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Proposal of novel Predicted No Effect Concentrations (PNEC) for metals in freshwater using Species Sensitivity Distribution for different taxonomic groups

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Water pollution by metals and metalloids promotes toxic effects to aquatic biota especially in mining regions. Environmental legislation applied to protect aquatic life from the toxicity of metals relies on the definition of protective values (PVs) for each compound. Among methods used to define PVs, Species Sensitivity Distribution (SSD) curves enable the derivation of the Predicted No Effect concentration (PNEC). In this context, this is one of the first studies to propose the construction of acute and chronic split SSD curves built separately for three groups of freshwater organisms (algae, invertebrates and fish) to derive PNEC values for the 14 metals most commonly observed in iron ore mining tailings. Data used to construct split SSD curves were derived from the USEPA ECOTOX knowledgebase and EnviroTox databases and segregated according to the freshwater organism group and as "acute" or "chronic" toxicity. Then, split SSD curves were built using a minimum of nine species for each group to determine the hazardous concentration to 5% of species (HC_5) and PNEC values for each group. Once PNEC were derived, a framework was proposed to calculate the Bioavailabity Factor (BioF) used to adjust values for local bioavailability conditions considering water quality characteristics in different regions. The lowest acute PNEC were observed for algae and invertebrates and corresponded to Silver (Ag). Nearly half of calculated PNEC were below current PVs in practice in Brazil, United States (US), United Kingdom (UK), Canada and European Union (EU). Results reinforce the pertinence of: (i) splitting SSD curves to define PVs for metals; and (ii) taking bioavailability into consideration to correct PNEC for local conditions. In addition, outcomes suggest that it is critical to rethink PVs related to metals for aquatic life protection, mainly in Brazil and Minas Gerais state, a region known for extensive mining activity. Finally, PNEC values obtained in this study may be used for ecological risk assessment studies, especially in areas affected by mining and other activities that result in pollution by metals and metalloids, such as Brazil.

Keywords Ecotoxicity, Mining, Bioavailability, Environmental legislation, Aquatic life protection

Mining activities are important sources of metals and metalloids to water[1,2]. These compounds can be carried to water bodies located close to mining areas via surface runoff, erosion, discharge of contaminated effluents or dust settlement[3,4], resulting in pollution and toxicity to aquatic biota[5]. Hence, it is critical to monitor water quality for physicochemical parameters and ecotoxicological effects in watersheds affected by metal contamination.

Ecotoxicological assays are important tools for environmental quality monitoring and impact assessment. They allow for the identification and quantification of the effects of natural or synthetic compounds and environmental samples upon living organisms, populations and communities from different trophic levels and

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environmental compartments (terrestrial or aquatic)[6,7]. However, these assays demand time and resources. In most cases, especially in low and middle-income countries, it is not possible to perform field monitoring programs which include frequent ecotoxicological analyses to detect dynamic changes in toxicity in lotic systems. This becomes even more challenging when considering sudden shifts imposed by extreme events associated with climate change[8] and disasters, such as mining dam ruptures[9–11].

In this context, indirect methodologies, such as Ecotoxicological Risk Assessment (ERA), allow for the estimation of risks to aquatic biota and identification of critical areas for ecotoxicological sampling and monitoring. In ERA, the Risk Quotient (RQ) is calculated by dividing the Measured Environmental Concentration (MEC) of a pollutant obtained from conventional surface water monitoring programs by the Predicted No Effect Concentration (PNEC) of a compound[12].

The PNEC is defined as the concentration of a toxic compound below which most (90–95% of species) of the exposed organisms and ecosystem functions are unlikely to suffer unacceptable damage[13,14]. PNEC values are generally obtained from extrapolations of data from ecotoxicological assays performed with, in some cases, a limited number of species at an individual level[15] and may be derived through extrapolation of laboratory data by using (i) the deterministic method or (ii) the Species Sensitivity Distribution (SSD) method[16,17].

In the deterministic method, the PNEC is derived by dividing the lowest value reported for acute (Lethal concentration to 50% of species—LC_{50} or Effect Concentration to 50% of species—EC_{50}) or chronic toxicity (No Observed Effect Concentration to test organisms—NOEC or Effect Concentration to 10% of species—EC_{10}) by an Assessment Factor (AF). The AF is used to account for uncertainties of extrapolating laboratory results for a single species to a multi-species ecosystem and may vary broadly (10–1,000) depending on the considered effect and the quantity and quality of available ecotoxicity data[12]. This method can be applied for any sample size (n), yet the bigger the n, the more protective is the derived PNEC as there is a higher chance of accounting for the most sensitive species. Furthermore, the deterministic method only considers the most sensitive species in the database. It does not account for variability between species and the fact that a more sensitive species may occur in a certain environment.

In contrast, the SSD method allows for the estimation of a chemical concentration which represents hazard to 5% (HC_5) of species used as input in a SSD curve. The HC_5 is the fifth percentile of the cumulative distribution function (SSD curve) built with NOECs, EC_{10} or $L(E)C_{50}$ values obtained in ecotoxicity assays carried out with different species[18]. Using the SSD method, the PNEC is derived by dividing the HC_5 by an AF that may vary from one to five depending on the quality, diversity and representativeness of data used to build the curve[16,19]. This method considers ecotoxicological risk uncertainties[16,20] as the PNEC value is based on effect concentrations reported for various species[21]. As reported by Sorgog and Kamo[16], the SSD method tends to be recommended when there is high variability among toxicity data (standard deviation > 0.9).

The SSD approach has become widely applied in the United States (US), Canada, Australia, New Zealand and the European Union (EU), as a method for derivation of protective values (PVs) (water quality standard, criteria, benchmarks, guidelines)[22] for aquatic life protection, as well as for the estimation of PNEC to be used in ecological risk assessment and for the characterization of effects of chemicals to aquatic biota[15,16,20,23]. Although applied in scientific research in Brazil[1,24], the SSD approach is not yet required for the derivation of water quality standards. Current PVs in practice for chemicals in Brazil were defined 20 years ago (in 2005)[25] and were mostly imported from Canada and the US as according to the most restrictive value among all water uses (drinking water, aquatic life protection, water for animal consumption, irrigation, and recreation)[26] rather than considering a specific PV for aquatic life protection.

