Oyster As, Cd, Cu, Hg, Pb and Zn Levels in the Northern South China Sea: Long-term Spatiotemporal Distributions, Interacting Effects, and Risk Assessment to Human Health

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Oyster As, Cd, Cu, Hg, Pb and Zn levels in the northern South China Sea: long-term spatiotemporal distributions, interacting effects, and risk assessment to human health

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Abstract

Estuarine and coastal ecosystems are often considered vulnerable due to the complex biogeochemical processes and the human disturbances through a variety of pollution. Among environmental contaminants, heavy metals in estuarine and coastal ecosystems have been of increasing concern in environmental conservation. Long-term exposure to heavy metal contamination, mainly through food and water, could be harmful to human health. It is therefore critical to understand the quantitative comparisons and interacting effects of different heavy metals in common seafood species, such as oysters. This work studied the long-term spatiotemporal trends and health risk assessment of oyster arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) levels in the coastal waters of northern South China Sea. Cultured oysters (*Crassostrea rivularis*) from 23 estuaries and harbors in the coastal areas of northern South China Sea in 1989-2015 were analyzed for the spatiotemporal trends of the six heavy metal levels. Metal pollution index (MPI), target hazard quotient (THQ) and hazard index (HI) were used for quantifying the exposure of the six heavy metals to human health through oyster consumption. Principal component analysis (PCA) was used for assessing the relative importance of the six metals in oyster heavy metal distribution patterns in the northern South China Sea. Overall, the As, Cd, Cu, Hg, Pb and Zn levels in oysters from the northern South China Sea generally declined from 1989 to 2015, stayed relatively high (MPI = 2.42-3.68) during 1989-2000, gradually decreased since 2000, and slightly increased after 2010. Oyster heavy metal levels were highest in the Pearl River Estuary (MPI = 1.20-5.52), followed by west Guangdong and east Guangdong, Guangxi, and Hainan coastal waters. This pattern is probably because economics and industry around the Pearl River Estuary have been growing faster than the other areas of this work in the recent two decades, and it should be taken as a hotspot for the monitoring of seafood safety in southern China. Principal component analysis indicated that Cu, Zn and Cd were the most important metals in the long-term distributions of oyster heavy metal levels in the northern South China Sea. Health risk assessment suggested that the risk of the six heavy metals exposure through oyster consumption were relatively high during 1989-2005 (THQ = 1.01-5.82), significantly decreased since 2005 (THQ < 1), and slightly increased after 2010.

Keywords Environmental conservation · Hazard index · Health risk assessment · Heavy metal pollution · Metal pollution index · Oyster *Crassostrea rivularis* · Principal component analysis · Seafood safety · Spatiotemporal distributions · Target hazard quotient

Introduction

Natural fishery resources have declined for more than ten times since commercial fishing became popular worldwide (Myers and Worm 2003). As the world population and living condition increasing nowadays, the need for high-quality protein, such as seafood, increases dramatically. Under the current global trade of seafood, seafood safety has drawn increasing concerns, especially when huge amounts of seafood imported to developed countries (e.g., German and Japan) are from developing countries (Kent 2003; Pauly and Jacquet 2019). Estuarine and coastal ecosystems are often taken as vulnerable due to the complex biogeochemical processes and the human disturbances through a variety of pollution (Bendell et al. 2020). Among environmental contaminants, heavy metals in estuarine and coastal ecosystems have been of increasing concern in environmental conservation (Jahan and Strezov 2019; Suami et al. 2019; Pinzón-Bedoya et al. 2020). Long-term exposure to heavy metal contamination, mainly through food and water, could be harmful to human health. The Bulletin of Marine Ecological Environment of China indicated that in 2016 the sediments from 25 out of 81 estuaries did not meet the environmental requirement of their respective marine functional zones (Chen 2018). Therefore, the monitoring of heavy metal pollution in marine organisms is critical for seafood safety, environmental evaluation, and aquaculture development (Azevedo et al. 2019; Djedjibegovic et al. 2020; Esilaba et al. 2020).

Marine bivalves and planktivorous fish have been serving as major prey for predators (e.g., sharks and marine mammals) in marine ecological systems. The rapid development of marine bivalves aquaculture has played an important role in the sustainable development of fisheries in China and the global trade and supply of seafood (Pauly and Jacquet 2019). China's marine aquaculture production grows from 1.58 million tons in 1989 to 18.76 million tons in 2015. Oysters have become one of the most popular seafood in coastal or even inland regions nowadays, because they are of high nutrients, affordable, and widely farmed (García-Rico and Tejeda-Valenzuela 2020). The oyster aquaculture production from the northern South China Sea took around 36.3% of China's total production of bivalves aquaculture in 2000, 2010, and 2015. The oyster aquaculture production from three provinces Guangdong, Guangxi and Hainan in the coastal areas of the northern South China Sea increases from 12.5 thousand tons in 1989 to 1.66 million tons in 2015. By 2015, the oyster aquaculture area in the three southern China provinces has been up to 49.9 thousand hectares, accounting for 35.2% of China's total area of oyster aquaculture.

Heavy metal accumulation in bivalve mollusks depends on not only the biological processes within organisms, but also the concentrations and bioavailability of heavy metals in ambient environment. Due to their limited dispersal ability, mollusks easily accumulate heavy metals from environment, and the heavy metal concentrations in their tissues could indicate the bioavailability of heavy metals and the heavy metal levels in the environment. Studies based on double-box kinetic model suggested that as heavy metal concentrations in ambient water increased, oysters' bioconcentration factor (BCF) for heavy metals decreased and the heavy metal levels in their tissues significantly increased at the state of equilibrium, which made oysters a good indicator species for cadmium, lead and mercury contamination (Wang et al. 2004). Principal component analysis (PCA) provides an ideal tool for identifying the sources and relations of multiple heavy metals (Zhou et al. 2007).

Heavy metal levels in marine invertebrates such as oysters are usually several orders of magnitude higher than those in seawater (Rainbow 1997). Different species have different accumulation and degradation capacities to heavy metals. Oysters typically have a stronger ability to accumulate zinc than mussels, and can store zinc as detoxified granules in tissues, whereas mussels often discharge the zinc they absorb (George et al. 1978). The heavy metal levels and accumulation processes in oysters depend on the marine environment and the type and species of heavy metals (Rainbow et al. 1993). There are various paths for heavy metals to be transferred from environment to organisms, and the absorption efficiency of different paths varies among species and environmental conditions (Rainbow et al. 1993). Heavy metal ions usually get into organisms through major ion channels, and as salinity decreases, the function of ion pumps increases, which increases the possibility for heavy metals being absorbed by organisms. Rainbow (1997) categorized Cu^{+} and Hg^{2+} as Class B, and As(III), Cd^{2+}, Cu^{2+}, Pb and Zn^{2+} as borderline ions. Copper and zinc are essential vector elements for organisms, and Class B and borderline ions both have potential toxicity, but Class B is typically considered as more toxic than borderline ions. An organic ligand can more easily and strongly bind with Cu than with Zn^{2+} (Rainbow 1997). George et al. (1978) examined the heavy metal species in green-colored oysters, and found that copper and zinc bound with sulfur and phosphorus respectively, and the formed Cu-S and Zn-P were stored in vesicles. Their study indicated that the copper in oysters' blood serum could be absorbed by granular amoebocytes and stored in vesicles, which significantly reduced the toxicity of copper in oysters. Some heavy metals absorbed by organisms could be taken into biological processes such as metabolisms, but any heavy metals that are nonessential or essential but beyond normal levels should go through temporary or permanent detoxification, or would harm normal biological activities. Studies suggested that infants and children's blood lead levels were significantly correlated with their intelligence quotient (IQ), and the IQ value would decrease for about 1-3 when the blood lead level increased for 100 μg/L (Wang et al. 2010; Taylor et al. 2017).

