Which metal represents the greatest risk to freshwater ecosystem in Bohai Region of China?

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Abstract. Metals discharged from industrial effluents, agricultural wastewater, and sewage runoff by rapid urbanization are of concern as contaminants of freshwater ecosystem because of their persistence and high toxicity to aquatic organisms. This study attempted to identify which metal posed the greatest risk to freshwater ecosystem in the Bohai Region, China. The metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), mercury (Hg), iron (Fe), and manganese (Mn) were compared against norfloxacin and gamma-hexachlorocyclohexane (lindane). By comparing the median reported environmental and ecotoxicity concentrations, it showed that Cu, Fe, Zn, Mn, and Cr were the top five metals of concern. Of these, Cu was deemed to represent the highest risk and Hg the lowest risk. The risks for all metals were higher than those for norfloxacin and lindane. Almost all the metals except Hg had water concentrations that exceeded levels where ecotoxicity effects had been recorded in the literature. A comparison with the measurements across the UK rivers suggested that all metals examined had water concentrations about 5- to 10-fold higher than the UK median values except for Cu, Fe, Cd, and Pb. The Fuyang River, a tributary of the Haihe River Basin, seemed to be the location with the highest metal concentrations. However, comparing the post-2010 period to 2000–2009, concentrations of all the metals had fallen except for Fe and Mn, so risks have decreased over the last 7 yr with the greatest improvements for Cd and Pb. While metals still pose high risks to freshwater ecosystem in this region, there is encouragement that some control measures are taken into effect.

Key words: *chemical pollution; freshwater ecosystem; metals; risk ranking.*

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Introduction

As industry, urbanization, and the economy have been developing over the last 60 yr, our consumption of chemicals has increased. More than 100,000 chemicals are in use worldwide, including metals, organic pollutants, pharmaceuticals, and nanoparticles (Holt 2000). In China, associated with the rapid development of economy in the last 30 yr, high levels of contaminants have been discharged into rivers (Song et al. 2013). But to better protect the environment, we must identify which chemical contaminants represent the greatest risk. With so many different chemicals to monitor and assess, it is difficult to see where we should focus our efforts (Sumpter 2009). It has been acknowledged globally that there is a need to develop a better understanding and management strategy with regard to the risk of chemicals to wildlife and human health (Anastas et al. 2010). Identifying the chemicals of greatest concern is a global challenge and has been highlighted as a priority topic to be solved by the Society of Environmental Toxicology and Chemistry (Brooks et al. 2013).

Heavy metals as well as trace metal elements in aquatic ecosystems have received extensive attention due to their persistence and high toxicity to many aquatic organisms (Zhuang and Gao 2014). They may be present in both water and sediment in a wide variety of physicochemical forms. Unlike most organic pollutants, heavy metals are particularly problematic because they are not biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain (Azevedo et al. 2009, Christophoridis et al. 2009, Song et al. 2013, Zhuang and Gao 2014, Lu et al. 2015).

Rapid urbanization and economic development are one of the outstanding features in China over the past 30 yr, particularly in coastal regions. Therefore, this project studied the rivers in the Bohai coastal region, which

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has benefitted from rapid urbanization and industrialization since the late 1970s (Fig. 1). The Bohai Sea and its adjacent coastal areas and estuaries have suffered metal pollution problems. With its proximity to Beijing (the capital of China) and Tianjin, the Bohai Sea is one of the busiest seaways in the world (Xu et al. 2013). Large quantities of contaminants including organic pollutants and heavy metals have been produced and discharged into rivers, such as the Yellow River, Liaohe River, and Xiaoqing River (Zhou et al. 2014). For instance, the Liaohe River was estimated to have discharged 390 tons of metals into the sea in 2002, and the Yellow River totally discharged 200 tons of metals in 2003 (Wang and Wang 2007). Severe deterioration in species diversity and abundance has been recorded in the freshwater and marine environments here which have been related to habitat loss and chemical pollution (Xu et al. 2013).