Considering the threat imposed by various metals to aquatic biota[27,28] and the risk of water contamination by metals, especially in regions of extensive mining extraction, aligned to the unfeasibility of frequent ecotoxicological monitoring in these regions, it is critical to propose novel PNEC values derived from robust ecotoxicology databases to be used as reference values in environmental risk assessment and for the definition of PVs aiming at aquatic life protection[26]. Considering advances in ecotoxicology in recent years due to the development of in vivo and in silico approaches, and more sensitive analytical methodologies which allow for the detection and quantification of lower concentrations of pollutants in environmental matrices, there is a critical need to update PVs to values that are more protective to aquatic biota. This is even more critical in low- and middle-income countries, such as Brazil, where PVs were derived from standards stablished elsewhere, and mining is one of the main economic activities.

Additionally, regulatory PVs derived from SSD methods are commonly based on singular (nonsplit) curves which consider all taxonomic groups simultaneously[29]. However, distinct taxonomic groups may show different sensitivities due to different modes of action of a similar compound[20,30]. Hence, a nonsplit SSD curve may present poor statistical fits to data and lead to higher HC_5 values compared to the HC_5 calculated from split SSD curves built exclusively with the most sensitive taxonomic groups, especially for acute toxicity[31]. Furthermore, environmental ecotoxicological assessments are carried out in laboratories for single taxonomic groups, since they present different responses to compounds[32], this justifies the construction of split SSD curves for different taxonomic groups. Oginah et al.[29] evaluated the effect of splitting or not splitting SSD curves for 180 compounds and identified that split SSD curves are scientifically more appropriate when data are available in high quantity and quality. Thus, split SSD curves may result in more accurate PVs and, consequently, in more reliable ecotoxicological risk assessments. The SSD method has been applied to derive PNEC values for metals and metalloids, such as Cadmium (Cd), Copper (Cu), Lead (Pb) and Zinc (Zn)[33]; Aluminum (Al), Cd, Cu, Manganese (Mn), Nickel (Ni), Pb, Selenium (Se) and Zn[34] and Cobalt (Co)[35]. However, all these studies proposed the derivation of PNEC from nonsplit SSD curves by using input data from all taxonomic groups available simultaneously in a single curve. Hence, the construction of split SSD curves for metals is one of the novelties of the present study.

Bioavailability is a fundamental factor for metals ecotoxicological assessments, as it directly reflects the fraction of the substance that is available for biological uptake. This fraction is usually limited for metals in aquatic systems under natural environmental conditions[36]. Water characteristics such as pH, hardness, temperature and Dissolved Organic Carbon (DOC) are directly affected by lithogeochemistry, which differs by watershed and region. These characteristics influence metal concentration and speciation, thus impacting metal bioavailability[37]. However, only a few studies in the scientific literature consider this important aspect to define HC_5 values and those which do so apply nonsplit SSD curves. Lathouri and Korre[36] evaluated temperature influence to HC_5 derived from Cu nonsplit SSD curves and observed lower HC_5 values in the cold season, since temperature has an effect on parameters that affect the Cu bioavailability, such as pH, dissolved solids, alkalinity and organic carbon concentration. Mebane et al.[28] evaluated Cu, Cd and Zn toxicity to aquatic insect communities, based on SSD curves and considering bioavailability.

Different procedures and tools, such as the Bio Ligand Model (BLM)[38], are available and currently used in some countries to correct PVs or build SSD curves considering water characteristics such as pH, hardness and DOC to better reflect bioavailability[39]. "User-friendly" tools, such as the Bio-met[40] and mBAT[41], allow for the calculation of the Bioavailabity Factor (BioF), which is a ratio of the "reference" HC_5 and the HC_5 adjusted for bioavailability. For instance, in the UK, there are specific requirements to adapt PVs for As, Cr, Cu, Fe, Mn and Zn by correcting bioavailability. Generally, these tools are used to adjust each endpoint, such as NOEC, previously to the construction of SSD curves to account for bioavailability[36]. Although water quality data is required for this process, it is not always available in ecotoxicological databases, such as EnviroTox database[42], the US EPA ECOTOX knowledgebase[43].

In this context, this study is the first to propose the derivation of acute and chronic PNEC values for the 14 metals and metalloids most commonly observed in iron ore mining tailings[11,44–46] by using split SSD curves for different taxonomic groups (algae, invertebrates and fish) with data from more than nine species per group. In addition, a framework to adapt PNEC values obtained for each metal based on split SSD as according to bioavailability in different locations is also presented and these values are discussed in light of PVs in practice worldwide.

Methodology

Development of SSD curves and PNEC values

Split SSD curves were constructed for each metal/metalloid for three groups: algae, invertebrates and fish, based on ecotoxicity data for acute and chronic effects which were filtered as according to the "endpoint". "Endpoints" reported as $EC_{50,}$ IC_{50} and LC_{50} were considered as acute toxicity assays, and "endpoints" reported as NOEC, EC_{10} and LOEC were considered as chronic assays, as these are usually the values used as input for determining environmental standards worldwide[47]. Ecotoxicity data used to build the 78 split SSD curves (14 metals and metalloids, three groups, acute and chronic effects) using at least nine different species from each group are presented in the Supplementary Material File 1 and were gathered from the EnviroTox database[42], and the US EPA ECOTOX knowledgebase[43], both of which perform a review process prior to data publication, and from general scientific databases. The only exceptions were: Ag—chronic fish, Co—acute fish, Fe—acute algae, Mn—acute algae, chronic invertebrates, chronic fish, and U—acute invertebrates and chronic fish, for which at least seven species were used due to lack of data. In addition, it was not possible to build split SSD curves for As—chronic;invertebrates, Hg—chronic,algae, Mn—chronic,algae and U—acute,chronic,algae and chronic,invertebrates as the minimum number of species was not reached in these cases.

After the search was performed for each metal, studies were screened as an extra quality check regarding the metal source, endpoint, concentration range and journal impact factor. Studies published in the last ten years were prioritized due to improvement of analytical chemistry techniques[33] and updates to standard ecotoxicity assays in the last decade[48]. Data published before this period was only used in case of lack of data to build split SSD curves. For example, studies published before 1980 were not considered due to lack of reliability in experimental and analytical techniques[33], except for chronic effects for Arsenic (As), Ag and Mn, for which older studies (post 1978) were necessary to reach at least seven species per taxonomic group. When more than one ecotoxicity value was available for the same species, the geometric mean was calculated and used as the species toxicity value.

The ETX software (version 2.3)[49] was used to construct split SSD curves and to determine acute and chronic HC_5 values for all the 14 metals/metalloids as according to Aldenberg and Jarowska[18]. The ETX software assumes a log-normal distribution of ecotoxicity data, so the Kolmogorov Smirnov test ($\alpha = 0.05$) included in the software package[50] was used to check for adequate deviations from log-normality distributions. For chronic effects of Mercury (Hg) and Mn to algae, and chronic effect of Uranium (U) and As to invertebrates, the chronic HC_5 value was calculated by dividing the acute HC_5 by ten, as reported by Hiki et al.[51], as the minimum number of seven different species was not reached.