Oysters can easily accumulate pollutants in ambient waterbodies because of their limited dispersal ability and filter-feeding strategy, and the pollutants can be further accumulated through food chain and harm consumers' health, making oysters one of the seafood of most concern. Although there have been studies on oyster arsenic (Wang et al. 2017), cadmium (Wang et al. 2012), copper (Wang et al. 2020) and mercury (Zong and Jia 1996) levels in the northern South China Sea, they usually focused on one single heavy metal and seldom considered the quantitative comparisons or interacting effects of multiple heavy metals in cultured oysters from this area. Given that oysters' accumulation and degradation capacity varies between heavy metals and the potential toxicity of heavy metals differs a lot, it is important to understand the interacting effects and health implications of multiple heavy metals in popular seafood species such as oysters. This work studied the long-term spatiotemporal trends and health risk assessment of oyster arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) levels in the coastal waters of the northern South China Sea from 1989 to 2015. The objectives were to investigate the spatiotemporal patterns and interacting effects of the six heavy metal levels in cultured oysters in this area in 1989-2015, and to assess the health risk of the six heavy metals exposure through oyster consumption. Results of this work could help further understand the past, current and future status of the six heavy metal levels in the northern South China Sea, provide guidance for pollution recovery and monitoring programs, and support sustainable development of fisheries and human well-being in this area.

Material and methods

Sampling and analytical procedures

Based on the major farming areas of cultured oysters (*Crassostrea rivularis*) in the three provinces (i.e., Guangdong, Guangxi, and Hainan) in the coastal areas of the northern South China Sea and the habitat characteristics of coastal key fishery waterbodies, oyster samples were collected from 23 estuaries and harbors in March and April from 1989 to 2015 (Fig. 1). Among the 23 sampling sites, 17 sites were in Guangdong and sampled in 1989-2015, and two and four sites were in Guangxi and Hainan respectively and sampled in 2006-2015 because of logistic constraints in early years of this work. The oyster samples were all at the age of two to three, and were made sure to meet the size requirement of southern China seafood markets. At each sampling location, the number of oysters collected were made sure to be more than 30. The oysters were rinsed using sea water *in situ* and dissected. The soft tissues were stored at -20 °C including body fluids. The entire sampling procedure referred to the China National Specification for Marine Monitoring (GB 17378-1998; GB 17378-2007).

Prior to analyzing heavy metal concentrations, the collected oysters were naturally defrosted to around 20 °C. Samples were homogenized and measured for wet weight (W_w), and then oven-dried for about 72 hours and measured for dry weight (W_d). Samples (0.500 ± 0.005 g) were ashed around 450 °C and digested using a solution of 1 mL H_2O_2 and 8 mL HNO_3. Samples were then filtered using springe filters (0.45 μm) and reconstituted to 10 mL in 2% HCl (Wang et al. 2020). Arsenic, cadmium, copper, mercury, lead and zinc concentrations of the samples were measured in HITACHI atomic absorption spectrophotometry (Model Z-2000). The measurement was conducted twice in the same environment for every sample, and were made sure their absolute difference no more than 10% of their arithmetic mean (Wang et al. 2020). For quality assurance, standard reference materials were analyzed regularly (China Standard - Oyster tissues GSBZ 19002-88). The analytical procedure referred to the China Methods of Food Hygienic Analysis – Physical and Chemical Section (GB/T 5009-2003).

Metal pollution assessment

Arsenic, cadmium, copper, mercury, lead and zinc concentrations of the collected oysters were expressed as geometric mean (Han et al. 1998). The locally weighted least squares regression scatterplot smoothing (LOWESS) was used to examine the temporal variation of the six heavy metal levels in sampled oysters. Metal pollution index (MPI) was calculated for assessing the heavy metal pollution status of cultured oysters from different area or time:

$$MPI = (MC_1, MC_2, \dots, \ MC_i)^{1/n} \tag{1}$$

where MPI is the metal pollution index, and MC_i is the concentration of metal i in the soft tissues of oysters (Denil et al. 2017). The criterion for evaluating heavy metal pollution status according to MPI was summarized in Table 1 (Jamil et al. 2014). Analysis was conducted using R software and the package of ggplot2 (R Development Core Team 2020).

Health risk assessment

Target hazard quotient (THQ) was calculated for quantifying the health risk of arsenic, cadmium, copper, mercury, lead and zinc exposure through oyster consumption:

$$THQ = \frac{\mathrm{EFr} \times \mathrm{EDtot} \times \mathrm{SFI} \times \mathrm{MCS}}{RfD \times BWa \times ATn} \times 10^{-3} \quad (2)$$

where EFr is the exposure frequency (182.5 days per year); EDtot is the total exposure duration (30 years), which means the exposure time of consuming oysters; SFI is the seafood ingestion which is taken as 26.8 g/person/day (Tang et al. 2009; Wang et al. 2012), and we assumed that all the seafood consumed was oyster soft tissues; MCS is the metal contents in edible portion of seafood; RfD is the reference dose by oral consuming in μg/g/day (Table 2); BWa is the average body weight 70 kg; and ATn is the average exposure time for noncarcinogenic (EDtot × 365 days = 10950 days).

Hazard index (HI) was used to analyze the total potential risk to consumers' health for the six heavy metals, which is the sum of THQ:

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

where HI is the hazard index, THQ_i is the target hazard quotient of metal i, and n is the number of target metals in oyster soft tissues.

Relative impact of multiple heavy metal levels

The relative impact and interacting effects of arsenic, cadmium, copper, mercury, lead and zinc in sampled oysters were assessed using principal component analysis (PCA), which maximizing the total variance of loading values for different factors through varimax rotation (Abdi and Williams 2010).

Results

Spatiotemporal distributions of six heavy metal levels in oysters

Heavy metal analysis of cultured oysters sampled from 23 sites in the coastal areas of the northern South China Sea in 1989-2015 suggested that the spatiotemporal distributions of arsenic, cadmium, copper, mercury, lead and zinc varied a lot between metals (Table 3, Fig. 2). The copper and zinc levels were 53.85 µg/g and 149.23 µg/g respectively (expressed as geometric mean, wet weight), and were three orders of magnitude higher than the cadmium (0.57 µg/g), arsenic (0.33 µg/g) and lead (0.31 µg/g) levels, and four orders of magnitude higher than the mercury level (0.01 µg/g). Overall, the six heavy metal levels in sampled oysters declined during 1989-2010 (e.g., arsenic, cadmium, copper, and lead; Fig. 2), and slightly increased in 2011-2015 (e.g., arsenic, copper, mercury, and lead; Fig. 1), especially that the arsenic and lead levels increased from 0.10 µg/g and 0.20 µg/g in 2006-2010 to 0.52 µg/g and 0.34 µg/g in 2011-2015, with an increase for 420% and 70% respectively. The temporal variation of the cadmium levels were less than the other five metals, with an increase to 1.58 µg/g in 1996-2000, a decrease for 50.6% (to 0.78 µg/g) in 2001-2005, and a slight increase in 2006-2015 (0.84 µg/g in 2006-2010 and 0.86 µg/g in 2011-2015; Table 2).