In Europe, as part of the Water Framework Directive, chemicals were identified as being of special concern (priority and hazardous substances) on the basis of several properties including persistence and different toxic properties. Most of the available studies on metal pollution in rivers of Bohai Region focused on the risk assessment of surface sediment, using typical methods such as the enrichment factor, potential ecological index, and geoaccumulation index methods (Chai et al. 2014, Wen and Gao 2015, Xie et al. 2016). There are few studies assessing the risks of metals in waters. Song et al. (2013) used hazard quotient to assess the risks of metals in surface water of Yellow River Delta, and suggested that zinc (Zn), manganese (Mn), cadmium (Cd), chromium (Cr), and nickel (Ni) were the top five metals of concern (Song et al. 2013). However, a recent approach has been proposed which argues that only two factors are critical—the proximity of the median exposure and toxicity concentrations, when evaluating relative risk (Donnachie et al. 2014, 2015). There is no perfect system of course, but the focus on only these two factors has the merit of simplicity and transparency. There is no doubt that the ability of a chemical to bioaccumulate is an undesirable property but it is not clear whether this in itself should trump toxicity. In this study, the environmental concentrations of metals that have been well monitored in the freshwater of the Bohai Region were compared with the available information on toxicity concentrations in order to provide a risk ranking. Previous studies on metals in the Bohai Region have tended to focus on Pb and Cd under the assumption that these posed greater threat to local wildlife (Wang and Wang 2007, Wei et al. 2008, 2010, Feng et al. 2011, Cheng et al. 2014, Kong et al. 2014, Shi et al. 2016). However, without an attempt at relative risk ranking, it is not yet possible to conclude this with certainty. The project had the following objectives:

1. Identify which metal represents the greatest risk to the freshwater ecosystem of Bohai Region.

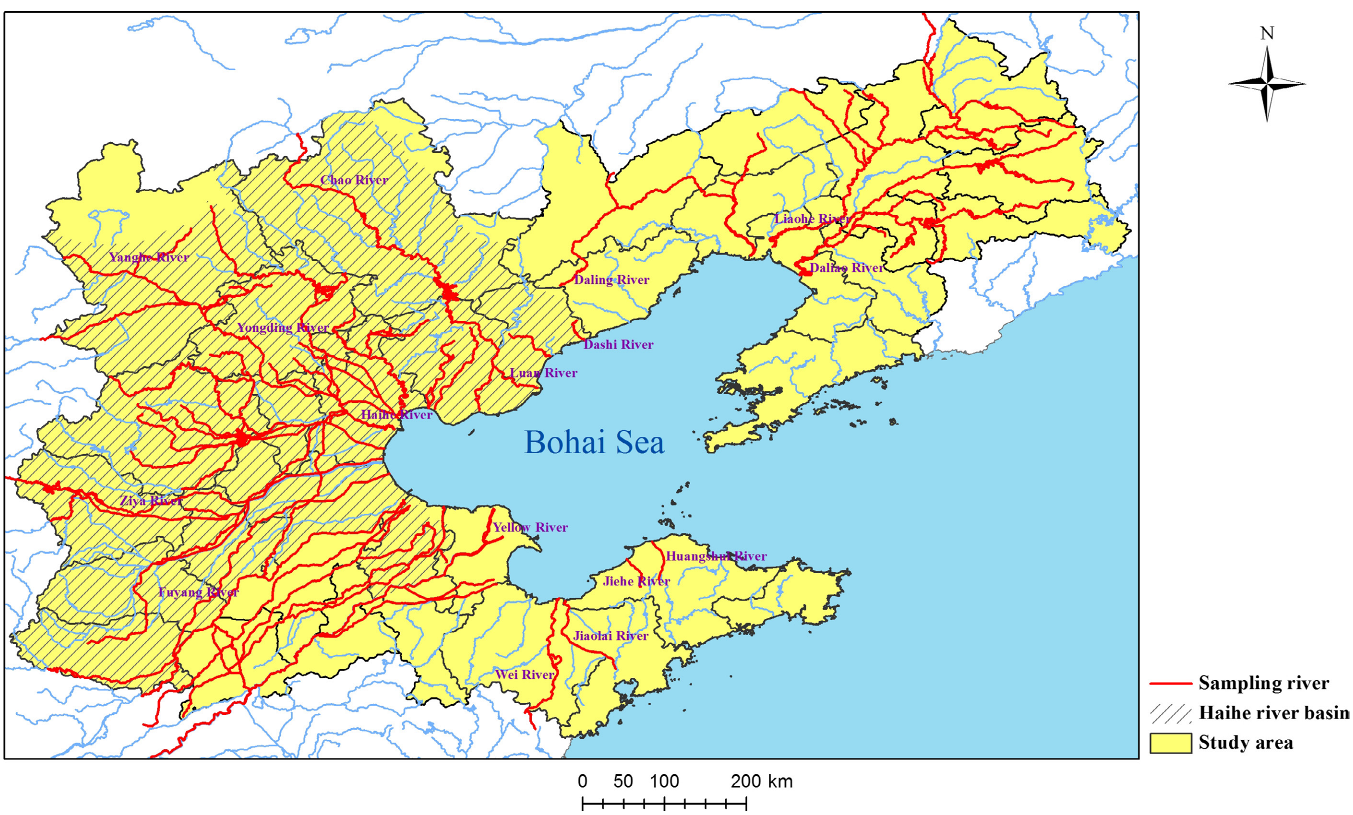

Fig. 1. Spatial distribution of rivers in the Bohai coastal region. Those where metals data were collected have been highlighted in red. Note: The names for some major rivers are marked in the figure.