Acute and chronic PNEC values were calculated based in Eq. 1 by dividing the HC_5 obtained for the most sensitive taxonomic group according to the SSD curves by an assessment factor (AF) that considers the uncertainties of extrapolating laboratory results from a single species to a multi-species in the environment[34,52].

$$PNEC = \frac{HC_5}{AF} \tag{1}$$

The European Technical Guidance Document on Risk Assessment states that the AF may vary from 1 to 5 according to data robustness. As split SSD curves were built separately for acute and chronic effects using at least nine species for each of the three different groups, the approach was considered as conservative and the AF applied in this study was equal to 1[12,34,36].

Evaluation of current PVs set for metals and metalloids in Brazil, US, UK, EU and Canada

To evaluate current PVs set for metals and metalloids (Ag, Al, As, Cd, Co, Cu, Chromium (Cr), Iron (Fe), Hg, Mn, Ni, Pb, U, Zn), PNEC values estimated for acute and chronic effects were compared to PVs set for freshwater in different regions of the world which comprise the Global South and North: (i) Resolution CONAMA n° 357/05[25] (Brazil); (ii) Normative Deliberation COPAM/CERH n° 08/22[53] (Minas Gerais, Brazil); (iii) Environmental Quality Standards from the European Union (EU)[54]; (iv) National Recommended Water Quality Criteria, from the US, defined between 1980 and 2016[43]; (v) Proposed Environmental Quality Standards UK[39,55–59]; and (vi) Canadian Water Quality Guidelines (WQG) for Aquatic Protection Life, defined between 1987 and 2019[60].

Correction of PNEC values for bioavailability

Bio-met and mBAT are freely available tools that allow for the calculation of BioF (bioavailability factor) values for some metals. The framework proposed in this study involves the calculation and use of the BioF to adjust PNEC values to reflect bioavailability ($PNEC_{bio}$) by considering local water quality parameters. Bio-met was used to calculate the BioF for Cu, Ni, Zn, Pb and Co[40] while M-BAT was used for Mn[41]. BioF values were calculated as according to the user guidelines by considering the pH, DOC and dissolved calcium (Ca) values shown in Table 1, which correspond to water quality in each region/watershed. Water quality data used as input for BioF calculation in Brazil, Canada and UK/EU corresponded to values reported for water quality parameters in the Paraopeba River[11], Lake Ontario[61] and Eden River[36], respectively. For the US, water quality data used to calculate the BioF were derived from the 50th percentile of over 20,000 observations (pH, DOC, alkalinity, hardness, Magnesium (Mg), Ca, Sodium (Na)) registered in the Water Quality Portal and which are representative of 65 out of the 84 ecoregions in the US[62]. This portal integrates water quality data from the US Environmental Protection Agency (EPA), the US Geological Survey (USGS) and over 400 agencies in the US—state, federal, and local[63] (Table 1).

Once the BioF was calculated for each region, PNEC values were adjusted for bioavailability ($PNEC_{bio}$) as according to Eq. 2, where PNEC is the value derived from SSD curves (Eq. 1); and BioF is the Bioavailability Factor obtained for each metal [40,41].

$$PNEC_{\mathrm{bio}} = \frac{PNEC}{BioF} \tag{2}$$

Results and discussion

Species Sensitivity Distribution and protective values

The split SSD curves for acute and chronic effects related to the 14 metals and metalloids are presented in the Supplementary Material File 2 (Figures S1 to S14). Considering all the evaluated metals and metalloids, the smallest acute HC_5 were defined by algae and invertebrates for 42.9% of compounds each and by fish for 14.3%. Regarding chronic HC_5, invertebrates defined the smallest HC_5 for 64.3% of metals and metalloids, while 35.7% were defined by algae. Table S7 in the Supplementary Material File 2 presents the most sensitive group for each metal/metalloid, considering acute and chronic effect, as well as the most sensitive species for each group. These results reflect the higher sensitivity of algae and invertebrates to metals when compared to fish[35,65], indicating that ecotoxicological assays performed with these groups and species should be prioritized for events involving contamination by metals. For instance, after one of the major mining disasters that occurred in Brazil (B1 Dam in Brumadinho), Vergilio et al.[11] observed that algae were the most sensitive among those exposed to water contaminated with tailings from an iron ore mining dam.

Concerning the construction of split SSD curves, literature data regarding ecotoxicological assays for chronic effects may be scarce, related to various endpoints, and based on a small group of standard species. Furthermore, although ecotoxicological assays are performed under standardized conditions (temperature, pH, DOC, and hardness), these are not always clearly presented in papers and do not necessarily reflect natural settings (metal concentration range, pH, hardness, water quality and temperature, among others). In addition, published studies rarely report the source of metal and whether they are reporting total or dissolved concentrations. Thus, it is important to carry out laboratory studies focused in obtaining data for SSD curves with diverse and native species representing each taxonomic group and under standardized conditions to overcome these limitations.

Table 2 shows acute and chronic HC_5 obtained through split SSD curves for each of the 14 metals and metalloids and three taxonomic groups, as well as current PVs in practice in Brazil, Minas Gerais state, UK, EU, US, and Canada PVs. Considering that an AF of 1 was adopted in this study, PNEC values are equivalent to HC_5.

1—Class 1—hardness: < 40 mg L^{-1} $CaCO_3$; 2—Hardness:136 mg L^{-1}; pH: 7.8; DOC: 3.5 mg L^{-1}[64]; 3—Hardness: 124 mg L^{-1}; pH: 8.2; DOC: 1.1 mg L^{-1}[64].

		BR—Paraopeba River[11]	CAN—Lake Ontario[64]	UK/EU—Eden River[36]	US[62]
pH		7.55	8.2	7.65	7.8
DOC	mg L^{-1}	6.16	1.1	6.91	3.5
Ca	mg L^{-1}	5.42	35	61.56	37

Table 1. Physiochemical parameters of freshwater bodies used as input to calculate the BioF (bioavailability factor) for Cu, Ni, Zn, Pb, Co and Mn in Brazil, Canada, the European Union and the United States of America.