Heavy metal analysis of cultured oysters sampled from five zones consisting of the Pearl River Estuary, west Guangdong, east Guangdong, Guangxi and Hainan in 1989-2015 indicated that the heavy metal levels in the Pearl River Estuary were significantly higher than those in the other four zones (Table 3, Fig. 2). Heavy metal levels in the Pearl River Estuary were generally higher than the overall levels in the northern South China Sea, except that the arsenic and mercury levels in the Pearl River Estuary were similar to those in the whole study area. The overall levels of arsenic, cadmium, copper, mercury, lead and zinc in the Pearl River Estuary in 1989-2015 were 0.32 µg/g, 1.49 µg/g, 122.35 µg/g, 0.01 µg/g, 0.42 µg/g and 210.49 µg/g respectively. The six heavy metal levels in the Pearl River Estuary were relatively high in 1989-2005, the arsenic, copper and cadmium levels decreased for 69.3%, 68.7% and 19.3% from 2001-2005 to 2006-2010, and the arsenic, copper and lead levels increased to 0.40 µg/g, 84.75 µg/g and 0.32 µg/g in 2011-2015 compared to those in 2006-2010. Heavy metal levels in west and east Guangdong were very similar to each other, and were relatively high in 1989-1990, 1991-1995 and 1996-2000. The heavy metal levels in west Guangdong were generally higher than those in east Guangdong during 2001-2005, except for the arsenic and lead levels. Due to logistic constraints, oyster heavy metal data from Guangxi and Hainan were not available until 2006, and heavy metal levels in the coastal waters of Guangxi were generally higher than those in Hainan. However, the heavy metal levels in Guangxi were higher in 2006-2010 than in 2011-2015, whereas the heavy metal levels in Hainan were lower in 2006-2010 than in 2011-2015. Heavy metal levels in Guangxi and

Hainan were close to the overall levels in the northern South China Sea, lower than those in the Pearl River Estuary, and similar to those in west and east Guangdong.

Metal pollution assessment of six heavy metal levels in oysters

The MPI analysis suggested that the oyster heavy metal levels in the northern South China Sea during 1989-2000 were in very low contamination (MPI = 1.6; Table 3). Heavy metal levels in this area declined in 1989-2015, with the MPI value decreasing for 75.1% from 3.82 in 1989-1990 to 0.95 in 2011-2015. The MPI value in this area was 3.82 in 1989-1990 and 3.68 in 1996-2000, both higher than 2.42 in 1991-1995. The degree of oyster heavy metal pollution in the northern South China Sea was considered as not impacted since 2001. Across the five zones and different time periods, oyster heavy metal levels in the Pearl River Estuary in 1996-2000 were the highest (MPI = 5.52) and in 1989-1990 were the second highest (MPI = 4.85). The MPI value in the coastal waters of west Guangdong was 4.17 in 1989-1990, and was 2.45, 3.40 and 2.62 in 1991-1995, 1996-2000 and 2001-2005 respectively, all higher than that in east Guangdong. The degree of oyster heavy metal pollution in the coastal waters of Guangxi and Hainan was assigned as not impacted according to MPI since 2006.

Health risk assessment of six heavy metal levels in oysters

The health risk of arsenic, cadmium, copper, mercury, lead and zinc exposure through oyster consumption in the coastal areas of the northern South China Sea in 1989-2015 according to THQ and HI was summarized in Table 4. Typically the health risk of heavy metal exposure is considered as high when HI > 1. The overall health risk of the six heavy metals exposure in the northern South China Sea was highest in 1989-1990 (HI = 3.336), gradually decreased since 1991 but still relatively high in 1991-1995 (HI = 1.309) and 1996-2000 (HI = 1.177), and became low during 2001-2015 (HI < 1) but slightly increased in 2011-2015 compared to 2006-2010.

For the health risk of individual heavy metal exposure, the risk of copper exposure in the study area in 1989-1990 was the highest (THQ_{Cu} = 2.055), due to the high risk of copper exposure in the Pearl River Estuary (THQ_{Cu} = 4.438) and west Guangdong (THQ_{Cu} = 2.454) during this time period. The risk of arsenic exposure in the study area in 1989-1990 was the second highest (THQ_{As} = 0.919), due to the high risk of arsenic exposure in east Guangdong (THQ_{As} = 1.091), west Guangdong (THQ_{As} = 0.900) and the Pearl River Estuary (THQ_{As} = 0.804) during this time period. The risk of cadmium exposure in the study area in 1996-2000 was the third highest (THQ_{Cd} = 0.302), due to the high risk of cadmium exposure in the Pearl River Estuary (THQ_{Cd} = 0.496) and west Guangdong (THQ_{Cd} = 0.327) during this time period. The risk of zinc exposure was ranked as the fourth, and the risk of lead and mercury exposure were relatively low.

For the health risk of heavy metal exposure in the five zones at different time periods, the risk of heavy metal exposure in the Pearl River Estuary was highest overall (HI = 1.236) except lower in 2006-2010 (HI < 1). The health risk in west Guangdong increased in 2011-2015 compared to 2001-2010. The risk of heavy metal exposure in east Guangdong became relatively low since 2001. The health risk in Guangxi and Hainan was low overall, but slightly increased in 2011-2015 compared to 2006-2010.

Overall, the HI value of the six heavy metals in the coastal areas of the northern South China Sea in 1989-2015 was 0.747; the health risk gradually decreased and became relatively low since 2001, but slightly increased in 2011-2015. The risk of copper exposure was the highest among the six heavy metals, followed by arsenic. The health risk of the six heavy metals exposure was highest in the Pearl River Estuary, relatively low in west Guangdong and east Guangdong, and low in Guangxi and Hainan.

Relative impact of six heavy metal levels in oysters

The PCA results based on the arsenic, cadmium, copper, mercury, lead and zinc levels in oysters from the northern South China Sea during 2006-2015 were summarized in Table 5 and Fig. 3. The first and second principal components explained 37.46% and 25.97% of the heavy metal variation in sampled oysters. The heavy metals contributed most to the first principal component were copper (29.78%), lead (23.76%) and mercury (22.77%). The heavy metals contributed most to the second principal component were zinc (46.60%), cadmium (29.02%) and arsenic (10.77%).

Discussion

Sources of heavy metals and pollution status in the northern South China Sea

Coastal waters are the key habitat for many important commercial fishery species such as oysters, and a critical component of marine ecosystems. As the industrialization and urbanization processes continue to accelerate in coastal areas, there have been increasing marine fishing pressure and environmental pollution, and coastal waters are impacted most (González-Macías et al. 2006). Due to their high toxicity, bioaccumulability and persistence, heavy metals can harm human health through food chains and therefore have drawn increasing attention in environmental science (Zhou et al. 2007).

This work analyzed six heavy metal levels in cultured oysters sampled from 23 sites in the coastal areas of the northern South China Sea in 1989-2015, which allowed us to be able to examine the status and trend of multiple heavy metals and their interacting effects at higher spatial and temporal scales, whereas previous studies often focused on one particular heavy metal (Wang et al. 2012; Wang et al. 2017). This work suggested that oysters from the northern South China Sea were most contaminated by copper and arsenic. Prior studies indicated that cultured oysters from the Jiaozhou Bay (Yellow Sea) were most contaminated by arsenic and mercury, followed by copper, cadmium, zinc and lead, probably caused by the discharge of industrial wastewaters (Chen 2018); cultured oysters from the Gulf of Yueqing (East China Sea) were most contaminated by copper, lead, zinc, cadmium and mercury. Different heavy metals typically have quite different potential sources; copper, lead and zinc usually come from the discharge of electroplating industry; zinc and lead are also highly related to the construction, maintenance and anchoring of vessels; cadmium and mercury are mainly from the discharge of coal-fired power stations (Tanner et al. 2000; Zhou et al. 2007). Therefore, anthropogenic sources are becoming the major sources of heavy metal pollution in coastal waters.

This work indicated that oysters from the northern South China Sea were most contaminated by copper. Pan et al. (2014) suggested that copper contamination has become an increasing problem for the coastal and estuarine environmental protection in China. Copper widely exists in the tissues of organisms, is an important structural element and a component of many proteins and enzymes in cells, and critical for metabolisms. However, copper above normal levels can be harmful for organisms. High concentrations of copper can directly or indirectly influence the oxidation-reduction state of cellular environment and assist produce reactive oxygen species, which could adversely affect cell structures, functions and metabolisms, or even damage cells. Nowadays copper is commonly used in electronics, construction, mechanics, electroplating, telecommunication, energy, petrochemistry and aquaculture. China's copper consumption has grown from 2.2 million tons in 2001 to 7.8 million tons in 2011, and its percentage in global copper consumption has increased steadily (Pan et al. 2014). The appearance of blue/green-colored oysters is a complex biological and ecological consequence of high copper levels, and suggests the problem of copper contamination in the coastal waters of China. In recent years, copper contamination started to lessen because of improved monitoring and management strategies. Wind power industry has increasingly developed as a substitute for coal-fired power, which also help reduce the discharge of heavy metals.

