, K. Yankson, *Bull. Environm. Contam. Toxicol.* **79** 544,(2007).
6. S. Obiri, *Environm. Monit. Assess.* **130,** 455, (2007).
7. N. Singh, J. Koku, B. Balfors, *J. Creative Commun.*, **2,** 361, (2007).
8. A. Demirbas, *J. Hazard Mater.* **157,** 220, (2008).
9. D.M. Templeton, F. Ariese, R. Cornelis, i.Q. Danielsson, H. Muntau, H.P. van Leeuwen, R. Lobiñski, *Pure Appl. Chem.*, **72,** 1453, (2000).
10. C. Pettersen, K. Hakanson, S. Karlson, B. Allard, *Water Res.* **27,** 863, (1993).

11. Z. Hseu, Z. Chen, C. Tsai, C. Tsui, S. Cheng, C. Liu, H. Lin, *Water Air Soil Pollut.,* **141,** 189, (2000).
12. A. Aksoy, D. Demirezen, F. Duman, *Water Air Soil Pollut.* **164**, 241, (2005).
13. H. l. Nguyen, M. Leermakers, J. Osán, S. Török, W. Baeyens, *Sci. Total Environ.,* **340,** 213, (2005).
14. L.K. Boamponsem, J. I. Adam, S.B. Dampare, E. Owusu-Ansah, G. Addae , *J. Chem. Pharm. Res*., **2,** 504, (2010).
15. C.p. Hawkins, M.L. Murphy, N.H. Anderson, *Ecology*, **63,** 1840, (1982).
16. Q.A. Hussain, A.K. Pandit, *Int. J. Fish. Aquat. Sci.,* **4,** 114, (2012).
17. A. Begum, S. Harikrishna, I. Khan, *Int. J. Chem. Tech. Res.* **1**, 245, (2009).
18. M. Klavinš, A. Briede, A. Parele, V. Rodinov, I. Klavina, *Chemospher,* **36,** 3043, (1998).
19. R.W. Merritt, K.W. Cummins, *An Introduction to the Aquatic Insects of North America* Second ed. Kendall Hunt, Bubuque, Iowa, (1984).
20. E.E. Dodge, T.L. Theis, *Environ. Sci. Technol.* **13,** 1287, (1979).
21. L. Hare, A. Tessier, P.G.C. Campbell, *Can. J. Fish. Aquat. Sci.* **48,** 1481, (1991).
22. C.Yoshimura, K. Tockner, T. Omura, O. Moog O 2006 *Limnology* , **7**, 63, (2006).
23. D.J.H. Phillips, P.S. Rainbow, *Biomonitoring of Trace Aquatic Contaminants*. Elsevier Applied Science, London. 371 p (1993).
24. E.T.H.M. Peeters, R. Gylstra, J.H. Vos, *Hydrobiologia,* **519**, 103, (2004).
25. T. Mangadze, *Sci. Total Environ*., **695**, 13391, (2019).
26. C. Wang, B. Viktória, C. Stenger-Kovács, X. Li, A. Abonyi, *Hydrobiologia*, **818**, 163, (2018).
27. A. Guilpart, J.M. Roussel, J. Aubin, T. Caquet, M. Marle, *Ecol. Indic.*, **23**, 356, (2012).
28. I.A. Wright, M.M. Ryan, *Hidrobiología*, **772**, 103, (2016).
29. A. Chakona, C. Phiri, C.H.D. Magadza, L. Brendonck, *Hydrobiologia* **607,** 199, (2008).
30. A. Chakona, C. Phiri, T. Chinamaringa, N. Muller, *Aquat. Ecol.,* **43,** 1095, (2009).
31. T. Bere, B.B. Nyamupingidza, *Hydrobiologia,* **722,** 223, (2014).
32. P.M. Kiffney, W.H. Clements, *Environ. Toxicol. Chem,* **15,** 1352 (1996).
33. P. M. Chapman, F. Wang, C. Janssen, G. Persoone, H. E. Allen, *Can. J. Fish. Aquat. Sci*., **55,** 2221, (1998).
34. L. Hare, *Crit. Rev. Toxicol,* **22,** 327, (1992).
35. P.M. Kiffney, W.H. Clements, *Environ Toxicol Chem,* **12,** 1507, (1993).
36. A.M. Farag, D.F. Woodward, J-N. Goldstein, W. Brumbaugh, J.S. Meyer, *Arch. Environ. Contam. Toxicol*. **34,** 119, (1998).
37. W.H. Clements, *Am. Benthol. Soc.*, **13,** 30, (1994).
38. W.H. Clements, *Ecol Appl.,* **9,** 1073, (1999).
39. D.M. Carlisle, *J. Aquat. Ecosyst. Stress Recovery*, **7,** 155, (2000).
40. A.H. Lorenzi, D.J. Cain, F. Parchaso, J.K. Thompson, S.N. Luoma, M.I. Hornberger, J.L. Dyke, *Water monitoring of trace metals and a benthic community near the Palo Alto Regional Water Quality Control Plant in south San Francisco Bay, California: 2007. U.S. Geological Survey Open File Report 2008*-1180. California: Menlo Park. 127 p (2008).
41. Dirección General de Aguas. *Diagnóstico y clasificación de los cursos y cuerpos de agua según objetivos de calidad, cuenca del Rio Maipo*. Ministerio de Obras Públicas, Gobierno de Chile, (2004).