Metal	HC$_5$ (PNEC) (μg L^{-1})						Brazil and Minas Gerais (μg L^{-1})[25,53]	Proposed PNEC (μg L^{-1}) WFD UK		EQSD (μg L^{-1}) EU[39]		NRWQC (μg L^{-1}) US[43]		WQG (μg L^{-1}) Canada[60]	
	Acute			Chronic											
	A	I	F	A	I	F		Acute	Chronic	Maximum	Annual Average	Acute	Chronic	Acute	Chronic
Ag	**0.51**	1.52	2.15	0.47	**0.02**	0.22	**10.0**	nd	nd	nd	nd	**3.2**	nd	nd	**0.25**
Al	569.80	186.20	**72.96**	24.45	**0.16**	30.99	**100.0**	nd	nd	nd	nd	**2,900**[2]	**960**[2]	nd	**100**[3]
As	**54.36**	370.60	11,960	**7.02**	37.06	1,200	**10.0**	8.0[57]	0.5[57]	nd	nd	**340**	**150**	nd	5
Cd	**2.04**	16.55	4.43	**0.31**	0.47	0.38	**1.0**	nd	nd	0.45[1]	0.08[1]	1.8	**0.72**	**2.6**[2]	0.19[3]
Co	**52.05**	1,430	714.40	1.86	**0.29**	65.48	**50.0**	nd	nd	nd	nd	nd	nd	nd	nd
Cr	16.76	**15.65**	5,208	**2.85**	6.39	23.88	**50.0**	2.0[59]	**3.4**[59]	nd	nd	**16**	**11**	nd	1
Cu	16.13	**4.69**	16.06	12.08	**2.62**	3.03	**9.0**	nd	**8.2**[55]	nd	nd	**18.70**[2]	**5.81**[2]	nd	**2.84**[3]
Fe	**23.07**	1,204	297.00	0.28	**0.16**	199.80	**300.0**	**41.0**[58]	**16.0**[58]	nd	nd	nd	**1,000**	nd	**300**
Hg	15.20	**3.41**	35.03	1.52	**0.56**	0.92	0.2	nd	nd	0.07	nd	1.4	**0.77**	nd	0.026
Mn	**113.70**	728.50	1,985	**11.37**	18.59	38.50	**100.0**	nd	**123.0**[58]	nd	nd	nd	nd	**8,040**[3]	**280**[3]
Ni	20.60	**6.64**	6,192	3.46	**0.68**	17.42	**25.0**	nd	nd	**34**	**4**	**470**	**52**	nd	**112.55**[3]
Pb	149.60	**98.42**	226.00	12.38	**1.46**	11.44	**10.0**	nd	nd	**14**	1.2	65	**2.5**	nd	1
U	-	**25.15**	500.60	-	**2.52**	17.09	**20.0**	nd	nd	nd	nd	nd	nd	**33**	**15**
Zn	**5.50**	98.11	267.00	**0.87**	3.63	14.39	**180.0**	nd	**10.9**[56]	nd	nd	**120**	**120**	**95.98**[3]	**12.74**[3]

Table 2. Acute and chronic HC$_5$ (PNEC) values obtained for dissolved metals and metalloids for algae, invertebrate and fishes through split Species Sensitivity Distribution curves (SSD) and current PVs in practice in Brazil, Minas Gerais state (Brazil), UK, EU, US and Canada. A = algae; I = invertebrates; F = fishes. Acute or chronic proposed PNEC values in bold: lowest value obtained for each metal; Water Quality standard values in bold are above the PNEC defined for each metal. nd: no data;

HC$_5$ values (Table 2) indicate that Ag is the most toxic metal as it presents the smallest PNEC for all groups and effects. The only exception was observed for chronic effects in algae, for which Fe was the most toxic. For the acute effect of Ag, algae were the most sensitive group (HC$_5$ of 0.51 μg L^{-1}), while invertebrates were the most sensitive group for chronic effects (HC$_5$ of 0.02 μg L^{-1}). Wang et al.[66] obtained an HC$_5$ of 0.88 μg L^{-1} for acute effects promoted by Ag derived from a nonsplit SSD curve built with 41 species among amphibians, invertebrates, and fish, yet no algae were present in the dataset. Despite considering all species in the same curve, the value reported by the authors is close to acute HC$_5$ values identified in this study. However, the value is still 172% higher than HC$_5$ value derived in this study from a split SSD curve built only for algae species.

(Al) With respect to Al (Table 2), fish was the most sensitive group for acute effects (HC$_5$ of 72.96 μg L^{-1}) while invertebrates were the most sensitive considering chronic effects (HC$_5$ of 0.16 μg L^{-1}). An acute toxicity study with Al by Hui et al.[67] also identified fish as the most sensitive group. Razak et al.[34] and Gebara et al.[24] obtained acute HC$_5$ values equivalent to 521.06 μg L^{-1} and 148 μg L^{-1} for Al, respectively. These values are close to results observed in the present study for algae and invertebrates (569.8 and 186.2 μg L^{-1}, respectively). However, the referenced authors used a nonsplit SSD curve for all species, and fish, the most sensitive group in the present study, would not be protected by values reported by these researchers. This reflects the fact that SSD curves built with all taxonomic groups simultaneously result in higher HC$_5$ values as resistant species push HC$_5$ values upwards.

(Cd) For Cd, algae were the most sensitive group for acute and chronic effects (HC$_5$ of 2.04 and 0.31 μg L^{-1}, respectively) (Table 2). Acute HC$_5$ values ranging from 3.1 to 23.8 μg L^{-1} Cd were reported by Park and Kim[33] who, as in most studies on Cd toxicity, have considered nonsplit SSD curves. These HC$_5$ values to protect algae as the most sensitive group to Cd[34]. Meanwhile, Arambawatta-Lekamge et al.[68] reported a chronic HC$_5$ value of 0.48 μg L^{-1} which is similar to chronic values obtained in the present study.

(Cu, Hg, Ni, Pb, Ni and U) As with Cd, algae were also the most sensitive group for acute and chronic effects promoted by Mn and Zn (Table 2). For Cu, Hg, Ni, Pb and U, invertebrates were the most sensitive organisms for both acute and chronic effects (Table 2). Similar results were observed by Lima et al.[50], for acute effects of Cu, Cd, and Hg, and by Razak et al.[34] for Cu and Pb. Regarding chronic SSD curves, Arambawatta-Lekamge et al.[68] also verified invertebrates as the most sensitive group for Cu.

(Co, Fe) For Co and Fe, algae were the most sensitive considering acute effects and invertebrates were the most sensitive for chronic effects, with respective HC$_5$ values of 0.29 and 0.16 μg L^{-1}. For Mn, algae and fish were, respectively, the most and least sensitive groups for both acute and chronic effects. These results are in accordance with Alho and collaborators[1]. Marks et al.[69] also verified fish as the least sensitive group for chronic effects of Mn.