Heavy metal pollution in the Pearl River Estuary is of the most concern in this work. Oyster heavy metal levels and the MPI values indicated that the heavy metal levels in the Pearl River Estuary were higher than the other zone of the study area in 1989-2015. One reason would be because oyster farming areas are mainly in coastal waters with depth < 10 m. The amount of sand brought through water flow to the Pearl River Estuary is 8.366×10^7 tons per year, about 20% of which remains in the Pearl River Delta and the other 80% sedimentates in the coastal area outside the delta (Lan 1989). Lots of sand and heavy metals are brought through the Pearl River flow to the sediments in coastal waters with depth < 10 m, whereas waters with depth > 10 m are less affected by land-source heavy metal input (Ma et al. 2014). Other reasons would be because sediments in the Pearl River Estuary are mainly land source and biological source; human activities around the estuary and the Pearl River strongly increase heavy metal input; and the hydrological and geographical characteristics of the Pearl River Estuary are suitable for the sedimentation of heavy metals (Ma et al. 2012). The copper, lead and zinc levels in the sediments of the Pearl River Estuary were (16.1 ± 4.0) µg/g, (21.9 ± 2.1) µg/g and (94.3 ± 11.2) µg/g (Ma et al. 2014); their levels in Guangdong coastal waters were 15.5 µg/g, 30.0 µg/g and 63.3 µg/g (He and Wen 1982); and those round the South China Sea Shelf area were 7.43 µg/g, 15.6 µg/g and 54.4 µg/g (Zhang and Du 2005). As a consequence of the water pollution in the Pearl River Estuary, nowadays there has been no more oyster farming area in the city of Shenzhen, which is located by the estuary. The current major areas for oyster farming are in east and west Guangdong, mostly in the cities of Yangjiang and Zhanjiang.

Risk of heavy metal exposure to human health through oyster consumption

Large amounts of heavy metals from the discharge of industrial and agricultural wastewaters can directly or indirectly harm human health (Sheehan et al. 2014). Coastal residents are usually more susceptible to heavy metal exposure from higher sea food consumption than other populations (Juric et al. 2017). There have been a variety of investigations on the health risk and toxicology of heavy metals (Morais 2012; Wang et al. 2018). With the application of new technologies in ecological toxicology in recent years, great achievement has been made in studies on the interacting effects of multiple heavy metals on oyster life history and the complex relationships between the chemical properties of different heavy metals, which could provide valuable guidance for oyster safety, safe consumption, heavy metal exposure risk and protecting oyster consumers' health (Wang et al. 2018).

Health risk assessment is to quantify the probability of adverse effects on human health due to a specific toxic agent exposure. The parameters of THQ through oyster consumption in this work were mainly from experiment and survey data. The assessment results depend mostly on the toxicity and exposure (frequency and duration) of heavy metals. Risk assessment of heavy metals is typically comprised of hazard assessment, dose-response assessment, exposure assessment, and risk assessment. The diet structure of seafood consumers varies a lot between different areas, and health risk assessment of heavy metal exposure should consider the heavy metal type and level and the diet structure (exposure frequency and duration). Oyster intake used in this work was based on a previous survey of 1626 samples from 12 coastal cities in Guangdong examining pollutant exposure through food consumption (Tang et al. 2009). Their survey indicated that residents around the coastal areas of the northern South China Sea consumed more crustaceans and mollusks such as mussels, oysters and scallops than fish, especially for males, and the intake of crustaceans and mollusks could be 76.1 g/day, which was 22.1 g/day more than fish intake. It has been reported that pollution cases such as cadmium contamination in Beijiang River and arsenic poisoning in the city of Yingde happened in Guangdong (Chen 2004; Tang et al. 2009). According to the risk assessment of diet structure (e.g., vegetables, meat, fish, crustaceans, mollusks, rice, and flour) for Guangdong residents, heavy metal pollution in seafood is of substantial concern, and the risk of cadmium exposure is high. This work suggested that the health risk of the six heavy metals exposure through oyster consumption varied between different zones of the study areas and different time periods, and the risk of copper exposure was the highest among the six heavy metals examined. The risk of the six heavy metals exposure to human health was relatively low during 2001-2015, but slightly increased in 2011-2015 compared to that in 2006-2010, and therefore oyster heavy metal levels should still be a key part in the monitoring of oyster safety. The health risk of the six heavy metals exposure was most due to copper, arsenic and cadmium, followed by lead and mercury; zinc has the lowest toxicity among the six heavy metals, and is an essential element for human body.

It is recommended that future research on the toxicity and toxicology effects of oysters should pay more attention to the interacting toxicity and ecological risk assessment of multiple heavy metals exposure, because heavy metal exposure not only puts oysters or oyster consumers at risk, but also has interacting and combined effects on many other aquatic species, and could provide information support for the improvement of water quality standard and ecological risk assessment. Studies based on species sensitivity distributions (SSDs) typically set the target of protecting the majority (usually 95%) of species in the environment when investigating the levels of chemicals such as heavy metals (van Straalen and van Rijn 1998). Future exploration combining SSDs and quantitative structure activity relationships (QSARs) to develop ecological risk assessment methods of chemical species and structure, especially to be applied around the coastal areas of China, could serve as a basis for the management of aquatic ecological environment and seafood safety (Feng et al. 2013).

Conclusions

With the increasing of world population and the need for seafood safety, how to improve the ecosystem service function of limited fishery waterbodies and the sustainable supply of high-quality seafood, is crucial for a healthy development of fisheries and human well-being. This work examined the long-term spatiotemporal trends and health risk assessment of oyster arsenic, cadmium, copper, mercury, lead and zinc levels in the northern South China Sea in 1989-2015. Unlike previous studies usually focusing on one single heavy metal level in cultured oysters from this area (Zong and Jia 1996; Wang et al. 2017; Wang et al. 2020), this work considered the quantitative comparisons, interacting effects and health implications of multiple heavy metals, and the results could serve as a basis for ongoing monitoring of mollusks safety and future development and design of oyster farming.

Results indicated that heavy metal pollution in oysters from the northern South China Sea was most due to copper, arsenic and cadmium, followed by lead and mercury. Across different time periods, oyster heavy metal levels were highest in 1989-1990, 1991-1995 and 1996-2000 (MPI = 2.42-3.68), and gradually decreased since 2001, but slightly increased in 2011-2015, which deserves further attention. Among the five zones, oyster heavy metal levels were generally highest in the Pearl River Estuary (MPI = 1.20-5.52), followed by the coastal waters of west and east Guangdong, Guangxi and Hainan. Health risk assessment according to the THQ and HI values indicated that the risk of the six heavy metals exposure was relatively high in 1989-2005, and decreased since 2006, but slightly increased in 2011-2015. The quantitative comparisons and time series analysis of multiple heavy metals in cultured oysters from the study area suggested that copper contamination in the coastal waters of the northern South China Sea should draw more attention. The Pearl River Estuary generally showed the highest heavy metal levels, probably because economics and industry around the Pearl River Estuary have been growing faster than the other areas of this work in the recent two decades, and it should be taken as a hotspot for the monitoring of seafood safety in southern China. The heavy metal pollution caused by increasing industrialization and urbanization processes in some areas might outcompete the ongoing environmental protection and recovery programs in the past decade. Therefore, the environmental protection and management of aquaculture and seafood safety should be a long-term focus for the sustainability of fishery ecosystems in China.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Availability of data and materials All data generated or analyzed during this study are included in this article. Source data of the South China Sea Mussel Watch Program are available from the corresponding authors upon reasonable request.

Competing interests The authors declare no competing interests.