42. C. Vega-Retter, P. Muñoz-Rojas, I. Vila, S.V. Copaja, D. Veliz, *Pop. Ecol*. **56,** 569,(2014) .
43. C. Vega-Retter, I. Vila, D. Veliz, *Evol. Biol*. **42,** 156, (2015).
44. C. Vega-Retter, N. Rojas-Hernandez, I. Vila, R. Espejo, D.E. Loyola**, S.V.** Copaja, M. Briones, A.W. Nolte, D. Veliz, *Sci Rep*, **8,** 4820, (2018).
45. M. Briones, *Efecto de la contaminación y el tipo de cauce sobre la estructura trófica del Río Maipo, usando como modelo a los macroinvertebrados bentónicos y al pejerrey Basilichthys microlepidotus*. Tesis Magister en Ciencias Biológicas, Facultad de Ciencias, Universidad de Chile, (2019).
46. R. Arocena, L. Aubriot, S. Bonilla, G. Chalar, D. Conde, G. Daners, F. Scasso, *Métodos en Ecología de aguas continentales, con ejemplos de limnología en uruguay*. Montevideo: DIRAC. EPA Method 3015, (1999).
47. S. Simpson, G. Batley, A. Chariton, J. Stauber, C. King, J. Chapman, W. Maher, *Handbook for Sediment Quality Assessment*, (2005).
48. H. Khademi, M. Gabarrón, A. Abbaspour, S. Martínez-Martínez, A. Faz, J.A. Acosta, *Chemosphere*, **217,** 705, (2019).
49. M.H.F. Monged, H.B. Hassan, S.A.El-Sayed, *Water Air. Soil Pollut.* **231,** 338, (2020).
50. G. Müller, *Geol J.,* **2,** 108, (1969).
51. N. Adimalla, J. Chen, H. Qian, *Ecotoxicol. Environ. Saf.*, **194,** 110406, (2020).
52. J.C.Egbueri, B.U. Ukah, O.E. Ubido, C.O. Unigwe, *Int. J. Environ. Anal. Chem* **98,** 1, (2020) .
53. C. Men, R. Liu, F. Xu, Q. Wang, L. Guo, Z. Shen, *Sci. Total Environ*., **612,** 138, (2018).
54. H. Khademi, M. Gabarrón, A. Abbaspour, S. Martínez-Martínez, A. Faz, J. A. Acosta, *Chemosphere*, **217,** 695, (2019).
55. D. Relic, S. Sakan, I. Andelkovic, A. Popovic, D. Dordevic, *Molecules*, **24,** 2139, (2019).
56. H-H. Jiang, L-M. Cai, H-H. Wen, G-C. Hu, L-G. Chen, J. Luo, *Sci. Total Environ.,* **701,** 134466, (2020).
57. D.L. Tomlinson, J.G. Wilson, C.R. Harris, D.W. Jeffrey, *Helol. Mees*., **33,** 566, (1980).
58. D. Relic, S. Sakan, I. Andelkovic , A. Popovic, D. Dordevic, *Molecules*, **24**, 2139, (2019).
59. J.C. Egbueri, B.U. Ukah, O.E. Ubido, C.O. Unigwe, *Int. J. Environ. Anal. Chem.*, **98,** 1, (2020).
60. L. Hakanson, *Water Res.*, **14,** 975, (1980).
61. Y. Gan, X. Huang, S. Li, N. Liu, Y.C. Li, A. Freidenreich, *J. Clean. Prod.*, **221,** 98, (2019).
62. J. Li, G. Wang, F. Liu, L. Cui, Y. Jiao, *Source Apportionment and Ecological-Health Risks Assessment of Heavy Metals in Topsoil Near a Factory Ecological-Health Risks Assessment of Heavy Metals in Topsoil Near a Factory, Central China*. Berlin: Springer, (2020)
63. D.D. MacDonald, C. Ingersoll, T. Berger, *Contam. Toxicol*. **39,** 20, (2000).
64. T. Zoumis, A. Schmidt, L. Grigorova, W. Calmano, *Sci Total Environ.,* **266,** 195, (2001).
65. L. Nizzetto, M. Macleod, K. Borgå, A. Cabrerizo, J. Dachs, A.D. Guardo, D. Ghirardello, K.M. Hansen, A. Jarvis, A. Lindroth, B. Ludwig, D. Monteith, J.A. Perlinger, M. Scheringer, L. Schwendenmann, K.T. Semple, L.Y. Wick, G. Zhang, K.C. Jones, *Environ. Sci. Technol.,* **44,** 6526, (2010).
66. W. Salomons, N.M. De Rooij, H. Kerdijk, J. Bril, *Hydrobiologia,* **149,** 13, (1987).
67. T.M. Remaili, S.L. Simpson, E.D. Amato, D.A. Spadaro, C.V. Jarolimek, D.F. Jolley, *Environ. Pollut.*, **208,** 590, (2016).
68. L. Mustajärvi, E. Eek, G. Cornelissen, A.K. Eriksson-Wiklund, E. Undeman, A. Sobek, *Environ. Pollut.*, **231,** 854, (2017).
69. P.M. Linnik, I.B. Zubenko, *Lakes Reserv. Res. Manag.*, **5,** 11,(2000).
70. J. Eggleton, K.V. Thomas, *Environ. Int.,* **30,** 973, (2004).
71. A. Sobek, K. Wiberg, K.L. Sundqvist, P. Haglund, P. Jonsson, G. Cornelissen, *Sci Total Environ.,* **487,** 46, (2014).
72. S.V. Copaja, G. DíaZ, R. Toro, R. Tessada, P. Miranda, J.R. Morales, *J. Chilean Chem. Soc*., **57,** 1199, (2012).
73. S.V. Copaja, F. Muñoz, *J Chilean Chem Soc.,* **63,** 3788, (2018).