(U) It was not possible to calculate HC$_5$ nor PNEC values for acute and chronic effects of U upon algae due to lack of data in the literature, besides health risks associated with U manipulation in the laboratory. This highlights the need for studies which carry out algae exposure assays to this metal. Considering the other taxonomic groups, HC$_5$ values were lower for invertebrates (Table 2).

(Mn) In the present study, acute HC$_5$ for Mn were 113.7 μg L^{-1} for algae, 728.5 μg L^{-1} for invertebrates and 1,985 μg L^{-1} for fish. Independent studies developed by Razak et al.[34], Alho et al.[1] and Harford et al.[70] using nonsplit SSD observed acute HC_5 values for Mn which were, respectively: 1,049 μg L^{-1}, 580 μg L^{-1} and 143 μg L^{-1}. The range of PNEC values reported for Mn is broad here and in referenced studies. It is important to note that results obtained through SSD curves are highly dependent on the number of species; the proportion of each taxonomic group in the ecotoxicity database; the endpoint considered for each toxicity test (for example, EC_{50}, LC_{50}, NOEC, EC_{10}); the variation between results obtained from different laboratories[71]; the adopted distribution model of SSD curves (normal, logistic, triangular, etc.), amongst other factors[72]. Thus, different studies may result in distinct HC_5 values for the same substance and the same toxic effect.

It is also important to highlight that acute and chronic HC_5 values obtained via nonsplit SSD curves[1,24,34,50,73] differ from HC_5 values derived from split SSD curves (present study). Split and nonsplit SSD curves constructed for Al, Fe and Zn for acute and chronic effects (Supplementary Material File 2 Figure S15) demonstrate that HC_5 derived from curves built exclusively with data corresponding to the most sensitive group were more conservative, as also observed by Oginah et al.[29] in a study conducted with 180 chemicals. Smallest HC_5 obtained for split SSD (Table 2) were plotted in the corresponding nonsplit SSD curve to assess the level of protection of these HC_5s in the combined SSD curve (Figure S15). For Al, the smallest acute and chronic HC_5 values obtained in split SSD would protect 98.03 and 99.79% of species from all groups from, respectively, acute and chronic effects of Al. Regarding Fe, the smallest HC_5 for acute and chronic effects (Table 2) would protect 99.82% and 98.48%, respectively, while for Zn protection would range from 99.92% for acute to 98.92% for chronic toxicity. Thus, confirming the robustness of HC_5 values derived from split SSD curves for the 14 metals evaluated in the present study.

Predicted No Effect Concentration and current protective values

Table 2, Figs. 1 and 2 show that 45 out of a total of 82 PNEC values proposed in this study were below current PVs set in Brazil and Minas Gerais state, mainly for chronic effects (78% of PNEC chronic values) when compared to acute (32% of PNEC acute values). For PVs set in the US, the difference was nearly 77% and 53% for chronic and acute PNEC, respectively. For the UK, 11% of acute and 56% of chronic PNEC values derived from this study were under the current PVs, and this occurred for the EU in 2 out of 9 chronic PNEC. In Canada 55% of acute and 47% of chronic PNEC values obtained in this study were under PVs. In other words, according to PNEC values obtained via split SSD curves built in this study, aquatic biota might not be protected from toxic effects promoted by metals and metalloids by the current evaluated PVs in 48% of all evaluated cases and this is mainly true for chronic effects.

All PNEC values for chronic effects were below Brazilian and Minas Gerais current PVs for Ag, Al, Cd, Cr, Fe, Mn, Ni, U and Zn (Fig. 1). This is probably a consequence of the method used for deriving PVs in Brazil which does not aim directly at aquatic life protection, yet considers all water uses simultaneously, thus resulting in higher values. Considering the other countries, this was also observed for chronic PNEC values obtained for Mn compared to PVs in practice in the UK; chronic PNEC values obtained for Cd, Fe, Ni and Zn and current PVs in the US; and chronic PNEC values obtained for Al, Fe, Mn, and Ni compared to current PVs in Canada. In these countries, where PVs are set specifically for aquatic life protection often using the SSD approach, differences between PVs and PNEC values derived in this study are probably a consequence of the use of split SSD curves with a high number of species in this study.

(Ag) Considering Ag, all current PVs in practice in Brazil, Minas Gerais state (10 μg L^{-1}) and in the other countries used as reference in this study are higher than acute and chronic PNEC values obtained by split SSD curves, except for chronic effects to algae (Table 2, Figs. 1 and 2). Although still below, aquatic life PVs adopted in the US (3.2 μg L^{-1}) and Canada (0.25 μg L^{-1}) were close to HC_5 obtained in this study, respectively, for acute and chronic effects. According to resulting split SSD curves, current PVs analyzed in this study protect 17% (Brazil—invertebrates), 48% (Brazil—algae), 92% (US—fish) and 98% (Canada – algae) of species from chronic and acute effects induced by Ag, respectively. An exception is observed for chronic effects to algae, which might be protected by the Canadian WQG[60]. As Ag is considered a noble metal[74,75] and up to 80% of this metal is recycled, it tends to be less discharged and, consequently, present in smaller concentrations in environmental compartments than other metals[76,77].

(Al and Fe) For Al and Fe, Brazil and Minas Gerais current PVs are equal to the Canadian WQG (100 and 300 μg L^{-1}, respectively). For these cases, current PVs may be protective of the aquatic biota only for acute effects to specific groups (Al: algae and invertebrates and Fe: invertebrates). In the ecological context, if the concentration of a metal reaches a PV that is not protective of the aquatic biota, ecosystem function might be at risk, potentially resulting in ecological imbalance. This is critical mainly considering intensive iron ore mining extraction in Minas Gerais state (Brazil) where two major dam collapses occurred in less than five years leading to various environmental, economic and social impacts, including extensive Fe contamination[9,46]. Still, it is important to consider that species residing in watersheds located in iron-rich soils, which is the case for some regions of Minas Gerais, might be adapted to naturally higher concentrations of these metals.

(As and Cd) Aquatic life PVs established for As in the UK (0.5 μg L^{-1}) and in Canada (5 μg L^{-1}) may not protect primary producers from chronic effects. In contrast, current PVs in Brazil and Minas Gerais (10 μg L^{-1}) are likely to protect aquatic biota as they are below PNEC obtained for all evaluated groups (algae, invertebrates and fishes), except for chronic effects to algae (7.02 μg L^{-1}). For Cd, PVs set by the EU and Canadian criteria (0.08 and 0.19 μg L^{-1}, respectively) are protective against chronic effects, yet those set by Brazilian and Minas Gerais standards (1 μg L^{-1}) are still above chronic PNEC obtained in this study.