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Author' contributions Lifei Wang and Xuefeng Wang designed the study and analyzed the data with input from the South China Sea Mussel Watch Program. Haigang Chen, Zenghuan Wang and Xiaoping Jia were in charge of the project collecting long-term data. All authors contributed to the preparation of the manuscript.

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Table 1 Values of metal pollution index (MPI) and criterion for pollution status

Index value	Degree of Pollution
$MPI \leq 2$	Not impacted
$2 < MPI \leq 5$	Very low contamination
$5 < MPI \leq 10$	Low contamination
$10 < MPI \leq 20$	Medium contamination
$20 < MPI \leq 50$	High contamination
$50 < MPI \leq 100$	Very high contamination
$MPI > 100$	Extreme contamination

Table 2 Reference dose (Rfd) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn)*

Metal	Cu	Zn	Pb	Cd	As	Hg
Rfd (µg/g/day)	0.0400	0.3000	0.0035	0.0010	0.0003	0.0005

*The Rfd values referred to US EPA (2013), United States Environmental Protection Agency, Integrated Risk Information System, http://www.epa.gov/iris. The Rfd value of arsenic was based on the value of inorganic arsenic.

Table 3 Mean concentrations (µg/g wet weight) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) in oysters from the northern South China Sea in 1989-2015. Oyster heavy metal levels in Guangxi and Hainan were not available until 2006 due to logistic constraints

Zone	Year	Cu	Zn	Pb	Cd	As	Hg	MPI
Northern South China Sea	1989-1990	429.45	166.98	0.72	1.05	1.44	0.04	**3.82**
	1991-1995	85.58	198.34	0.67	0.62	0.95	0.03	**2.42**
	1996-2000	43.33	127.94	0.32	1.58	0.89	NaN	**3.68**
	2001-2005	47.34	140.47	0.21	0.78	0.34	0.02	1.4
	2006-2010	28.76	153.72	0.2	0.84	0.1	0.01	0.95
	2011-2015	80.02	135.86	0.34	0.86	0.52	0.01	1.6
	Overall	53.85	149.23	0.31	0.85	0.33	0.01	1.38
East Guangdong	1989-1990	139.45	71.35	0.8	0.57	1.71	0.05	**2.7**
	1991-1995	63.29	217.03	0.55	0.43	1.15	0.03	**2.2**
	1996-2000	32.33	117.40	0.37	1.22	0.92	NA	**3.41**
	2001-2005	32.02	127.44	0.25	0.46	0.38	0.02	1.24
	2006-2010	24.29	151.96	0.19	0.75	0.12	0.01	0.93
	2011-2015	74.59	141.49	0.38	0.81	0.51	0.01	1.6
	Overall	42.25	146.19	0.32	0.65	0.4	0.01	1.31
Pearl River Estuary	1989-1990	927.44	293.82	0.71	1.79	1.26	0.03	**4.85**
	1991-1995	162.7	294.5	0.77	0.95	0.89	0.03	**3.13**
	1996-2000	117.62	203.55	0.52	2.59	0.88	NaN	**5.52**
	2001-2005	191.92	232.65	0.32	2.09	0.27	0.02	**2.33**
	2006-2010	59.99	185.18	0.27	1.39	0.07	0.01	1.2
	2011-2015	84.75	158.37	0.32	1.17	0.4	0.01	1.65
	Overall	122.35	210.49	0.42	1.49	0.32	0.01	1.93
West Guangdong	1989-1990	512.83	192.58	0.69	1.1	1.41	0.05	**4.17**
	1991-1995	92.95	162.11	0.77	0.78	0.8	0.03	**2.45**
	1996-2000	39.7	116.46	0.23	1.71	0.85	NaN	**3.4**
	2001-2005	48.7	134.24	0.15	1.04	0.32	0..02	**2.62**
	2006-2010	33.9	148.96	0.18	0.94	0.1	0.01	0.97
	2011-2015	88.54	133.75	0.34	0.91	0.6	0.01	1.67
	Overall	59.64	141.85	0.29	0.98	0.35	0.02	1.6
Guangxi	2006-2010	30.9	224.6	0.18	1.29	0.11	0.01	1.1
	2011-2015	79.23	155.4	0.34	0.79	0.52	0.01	1.61
	Overall	49.48	186.61	0.25	1.01	0.24	0.01	1.33
Hainan	2006-2010	18.79	125.7	0.24	0.53	0.09	0.01	0.8
	2011-2015	72.77	113.98	0.27	0.8	0.47	0.02	1.6
	Overall	36.98	119.7	0.26	0.65	0.21	0.02	1.21

NaN: not available

Table 4 Target hazard quotient (THQ) and hazard index (HI) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) exposure through oyster consumption in the coastal areas of the northern South China Sea in 1989-2015

Zone	Year	THQ_{Cu}	THQ_{Zn}	THQ_{Pb}	THQ_{Cd}	THQ_{As}	THQ_{Hg}	HI
Northern South China Sea	1989-1990	2.055	0.107	0.039	0.201	0.919	0.015	**3.336**
	1991-1995	0.410	0.127	0.037	0.119	0.606	0.011	**1.309**
	1996-2000	0.207	0.082	0.018	0.302	0.568		**1.177**
	2001-2005	0.227	0.090	0.011	0.149	0.217	0.008	0.702
	2006-2010	0.138	0.098	0.011	0.161	0.064	0.004	0.475
	2011-2015	0.383	0.087	0.019	0.165	0.332	0.004	0.989
	Overall	0.258	0.095	0.017	0.163	0.211	0.004	0.747
East Guangdong	1989-1990	0.667	0.046	0.044	0.109	1.091	0.019	**1.976**
	1991-1995	0.303	0.138	0.030	0.082	0.734	0.011	**1.299**
	1996-2000	0.155	0.075	0.020	0.234	0.587		**1.070**
	2001-2005	0.153	0.081	0.014	0.088	0.242	0.008	0.586
	2006-2010	0.116	0.097	0.010	0.144	0.077	0.004	0.448
	2011-2015	0.357	0.090	0.021	0.155	0.325	0.004	0.952
	Overall	0.202	0.093	0.018	0.124	0.255	0.004	0.696
Pearl River Estuary	1989-1990	4.438	0.187	0.039	0.343	0.804	0.011	**5.823**
	1991-1995	0.779	0.188	0.042	0.182	0.568	0.011	**1.770**
	1996-2000	0.563	0.130	0.028	0.496	0.562		**1.779**
	2001-2005	0.918	0.148	0.018	0.400	0.172	0.008	**1.664**
	2006-2010	0.287	0.118	0.015	0.266	0.045	0.004	0.735
	2011-2015	0.406	0.101	0.018	0.224	0.255	0.004	**1.007**
	Overall	0.586	0.134	0.023	0.285	0.204	0.004	**1.236**
West Guangdong	1989-1990	2.454	0.123	0.038	0.211	0.900	0.019	**3.744**
	1991-1995	0.445	0.103	0.042	0.149	0.510	0.011	**1.262**
	1996-2000	0.190	0.074	0.013	0.327	0.542		**1.147**
	2001-2005	0.233	0.086	0.008	0.199	0.204		0.730
	2006-2010	0.162	0.095	0.010	0.180	0.064	0.004	0.515
	2011-2015	0.424	0.085	0.019	0.174	0.383	0.004	**1.089**
	Overall	0.285	0.091	0.016	0.188	0.223	0.008	0.810
Guangxi	2006-2010	0.148	0.143	0.010	0.247	0.070	0.004	0.622
	2011-2015	0.379	0.099	0.019	0.151	0.332	0.004	0.984
	Overall	0.237	0.119	0.014	0.193	0.153	0.004	0.720
Hainan	2006-2010	0.090	0.080	0.013	0.101	0.057	0.004	0.346
	2011-2015	0.348	0.073	0.015	0.153	0.300	0.008	0.896
	Overall	0.177	0.076	0.014	0.124	0.134	0.008	0.534

Table 5 Contributions of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) to the principal components (PC) in principal component analysis (PCA) for oyster heavy metal levels in the northern South China Sea in 2006-2015