2. Compare the relative risk of metals in the Bohai Region of China with that analyzed for the UK.
3. Identify the rivers in the Bohai Region at greatest risk from metals.
4. Assess whether the risk from metals is increasing or decreasing over time.

This study is able to support the effort for enhancing the Surface Water Environmental Quality Standards of the People's Republic of China (GB 3838-2002), which sets targets to prevent water pollution and safeguard human health.

Materials and Methods

Metals selected for this study

The selection of metals was determined by the availability and quality of measured elements. The metals considered in this research were arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), mercury (Hg), iron (Fe), and manganese (Mn). They were the 10 most monitored metals in China. Measured concentrations of these metals in freshwater in the Bohai Region were searched from the literature in the Web of Science database for English publications and China National Knowledge Infrastructure (CNKI) database for Chinese publications together with the database in the China National Environmental Monitoring Center (CNEMC) in 2013. Only monitoring data collected in the period 2010–2016 was used, because there are abundant freshwater sampling sites with a sufficient geographic distribution spread across the Bohai Region.

Environmental observed concentration information collection

For all the studied metals, information about total concentrations of metals in freshwater of the Bohai Region was collected. For observed concentrations in literature publications, data in both Web of Science for all English papers and CNKI databases were included. From CNKI database, papers for almost all the Chinese journals, PhD dissertations, and master thesis were collected. Freshwater and sea water were taken into consideration separately. This study only focused on the freshwater system. The period for review was from 1 January 2010 to 1 January 2016. The concentrations reported in drainage rivers such as Dagu Drainage River were excluded. The concentrations below the limit of detection were also included by regarding them as LOD/sqrt(2). The CNEMC database provided concentration data on all the metals except Cr and Ni for almost all the rivers in Haihe River Basin, such as Yongding River, Qingshui River, Chao River, Guishui River, and Liaohe River Basin such as Hunhe River, Daliao River, Daling River (Fig. 1). It is acknowledged that chemistry of metals is complex and that the bioavailable fraction (and risk) will be less than that recorded due to the local river conditions, such as pH, complexing organic matter, and calcium carbonates (Merrington et al. 2016). These factors may influence the relative risk of the metals between one another slightly, but will not be important where the relative risks are over 1000-fold different.

Ecotoxicity data collection

With regard to the reported effect concentrations, the ecotoxicity database ECOTOX https://cfpub.epa.gov/ecotox/ gathered by the U.S. Environmental Protection Agency was the main initial source of information. Firstly, toxicity data for freshwater species were extracted from the database. Only species that are relevant to China and the common test species that have been approved as standard test species were selected (Farre and Barcelo 2003, Donnachie et al. 2014). Representatives from algae, plants, fishes, invertebrates, and insects (with aquatic life-stage) were found for each metal. Appendix S1: Table S1 shows all the species used in this study. A wide range of endpoints were considered (sub-lethal as well as lethal), to ensure that a representative picture of species and possible effects were obtained. In this study, effect concentration 50 (EC50) was selected as preferred endpoint, followed by lethal concentration 50 (LC50) and then the lowest observed effect concentration (LOEC). If the fortune position arose were more than one ecotoxicity value existed for one endpoint for one species, then the lowest effect concentration was finally selected. So for each one species, only one effect concentration data were recorded from the database. In this study, the ecotoxicity dataset ranged from 11 (Fe) to 71 (Cu) entries for the metals.

Risk assessment

After the data were collected, the risks of each metal were ranked using a risk ratio approach. The effect concentrations and observed water concentrations in the rivers for each metal were plotted individually. Thus, it created two sub-sets of data, the effect data and the observed concentration data. The median of the ecotoxicity effect concentrations used in the study (including all species and all endpoints) and the median of all the freshwater measured concentrations were identified for each metal/chemical. A median derived from a representative ecotoxicity dataset should vary little if more data were added, certainly not by several orders of magnitude if more references were added. Of course, where the median ecotoxicity values of metals are quite similar, the ranking should not be seen as absolute.