(Pb) PNEC values calculated for Pb (Table 2, Figs. 1 and 2) are above aquatic life PVs in practice in Canada (1 μg L^{-1}) and the EU (14 and 1.2 μg L^{-1} for acute and chronic effects, respectively). On the other hand, current PVs in Brazil/ Minas Gerais (10 μg L^{-1}) and US (65 and 2.5 μg L^{-1} acute and chronic, respectively) are lower than PNEC obtained for all evaluated groups (algae, invertebrates and fishes). The only exception is chronic effects to invertebrates, for which the PNEC is 1.46 μg L^{-1}. According to split SSD curves built in this study, the

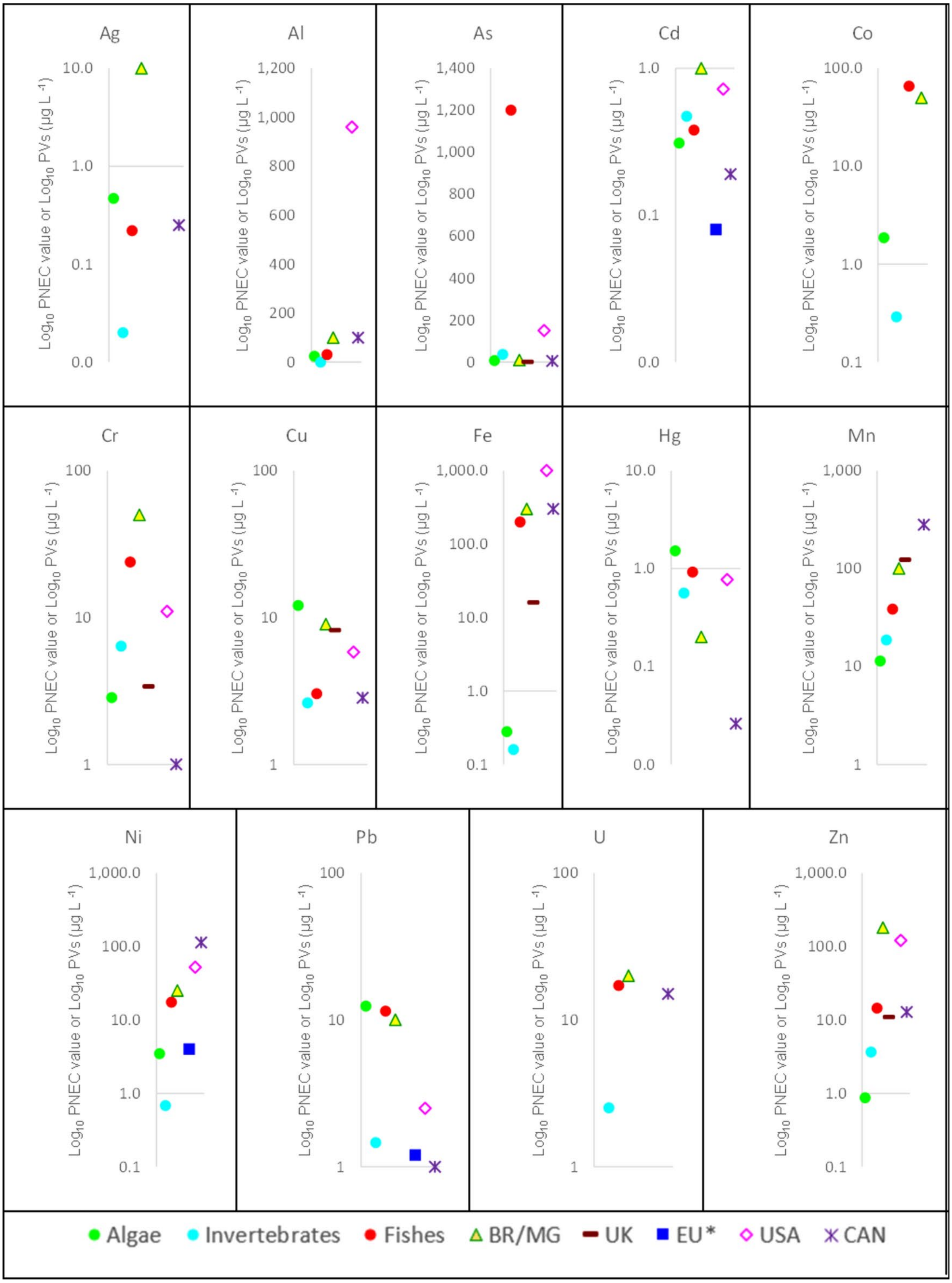

Fig. 1. Log_{10} PNEC values obtained in this study for chronic toxicity of dissolved metals and metalloids to algae, invertebrate and fishes in comparison to current PVs in Brazil, Minas Gerais, US, UK, EU and Canada. EU*: Chronic = Annual Average.

US and Brazil/MG state PVs, respectively, would protect 93% and 84% of aquatic invertebrates against chronic effects of Pb.

(Cr) Regarding Cr, PNEC values obtained by split SSD curves are higher than current PVs in UK and Canada for almost all groups and effects. In contrast, Brazilian PV (50 μg L^{-1}) is above PNEC values obtained for all