	PC1	PC2	PC3	PC4	PC5	PC6
Cu	29.78	0.92	5.8	22.87	0.24	40.39
Zn	1.02	46.6	1.59	0.01	47.26	3.52
Pb	23.76	0.31	36.71	13.82	5.9	19.5
Cd	3.8	39.02	8.61	6.53	40.3	1.74
As	18.87	10.77	37.74	0.6	5.42	26.6
Hg	22.77	2.38	9.54	56.16	0.88	8.26

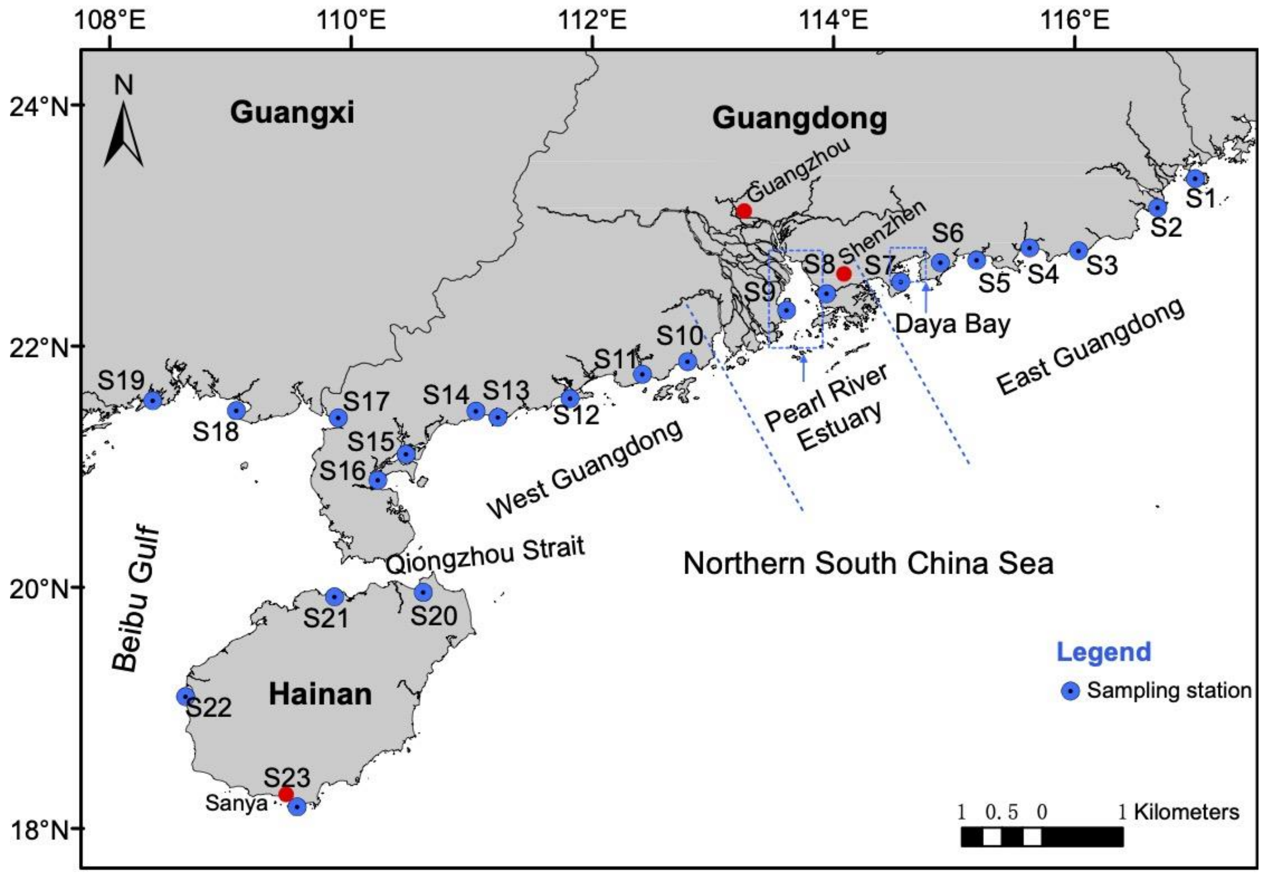

Fig. 1 Map of 23 sampling sites for cultured oysters collected from the northern South China Sea in 1989-2015. Sampling sites S1 to S23 were Zhelin Bay, Guangao Bay, Jiazi Harbor, Jieshi Bay, Changsha Bay, Kaoyang Estuary, Yaling Bay, Shenzhen Bay, Tangjia Bay, Guanghai Bay, Zhenhai Bay, Mawei Bay, Bohe Harbor, Shuidong Harbor, Zhanjiang Harbor, Leizhou Bay, Anpu Harbor, Beihai Harbor, Fangcheng Harbor, Dongzhai Harbor, Maniao Harbor, Basuo Harbor, and Yulin Harbor. S1-S7 were in east Guangdong, S8 and S9 were in the Pearl River Estuary, S10-S17 were in west Guangdong, S18 and S19 were in Guangxi, and S20-S23 were in Hainan