The degree of separation between the median values was used to rank metals on the basis of risk (Eq. 1). It could be described as a risk ratio, which could be used to rank concern—the larger the value, the greater the concern (Donnachie et al. 2014).

$$\text{Risk} = \frac{mW}{mT} \quad (1)$$

where mW is the median water concentration (μg/L) and mT is the median effect concentration (μg/L).

As a comparison of exposure with a European scenario, the measured data and medians for metals in UK rivers were also plotted.

Study area

The Bohai Region in this study covers Beijing City, Tianjin City, Hebei Province, and coastal cities of Huludao, Jinzhou, Panjin, Yingkou, Dalian, Chaoyang, Fuxin, Shenyang, Tieling, Fushun, Benxi, Liaoyang, Anshan in Liaoning Province, Binzhou, Dongying, Weifang, Qingdao, Yantai, Weihai, Dezhou, Jinan, Zibo, Liaocheng in Shandong Province. Measured rivers included rivers in the southern Bohai Sea, the Bohai Bay, the Haihe River Basin, and the Liaohe River Basin (Fig. 1). It is one of the most prosperous regions in China because of its coastal advantages. A wide range of industries are distributed in this region, including textile treatment, metal plating, and metal smelting (Liu et al. 2015). The rapid development of the regional industries has caused a great increase in energy consumptions and pollutants emissions, leading to a series of ecological and environmental problems.

Results and Discussion

Risk ranking of metals based on exposure and effect concentrations

Risk ranking of metals based on comparison of median ecotoxicity and freshwater concentrations

When ranking the risk of metals by ratios in the Bohai Region, on the basis of the comparison of the medium ecotoxicity and freshwater concentrations (Song et al. 2013, Xu et al. 2013, Tan et al. 2014, Wu 2014, Wu et al. 2014), Cu emerged as posing the highest risk to organisms. The method put Fe and Zn in the same high-risk group as Cu, while Pb, Cd, As, and Hg were between one and two orders of magnitude lower risk (Figs. 2 and 3). It is important to state that this study does not imply that the traditional heavy metals of Cd, Pb, and Hg are of no risk or interest, simply that by this type of analysis they are lower risk. Although it is not used in the ranking, a high degree of overlap between some reported metal concentrations and known effect concentrations was apparent (Fig. 2). Concentrations of Cu, Fe, Zn, and Cr in some rivers clearly exceed even the median ecotoxicity value. More details about median ecotoxicity and freshwater concentrations of all metals can be found in Appendix S1: Table S2.

When comparing the metal concentrations with the UK rivers in the same time scale, the median river