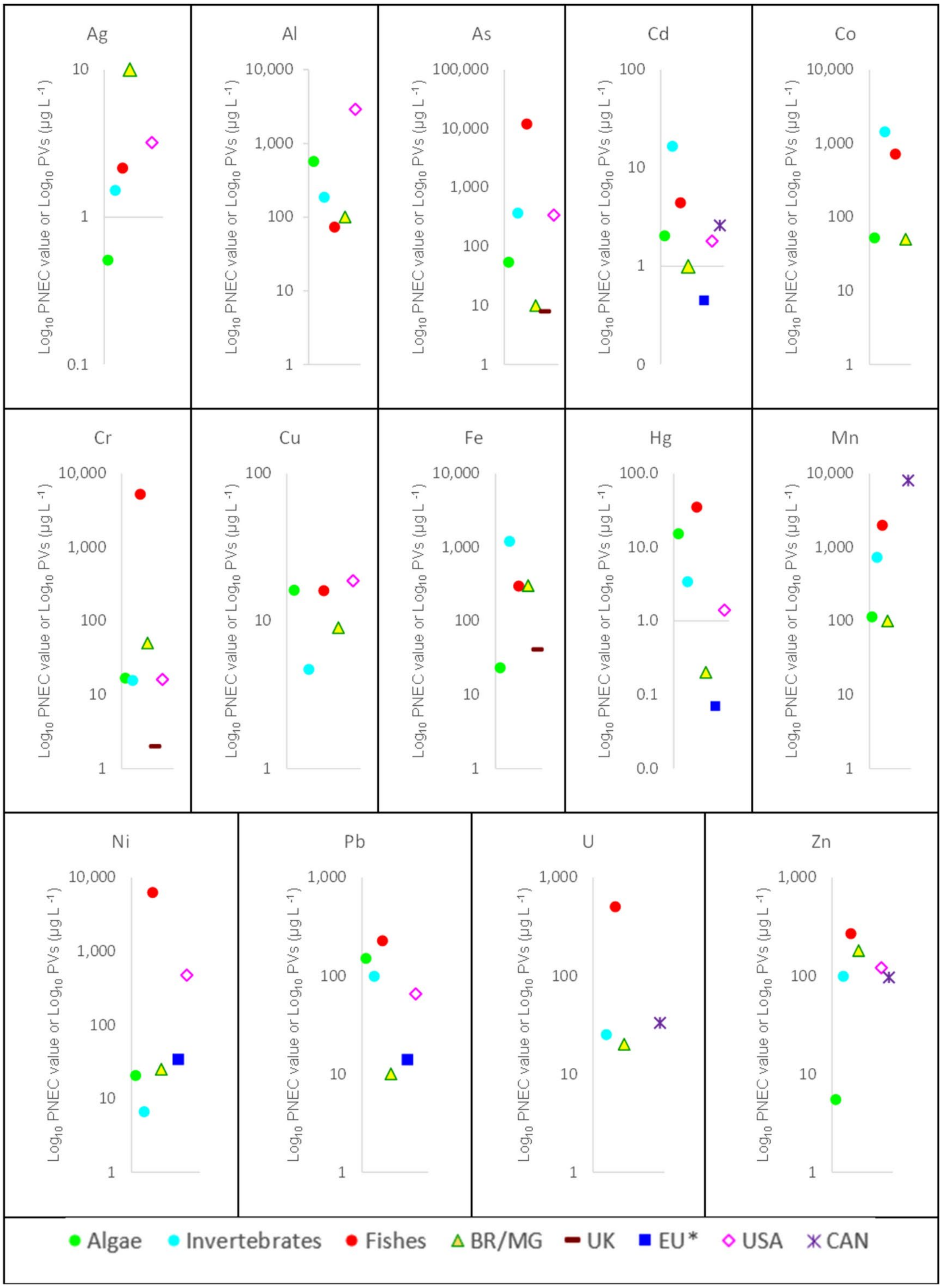

Fig. 2. Log_{10} PNEC values obtained in this study for acute toxicity of dissolved metals and metalloids to algae, invertebrate and fishes in comparison to current PVs in Brazil, Minas Gerais and US, UK, EU and Canada. EU*: Acute = Maximum Concentration.

groups and effects, except for acute response in fish. Thus, the current Brazilian PV may underprotect these groups (Table 2, Figs. 1 and 2).

(Hg) For Hg, all PVs are below PNEC values obtained in the present study (Table 2, Figs. 1 and 2). This may be a consequence of historical concerns related to environmental and human health hazards promoted by Hg contamination and bioaccumulation, such as the Minamata Bay case in Japan, where consumption of contaminated fish with methylmercury resulted in neurological disease due to poisoning by this heavy metal[78].

(Zn) For Zn, only the PNEC obtained for acute effects in fish (267 µg L^{-1}) (Table 2 and Fig. 2) was higher than the Brazilian CONAMA Resolution n° 357/05[25] and Minas Gerais COPAM/CERH n° 08/2022[53] PVs (180 µg L^{-1}) and higher than the US National Recommended Water Quality Criteria (120 µg L^{-1}). For acute effects, Brazilian and Minas Gerais PVs are nearly 33-fold higher than the acute PNEC found in this study for algae and 1.8-fold higher than acute PNEC value for invertebrates. Gebara et al.[24] also observed that current CONAMA n° 357/05 PVs for Zn may not be protective to 95% of the species, since acute HC_5 obtained for Zn (62 µg L^{-1}) by this author from a nonsplit SSD curve was about threefold smaller than current PVs. In relation to chronic effects (Fig. 1), Brazilian and US PVs are, respectively, 29-fold and 19-fold higher than the average PNEC derived in this study for Zn, considering each of the three taxonomic groups. UK (10.9 µg L^{-1}) and Canadian PVs (12.74 µg L^{-1}) might only be protective against chronic effects to fish.

An organism subjected to concentrations higher than PNEC values or even PVs will not necessarily suffer acute or chronic effects as split SSD curves built in the present study were developed considering results reported in the literature from ecotoxicological assays carried out with single species and metals while organisms are generally exposed to a mixture of metals and other substances in the environment[79]. Nevertheless, PVs are still set based on the PNEC for individual substances, thus supporting the feasibility of the split SSD approach proposed in this study. Constructing SSD curves for mixtures of metals can be an alternative for future studies to allow for the definition of HC_5 and PNEC values which reflect the mix of metals occurring in environmental waters[80].

The manifestation of effects also depends on biodynamics, exposure routes, metal accumulation in each species, time of exposure, feeding relationships, species sensitivity, bioavailability, additive or synergistic toxic effects of mixtures of substances, amongst other factors[81,82]. PNEC values obtained in the present study should be seen as a warning for the need to revise Brazilian and Minas Gerais PVs related to metals and metalloids aiming at aquatic life protection, especially for Ag, Al, Cr and Zn for which PNEC obtained in this study were much lower than current values. This perspective is adopted in other countries, such as the US and Canada, where different PVs are adopted according to water use purpose and local water characteristics, instead of one PV based on the most restrictive water use, as it is currently done for Brazil and in Minas Gerais[26].

Nevertheless, PNEC values obtained in this study should not be used to replace laboratory exposure assays, yet applied in ecotoxicological risk assessments as guides to define priority metals, test organisms, and critical regions within a watershed to be prioritized for ecotoxicological studies, especially in areas dominated by mining and other activities that culminate in environmental contamination by metals, such as in the state of Minas Gerais, Brazil. Despite recent updates to Minas Gerais state water quality PVs in November 2022 by the publication of Normative Deliberation COPAM/CERH n° 08/22[53], PVs for metals and metalloids were not updated in the occasion. In addition, future data should consider the use of native and residing species in bioassays.