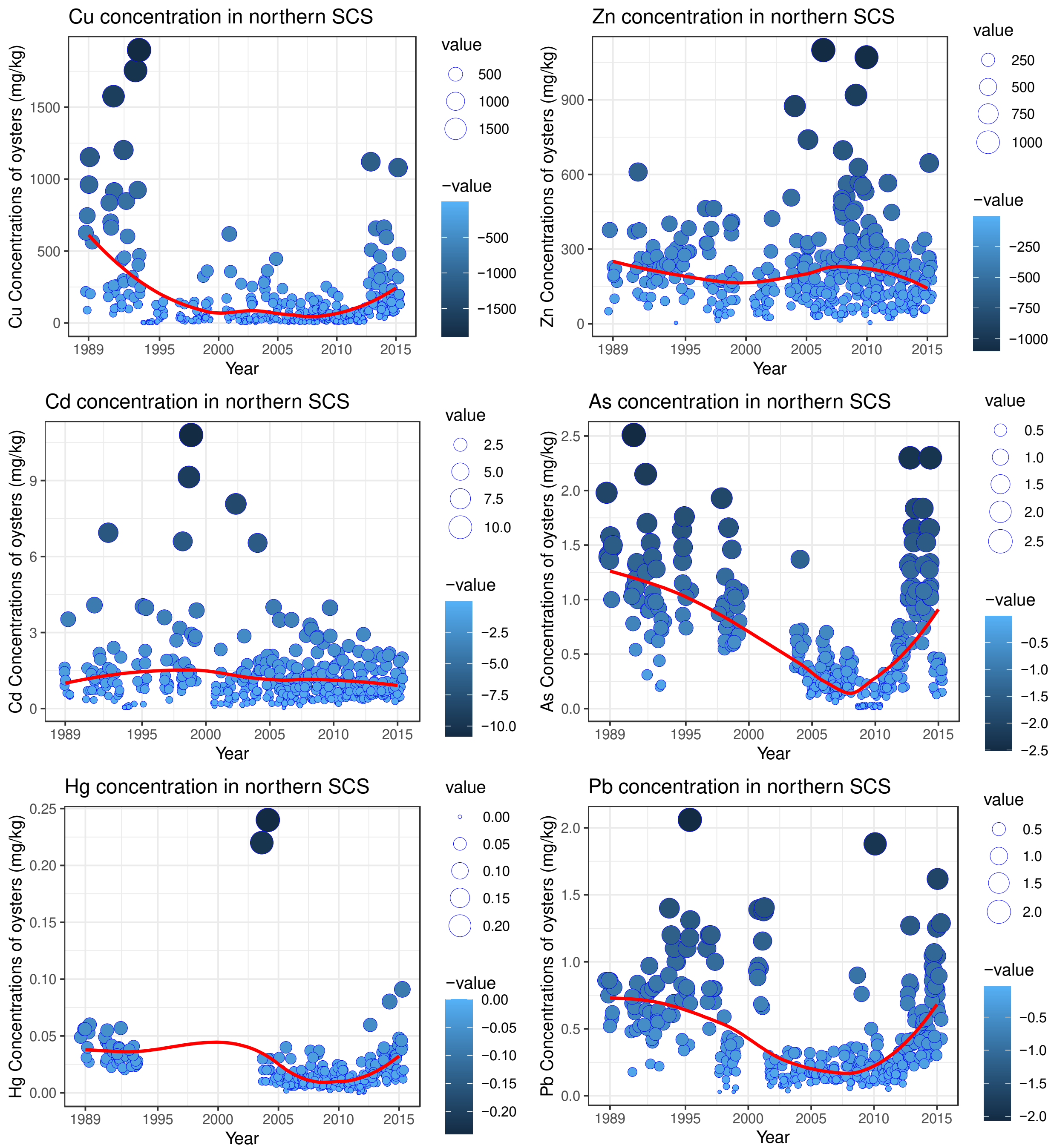

Fig. 2 Temporal variation of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) in oysters from the northern South China Sea (SCS) in 1989-2015, according to locally weighted least squares regression scatterplot smoothing (LOWESS)

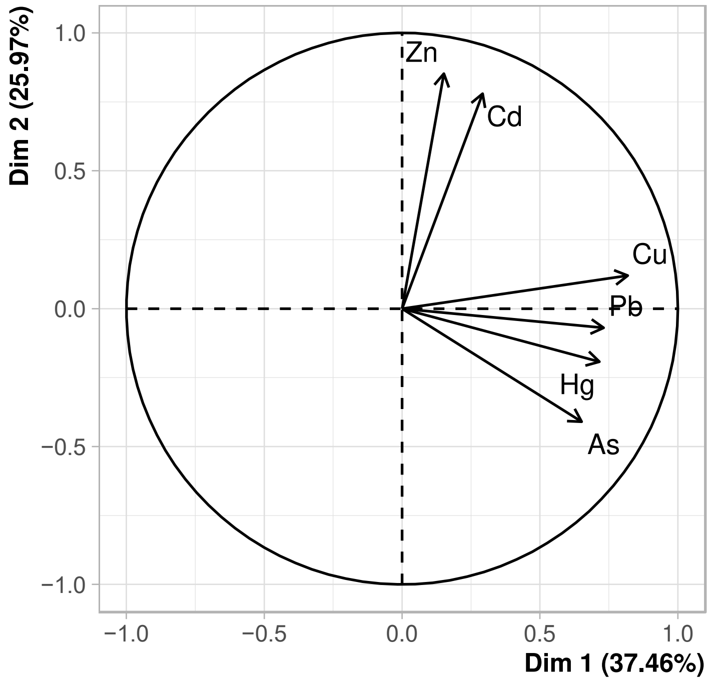

Fig. 3 Relationships between arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) based on the first two principal components (PC) in principal component analysis (PCA) for oyster heavy metal levels in the northern South China Sea in 2006-2015

Figures

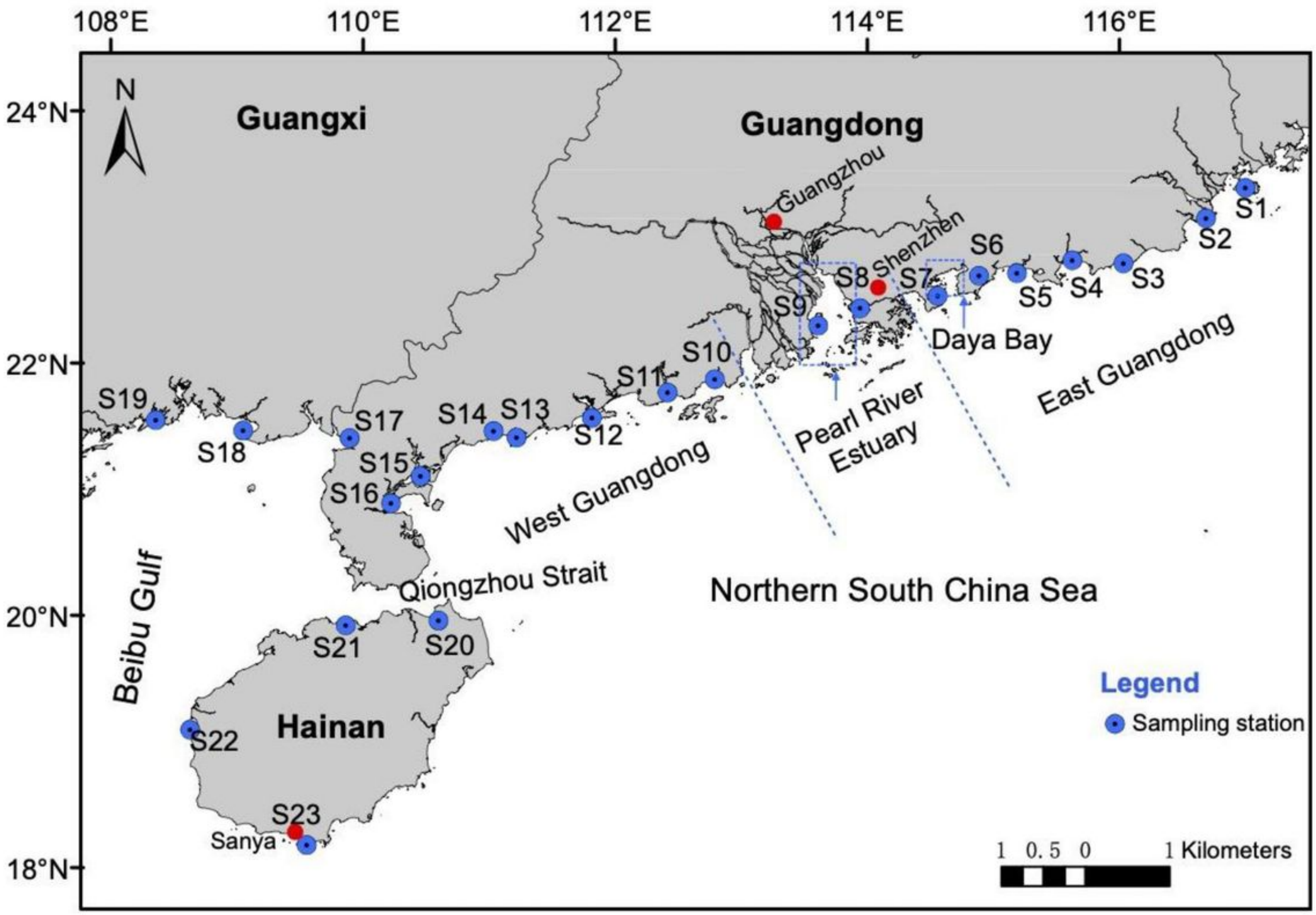

Figure 1

Map of 23 sampling sites for cultured oysters collected from the northern South China Sea in 1989-2015. Sampling sites S1 to S23 were Zhelin Bay, Guangao Bay, Jiazi Harbor, Jieshi Bay, Changsha Bay, Kaoyang Estuary, Yaling Bay, Shenzhen Bay, Tangjia Bay, Guanghai Bay, Zhenhai Bay, Mawei Bay, Bohe Harbor, Shuidong Harbor, Zhanjiang Harbor, Leizhou Bay, Anpu Harbor, Beihai Harbor, Fangcheng Harbor, Dongzhai Harbor, Maniao Harbor, Basuo Harbor, and Yulin Harbor. S1-S7 were in east Guangdong, S8 and S9 were in the Pearl River Estuary, S10-S17 were in west Guangdong, S18 and S19 were in Guangxi, and S20-S23 were in Hainan Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