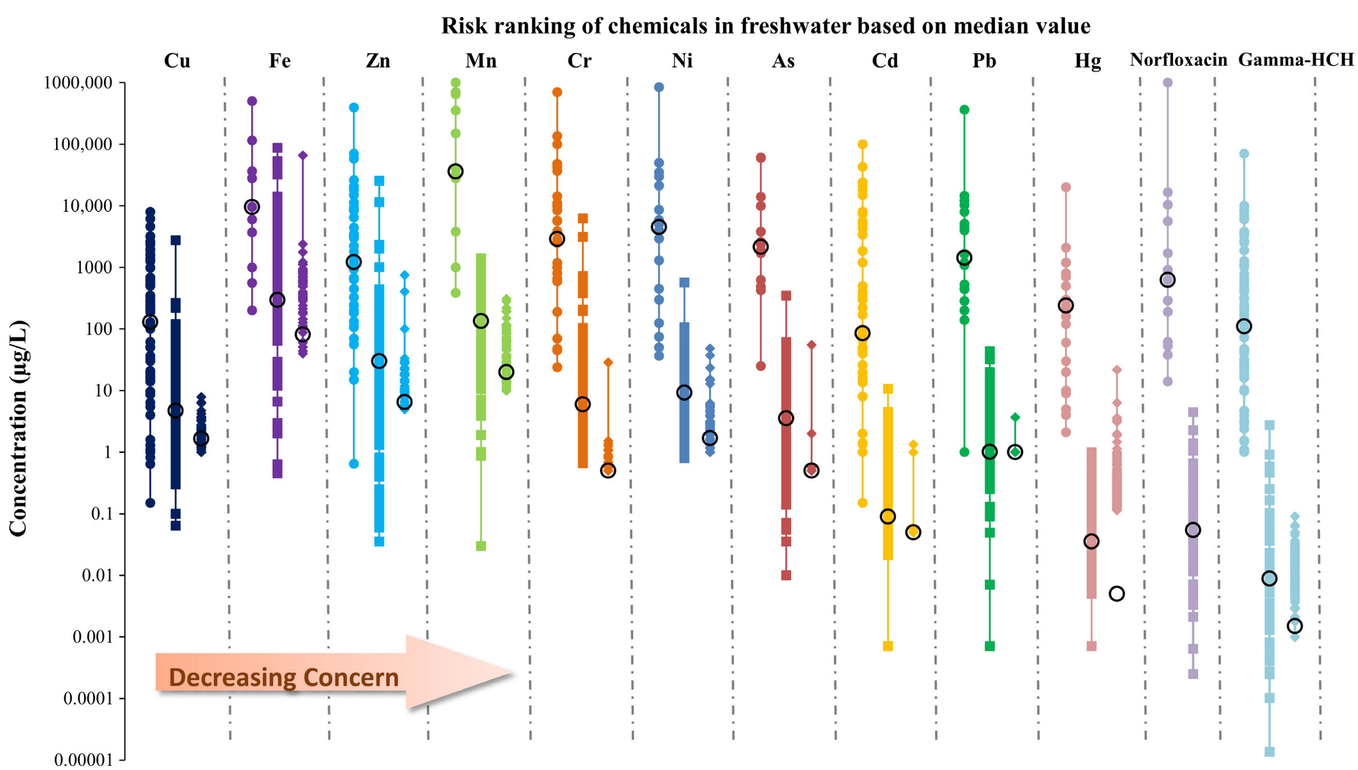

Fig. 2. Risk ranking of the metals and norfloxacin and gamma-HCH in freshwater in the Bohai Region, and their comparison with the UK rivers. Solid filled circle: effect concentrations reported. Solid filled square: freshwater concentrations in the Bohai Region. Solid filled diamond: water concentrations in the UK rivers (the third and final dataset). Hollow black circle: median points.

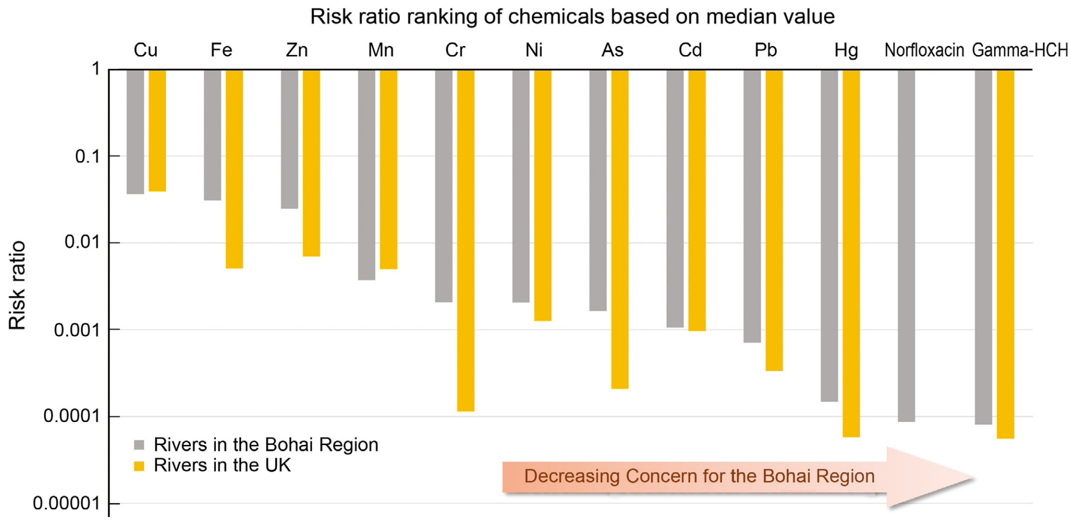

Fig. 3. Risk ratio ranking of the chemicals found in the freshwater in the Bohai Region compared with that for UK rivers based on median data.

concentrations for all metals in the rivers of the Bohai Region were higher, by a factor of 5–10, except for Cu, Fe, Cd, and Pb (Fig. 2). Interestingly, the top four high-risk metals identified for the UK and Bohai Region of China were the same. This raises the intriguing possibility that this might be the same situation worldwide.