Bioavailability and PNEC values

The bioavailability of metals and metalloids in the natural environment is influenced by physicochemical aspects such as pH, DOC and hardness, which affect metal/metalloid physical state, solubility, and speciation, thus, influencing their interaction with aquatic biota and, consequently, their toxicity[83]. $L(E)C_{50}$, NOEC, EC_{10} and LOEC values used to construct acute and chronic split SSD curves were derived from toxicity assays carried out under standard conditions of pH, hardness and organic content by following standard protocols defined for each test-organism. Hence, PNEC should be adapted to better reflect bioavailability ($PNEC_{bio}$) according to local physicochemical conditions at the study area. Different methods have been recommended to account for the bioavailability of Al, Cd, Cr, Cu, Mn, Ni and Zn during the derivation of PVs in Europe[84], Canada[60] and in the US[43].

The adaptation of PNEC values used in risk assessments would also make them more realistic to environmental conditions in each area/watershed. Even so, most scientific studies on the assessment of ecotoxicological risks do not account for bioavailability as (i) this makes results less comparable across studies and very specific to the area under study and (ii) freely available bioavailability tools are restricted to a few metals. In the current study, the framework proposed to adjust the PNEC into $PNEC_{bio}$ was conducted for Mn, Cu, Ni, Zn, Pb and Co for waters from different regions of the world based on the existence of bioavailability conversion tools for these metals[40,41].

Table S8 shows PNEC and $PNEC_{bio}$ values, as well as the BioF calculated for each metal (Co, Cu, Mn, Ni, Pb and Zn) for Brazil, Canada, UK and US, based on specific local physicochemical water quality (Table 1). It is important to emphasize that these results refer to the contexts of Paraopeba River, Lake Ontario, Eden River and the compilation of water chemistry data from US. Different results may be observed if these same metals are evaluated for other waterbodies or even for these same ones, yet with data from other periods.

When bioavailability was considered by applying the BioF, $PNEC_{bio}$ increased for all watersheds (Table S8), thus being higher than PNEC. This occurs because the BioF considers the portion of the metal that is available to interact with the test-organism and cause toxicity under defined conditions of pH, hardness and organic content existing in each watershed. For Cu, for instance, when bioavailability was considered, PNEC increased nearly 40-fold for the Paraopeba River and 30-fold for Eden River. This was the greatest rise amongst the evaluated metals. On the other hand, regarding Co, when bioavailability was taken into consideration, PNEC barely doubled considering the values of pH, DOC and hardness used as a reference for Brazil, UK and US. Despite the bioavailability adjustment, $PNEC_{bio}$ values obtained for Co were still lower than Brazilian and Minas Gerais state PVs for acute effects to invertebrates and chronic effects to algae and invertebrates.

Regarding Ni, the highest increase in $PNEC_{bio}$ value was observed for Paraopeba River (13.7-fold PNEC) (Table S8) and the smallest increase was observed for Lake Ontario (2.3-fold). The lowest $PNEC_{bio}$ observed for this metal (1.58 µg Ni L^{-1}) was related to chronic effects to invertebrates for Lake Ontario and was nearly 70-fold smaller than the Canadian Water Quality Guideline[60]. In contrast, considering bioavailability in the Paraopeba River (pH, DOC and Ca), $PNEC_{bio}$ values were higher than Brazilian and Minas Gerais current PV (25 µg Ni L^{-1}), except for chronic effects to invertebrates, for which $PNEC_{bio}$ were still lower than current PVs.

In the case of Mn and Pb, BioF values were equal to 1 for Lake Ontario characteristics. The Canadian legislation[60] is the only one amongst all PVs evaluated in this study (Table 2) that considers bioavailability to define water quality guidelines for these metals. According to their procedure, a modelling equation which considers hardness is used to calculate the PV for Pb, and hardness and pH are considered for the definition of WQG for Mn. When representative values of pH seen in the Paraopeba River (7.55) were used as input on the Canadian model for different conditions of hardness (25 and 670 mg L^{-1} of $CaCO_3$) the long term WQG for Mn varied from 320 to 720 µg Mn L^{-1}. When Ca concentration was set to the value observed in the Paraopeba River during the evaluated period (5.42 mg L^{-1}) and pH varied from 5.8 to 8.4, the PNEC value ranged between 190 to 160 µg Mn L^{-1}. Thus, for Mn, it is possible to observe that hardness has a direct influence on bioavailability and that its effect is opposite to that of pH.

Results obtained in this study emphasize the relevance of considering bioavailability when setting PVs and conducting risk assessment studies worldwide, mainly in Brazil, where such perspective is still incipient. Bioavailability might be the key to differences in toxicity effects observed in laboratory conditions compared to the natural environment. After all, organisms are generally exposed to different conditions of water quality in the environment compared to conditions standardized for laboratory assays. Still, it is critical to keep and constantly update PVs for each substance while considering the influence of environmental conditions upon metal solubility, complexation, oxidative state, and bioavailability to define effective PVs[83].

Conclusions

This study proposes acute and chronic PNEC values for 14 metals based on split SSD, thus contributing to the knowledge field on ecotoxicology and risk assessment. This is the first study to build split SSD curves for the 14 metals and metalloids most commonly observed in iron ore mining tailings, thus delivering novel and reliable reference values to be used by the scientific community and environmental agencies for risk assessment studies and as references to set PVs. PNEC values proposed in this study should not replace ecotoxicity assays, yet they may be used to indicate priority metals/metalloids and taxonomic groups in the context of ecological risk assessment, and to subsidize the development of new legislation directives and laboratory studies.

Almost half of calculated PVs for metals and metalloids in practice worldwide are above PNEC obtained in this study, mainly for chronic effects. For Brazil, US, UK, Canada and EU, chronic PVs are above proposed PNEC in, respectively, 78%, 71%, 56%, 46% and 18% of the evaluated cases. Values obtained in this study could be used as reference to advocate the revision of current PVs, while considering bioavailability, analytical feasibility and background concentration of each of these metals in different regions or countries. As far as Brazil is concerned, as protective values for metals and metalloids were proposed more than 19 years ago[25], the revision of PVs is critical. Ag, Al, Cr and Zn need special attention, since PNEC values derived in this study were much lower than current PVs.

In addition, this study showed that bioavailability strongly influences PNEC values. For instance, when pH, DOC and hardness for Eden River (UK) and Paraopeba River (Brazil) were considered, $PNEC_{bio}$ calculated for Cu were, respectively, 31 and 40 times higher than PNEC. So, it is critical to take this aspect into account by applying the framework proposed in this study for local water quality conditions when setting PVs and performing risk assessment studies in each watershed. This is challenging as no available tools enable bioavailability conversion for all metals and metalloids. Furthermore, water characteristics that influence bioavailability, such as pH, DOC and hardness, change along a watershed and in time.

Data availability

Data used in this manuscript are available as Supplementary Material.

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