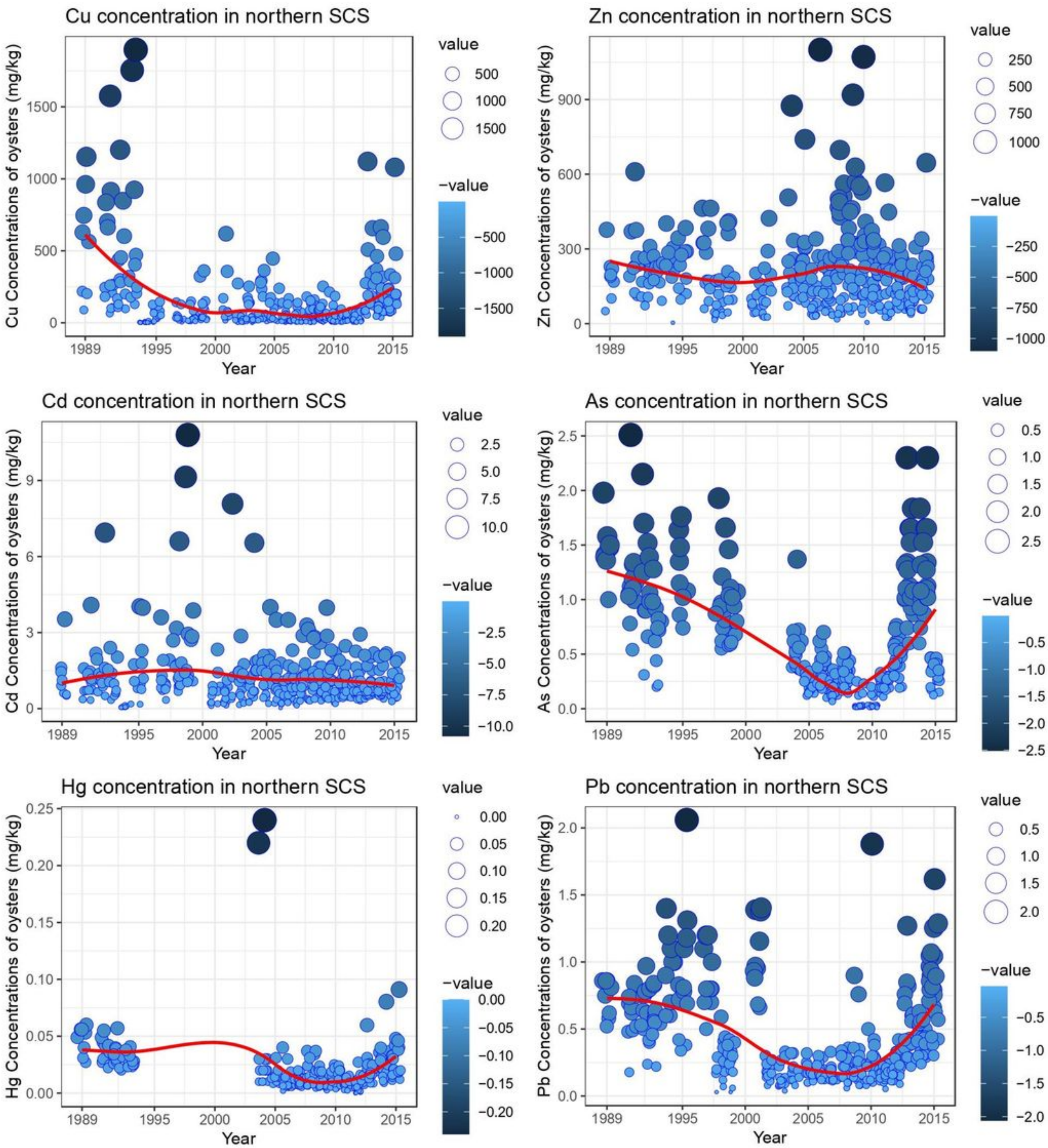

Figure 2

Temporal variation of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) in oysters from the northern South China Sea (SCS) in 1989-2015, according to locally weighted least squares regression scatterplot smoothing (LOWESS)

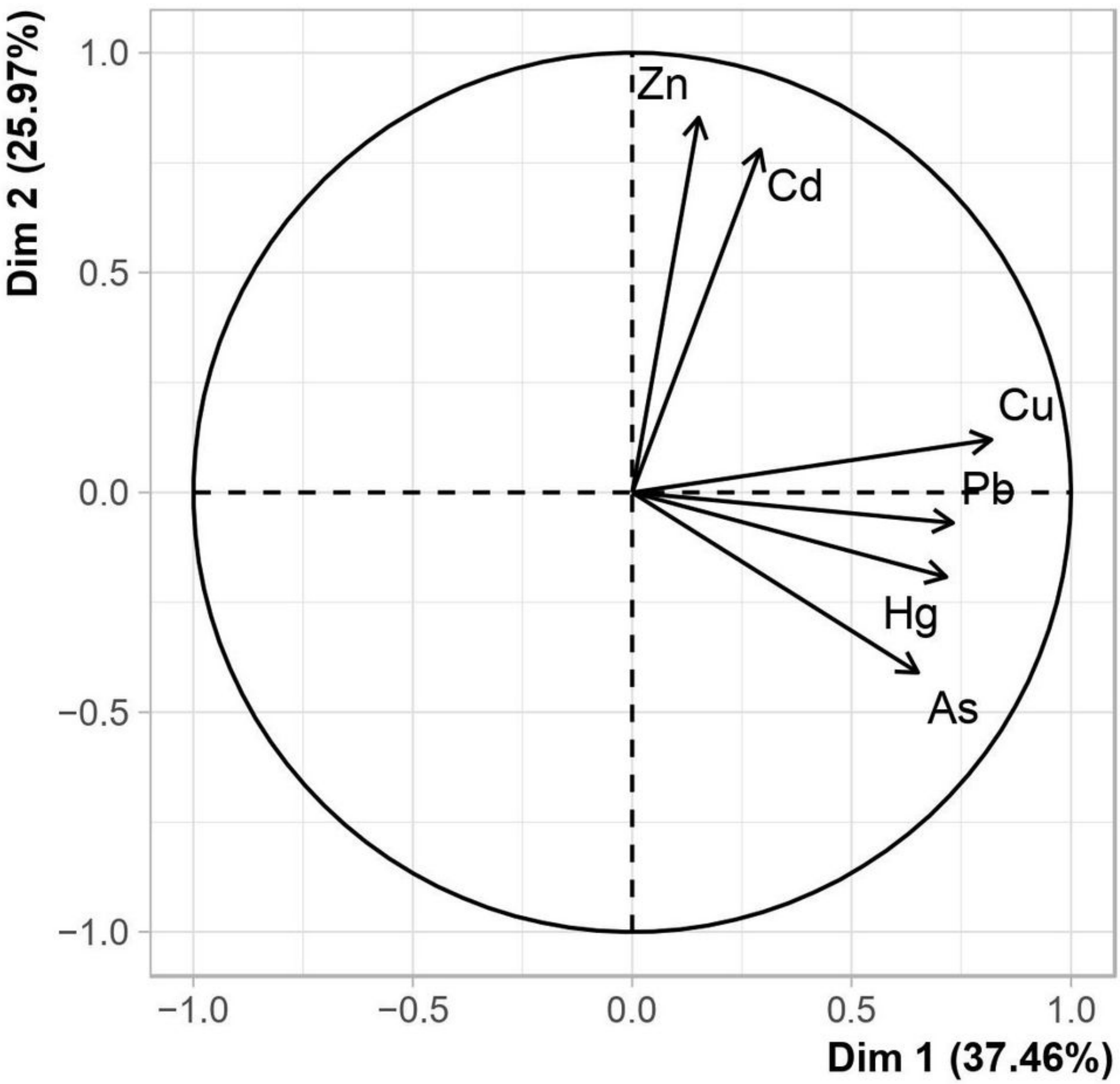

Figure 3

Relationships between arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) based on the first two principal components (PC) in principal component analysis (PCA) for oyster heavy metal levels in the northern South China Sea in 2006-2015