By way of comparison, the risk for norfloxacin (fluoroquinolone class of antibiotics), a commonly used broad-spectrum antibacterial agent for human therapy, veterinary husbandry, and aquaculture was examined (Tolls 2001, Kemp et al. 2009, Jin et al. 2011). Similarly, hexachlorocyclohexanes (HCHs), typical organochlorine pesticide widely used in China from the 1950s, were assessed for comparative risk. Gamma-HCH (lindane), one isomer of HCHs, is selected because it is the main insecticidal component, and it ranked in the middle position in the risk ranking of chemicals in the UK rivers (Donnachie et al. 2014). It could be seen that these two selected organic contaminants with risk values of 0.00009 and 0.00008, respectively, were almost 1000-fold lower relative risk than the metals (Figs. 2 and 3). The measured concentrations of organic chemicals were referred to Hao et al. (2011), Jin et al. (2011), Li et al. (2013), Wang et al. (2013), Bai et al. (2014), Gao et al. (2014, 2015), Guo (2015), Qin et al. (2015), and Zhang et al. (2015).

Overlap: the group of organisms likely to be suffering adverse effects in Bohai Region freshwater ecosystem

While there is a difference of 10- to 1000-fold between the median ecotoxicity and river concentrations, there are overlaps between the two datasets (Fig. 2). Thus, all of the metals except Hg in some locations of the study area had concentrations exceeding the effect-level thresholds.

The metal Cu was identified as providing the greatest threat to aquatic wildlife, and a considerable overlap between the effects and freshwater measured data can be seen (Fig. 2). Cu was reported in Yanghe River, Fuyang River, Hutuo River in Hebei; Chao River, Dashi River, and other rivers in Beijing City; and many other rivers in the Haihe Basin and the southern Bohai Sea. The number of samples was 838. Its measured concentration in the study area ranged from 0.0007 to 2,755 μg/L, while the median value was 4.73 μg/L (Table S2). The wildlife group most at risk were fishes and algae. However, the lowest reported effect concentration that had an adverse impact on organisms was 0.15 μg/L, for *tubifex tubifex* (Das et al. 1993).

The metal Fe posed the second greatest threat to aquatic wildlife in this ranking. The number of samples was 121. The observed Fe concentrations in Bohai Region had a wide range from 0.45 to 87,390 μg/L, with a median value of 295.8 μg/L, about 12-fold lower than the median effect concentration. The sampling sites with higher concentrations were found in Fuyang River. Fe exposure concentrations had a considerable overlap with effect concentrations for fish. *Goldfish* was the most sensitive species to Fe, with a lethal potential at 200 μg/L (Alam and Maughan 1995).

Zinc was ranked in the third place, with a median value of 30 μg/L and a concentration range in the Bohai Region from 0.035 to 25,370 μg/L. The exposure concentrations overlapped a significant proportion of effect concentrations for all species, particularly for fish and insects. The median value of exposure concentrations was 30-fold lower than the median effect concentration. The most sensitive species for Zn was *Microcystis aeruginosa*, a blue-green algae, with the lowest effect concentration level at 0.65 μg/L (Gouvêa et al. 2008).

For other metals, the most sensitive species were *Oncorhynchus mykiss* (fish, standard species), *Oncorhynchus tshawytscha* (fish, standard species), *Scenedesmus acutus* (green algae), *Chlorella vulgaris* (green algae), *Hyalella azteca* (a crustacean, standard species), *Ceriodaphnia reticulata* (a crustacean), *H. azteca* (a crustacean, standard species) for Mn, Cr, Ni, Cd, Pb, As, and Hg, respectively (Birge et al. 1981, Jin et al. 1996, Borgmann et al. 2005, Farag et al. 2006, Jain 2009). In conclusion, fishes, algae, and crustaceans were the most three sensitive species. As some freshwater fishes and crustaceans are consumed in China, potential risks to human health exist.

Identifying the geographic areas is of the greatest concern

The highest concentrations found in rivers in the Bohai Region are shown in Table 1. Reviewing the rivers where the highest concentration of each metal was reported, Fuyang River in Hebei Province, a tributary of the Haihe River Basin (Fig. 1), seemed to be the top hot-spot river where five metals (Fe, Zn, Ni, Pb, and Cr) were found at their highest concentrations. In this sub-catchment, there are believed to be up to 90 leather factories, 43 steel plants, 136 electroplating plants, 94 thermal power plants, and 208 cement production plants (Wu 2014). Yongnian County in Handan City, located in the upstream of Fuyang watershed, is the largest standard component production base in China (Wu 2014). It was estimated that there was more than 5 billion tons of wastewater which was minimally treated and directly discharged into the river each year, in which municipal wastewater and industrial wastewater contributed equally (Wang and Shan 2012). It is probable that these large domestic and industrial effluents with poor wastewater treatment were linked to these high metal concentrations.

The other hot-spot was Jiehe River in the southern part of the Bohai Region (Fig. 1), with the highest concentrations of Cu and As. Information suggests that there are abundant gold, copper, and iron mining activities in the Jiehe River Basin (Cao et al. 2001). It is known that the metal mining industry was closely related to the waste generation and metal pollution. Thus, this river might also suffer from severe ecological risk.

Temporal changes in metals' risk ranking: Haihe River Basin as a case

With a particularly long time-series of data available and its large proportion in the study area (Fig. 1), a temporal comparison of metals' risk ranking in the Haihe River Basin was made between the 2000–2009 period and the recent 2010–2016 period using the same risk ratio approach (Xiaoduan et al., Xiong 2005, Wang et al. 2011, Tang et al. 2013; Fig. 4). Compared to 2000–2009, risks of all the metals (unfortunately no data for Fe were available for the 2000–2009 period) decreased over the last 7 yr except for Mn. The largest reductions were observed for Cd and Pb, which decreased by 200-fold and 40-fold, respectively. The metals Cd and Pb have been considered as top priority pollutants among all the heavy metals in the Bohai Sea and its costal region (Xu et al. 2013). This temporal difference indicates that the regulation and control measures on Cd and Pb were helpful. But further efforts should be directed now to Mn and Fe.

Risk ranking vs. the Chinese water quality standard risk results

Across the world, countries typically select chemical quality standards based on a combination of the lowest effect concentrations together with other considerations such as bioconcentration factors and human health concerns. China has the Surface Water Environmental Quality Standard (GB 3838-2002), which includes three parts, that is, basic surface water environmental quality standard item, supplementary central drinking water surface source item, and particular central drinking water surface source item (GB 3838-2002). In the latter two cases, a quality sufficient to protect human health is the main aim. Thus, the most comparable standard to the aim of this study, which is assessing risk to aquatic wildlife, would be the Grade III in the basic surface water environmental quality standard item (Appendix S1: Table S3). Grade III standards for Cu, Zn, As, Hg, Cd, Cr, and Pb are available (while Fe, Mn, and Ni are not listed in the standard). The limit values of metals in basic surface water environmental quality standards are shown in Appendix S1: Table S3.

If the median freshwater concentration for the metals are compared to these limits, as calculated by Eq. 2:

$$\text{Risk} = \frac{mW}{L} \quad (2)$$

Table 1. Rivers with the highest reported metal concentrations.

ID	Metal	The highest concentration (μg/L)	Corresponding sampling river	References
1	Iron	87,390	Fuyang River in Hebei Province	Wu (2014)
2	Copper	2,755	Jiehe River in southern Bohai Sea	Xu et al. (2013)
3	Zinc	25,370	Fuyang River in Hebei Province	Wu (2014)
4	Manganese	1,720	Yellow River Delta	Song et al. (2013)
5	Chromium	6,226	Fuyang River in Hebei Province	Wu (2014)
6	Nickel	571	Fuyang River in Hebei Province	Wu (2014)
7	Cadmium	10.70	Weiyun River in Haihe Basin	China National Environmental Monitoring Center
8	Lead	43.43	Fuyang River in Hebei Province	Wu (2014)
9	Arsenic	347.70	Jiehe River in southern Bohai Sea	Xu et al. (2013)
10	Mercury	0.99	Yanghe River in Hebei Province	Tan et al. (2014)

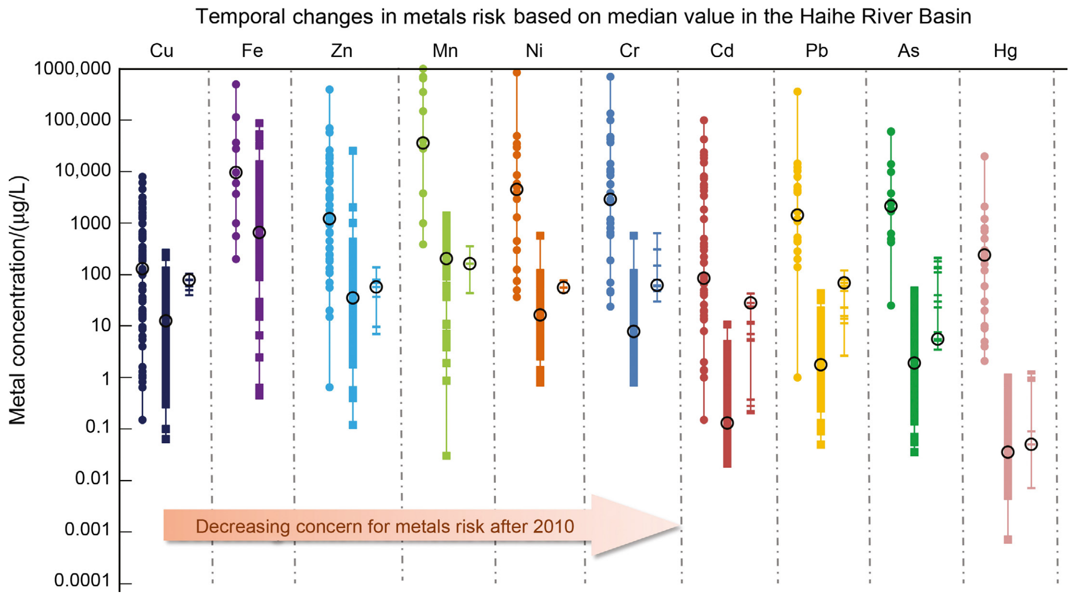

Fig. 4. Temporal changes of metals' risk ranking based on median values only for the Haihe River Basin. For each metal going from left to right, the solid filled circle: effect concentrations reported; the solid filled square: the most recent freshwater measurements since 2010. Finally, the horizontal line: older freshwater concentrations from 2000 to 2009. Hollow black circle: median points. There was a lack of Fe concentrations from 2000 to 2009.

where mW was the median river water concentration (μg/L) and L was the limit value of metal (μg/L). For Cu, Zn, As, Hg, Cd, Cr, and Pb, L were the limit values of Grade III in Appendix S1: Table S3 (GB 3838-2002). As the values of Grade III have not been set for Fe and Mn, we can use the higher standard values that are set for supplementary central drinking water surface source item, that is, 300 and 100 μg/L, respectively. Thus, according to the Chinese regulations, the metals of greatest concern in order would be as follows: Mn (1.34) > Fe (0.986) > Hg (0.35) > Cr (0.12) > As (0.046) > Zn (0.035) > Pb (0.034) > Cd (0.024) > Cu (0.007). This is a somewhat different risk ranking to the method used in the study. Thus, the current Chinese water quality standards would appear to operate in a different manner. Given the review of Cu ecotoxicity values used in this study, it could be argued that the current Chinese standards under-rate the risk from Cu and Ni and should not be neglected.

Conclusion

This study utilized large amount of information available to explore how metals could be ranked based on current knowledge. Based on a comparison of the median ecotoxicity and freshwater concentrations, Cu, Fe, Zn, Mn, and Cr were the metals of highest risk to the Bohai Region. This ranking of concern is somewhat different from the Chinese Surface Water Environmental Quality Standard (GB 3838-2002) that was applied to the measured metal concentrations in this region. This Chinese standard predicts a much lower risk from Cu than would be warranted by available ecotoxicity data. By way of comparison, the risk levels of metals were much higher than the two selected organic contaminants norfloxacin and gamma-HCH. All metals examined in the Bohai Region had concentrations about 5- to 10-fold higher than the UK median values except for Cu, Fe, Cd, and Pb. All of the metals could be found at levels in some places (except Hg) that would exceed some of the effect-level thresholds for wildlife. Thus, it would be expected that a broad range of aquatic organisms will suffer from different degrees of metal toxicity in the Bohai Region, although bioavailability factors might reduce this. Compared to 2000–2009, except for Fe and Mn, risk of all the metals decreased over the last 7 yr in the Haihe River Basin, particularly for Cd and Pb, which indicated that the regulation and control measures on Cd and Pb were helpful.

Given sufficient Chinese freshwater chemicals monitoring data, and by combining this with a review of ecotoxicity data, it will be possible to identify the greatest threats to Chinese freshwater ecosystem and to give powerful support to the establishment of Chinese Surface Water Environmental Quality Standard (GB 3838-2002). At this stage of this risk ranking analysis, it would appear that the historic concern by environmental scientists, decision makers, and regulators on metals has been entirely justified. In the future, more pesticides, pharmaceuticals, surfactants, and POPs will be included in the comparison.

Acknowledgments

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