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**Title:** Ecological risk assessment at the food web scale: A case study of a mercury contaminated oilfield

**Abstract:** Mercury, particularly methylmercury, can accumulate through food webs and generate high risks for species at higher trophic levels. Inorganic mercury can be methylated into the organic species methylmercury if suitable reducing conditions exist, for example, in hotspots like oilfields. We developed a conceptual model to conduct an ecological risk assessment based on the food web structure of the Shengli oilfield area, China. The model can identify species at risk and elucidate the sources of risks according to their diet. A risk rating criteria was developed based on the food web structure to categorize the different levels of risks for different species. As expected, the results indicate increasing risks for the biota higher in the food web hierarchy. Grasshoppers were mostly at no risk throughout the study area, whereas grubs at southwest were at minimal risks due to local high Hg concentration in the soil. Mantises, which are insect predators, were also at minimal risk. Herbivorous birds with similar feeding habits than grasshoppers were at no risk, but omnivorous and carnivorous birds were at moderate risk. The conceptual model is a useful tool to improve pollution remediation and establish risk control strategies based on ecological risks of the food web rather than just Hg concentrations in the environment.

**Keywords:** bioaccumulation; trophic level; hazard quotient; no observable adverse effect level; Shengli oilfield area.

## 1. Introduction

Mercury (Hg) is an environmental pollutant of global concern, as it can cause significant adverse effects to ecosystems and human health (Mergler et al., 2007). Dietary intake, such as through consumption of fish (Sunderland and Selin, 2013), rice (Li et al., 2015; Tang et al., 2018), and mushrooms (Falandysz et al., 2019a; Falandysz et al., 2019b), is the most important route of Hg exposure for humans and other beings. There is sufficient evidence showing that Hg and its compounds pose significant threats to both humans (Warkany and Hubbard, 1953; Wheatley et al., 1979) and other living organisms (Scheuhammer et al., 2007; Wolfe et al., 1998). Both inorganic Hg and its organic form can be taken up by plants, such as mushrooms (Falandysz et al., 2015; Falandysz et al., 2007). Once enters into the food web, Hg especially its more toxic organic form can be biomagnified in animals at higher trophic levels and thus cause high risks for the whole food web (Bloom, 1992). An effective method to assess the risk of Hg exposure is then needed. The concentration of Hg in hair and urine have been widely used as simple means to assess the risk of Hg exposure for humans (Airey, 1983; Akagi et al., 1995). Hg concentrations in biota tissues have also been widely studied. For piscivorous birds, significant risk is expected when the Hg blood concentration is over 4 mg $kg^{-1}$ (Scheuhammer et al., 2007; Evers et al., 1998).

Though there are sufficient studies that document the risk of Hg exposure on individual levels, there are few studies that analyze the risk of Hg exposure at a terrestrial food web level of Hg hotspot areas, such as oil extraction fields. Inorganic Hg can be methylated into the organic species MeHg if suitable reducing conditions exist in hotspots such as oil extraction fields (Feng et al., 2008). MeHg has a significantly higher availability to organisms, which increases its potential for bioaccumulation in biological tissues (Bloom, 1992). Therefore, Hg can pose higher risks for animals in higher trophic levels of the food web. In an oilfield environment, there is a large number of high-sulfur reducing bacteria. Therefore, it is more likely for methylation of mercury to occur, and the toxicity of the produced MeHg (neurotoxicity, genotoxicity and immunotoxicity) will be passed through the food chain. Level enrichment leads to significant harm to the ecological environment and human health through exposure routes such as diet and breathing. Therefore, a risk assessment of mercury in oilfield environments is necessary.

Traditional risk assessment largely depends on comparing individual mercury concentrations in hotspot areas with a reference point. In the risk assessment literature, several terms are used to report and describe observed object effect concentrations and provide meaningful guidelines of risk. Commonly reported terms include 1) no observable adverse effect level (NOAEL), 2) lowest observable adverse effect level (LOAEL), 3) specific effect concentrations (EC) on growth or reproduction, or 4) lethal concentration at which 50% of the population dies ($LC_{50}$). All of these terms are used for documenting Hg risk to specific species. The results usually provide a simple conclusion on whether the subject is at risk nor not. However, this method overlooks the fact that a species whose tissue concentrations lower than the reference point may still be at a potential risk due to their high trophic level. When having a diet with risky levels of mercury, a species can be at risks due to long-term bioaccumulation. A conceptual model based on food web can be an effective tool to assess ecological risk from a food chain level (Chen et al., 2013) and it has already been applied in some ecological risk assessments. Nevalainen et al. (2017) introduced a probabilistic framework based on a general food web approach to analyze ecological impacts of oil spills. Wang et al. (2011a) conducted a probabilistic ecological risk assessment of dichlorodiphenyltrichloroethanes in the Bohai Bay based on a food web bioaccumulation model.

This study developed a concept model based on a food web to assess the ecological risk of Hg exposure and elucidate the extent of Hg biomagnification through the food web in an oilfield. The framework can determine if the subject is at risk and identify possible risks based on the food web structure. The exposure level of Hg to the terrestrial food web in this study was determined by quantifying Hg in different media, including soil and different biotic components. NOAEL was used as benchmark values in the risk assessment unless a NOAEL value was not available. The main objectives were to i) develop a concept model for conducting a food web risk assessment; ii) and apply the model at a demonstration case.

## 2. Materials and Methods

### *2.1 Concept Model Setup*

A concept model based on the web structure should be established to determine the predator-prey relationship of the biota of an ecosystem. The predator-prey relationship will later determine the transfer direction of Hg exposure risk from lower to higher positions in the food web.

To test the model at different exposure levels and assess the Hg exposure level of the terrestrial food web, an oilfield located in the coastal area of Shandong Province, China, was selected as the case study due to the changing gradient of Hg concentrations in the environment from land to sea. The Shengli oilfield area (SLOA) covers an area of 44,000 km$^2$, located in the Yellow River Delta, near the southwestern coast of the Bohai Sea, which has a long history of oil extraction and smelting. Most of the study area is on both sides of the Yellow River estuary. Due to the historical mining and delta sedimentary activities, there was a rapid accumulation of heavy metals in the soil, which may cause environmental problems.

The case study site consists of eight areas, namely YanWo, ChenZhuang, TingLuo, LiuHe, HeKou, XianHe, GuDao, and DongYing port. They allow for frequent human activities and are spread along the Lijin Section of Yellow River (A1—A8), Caoqiao ditch (B1—B8), and Shenxian ditch (C1—C8) (Figure 1). The climate type is temperate continental and soils are mainly solonchak and inceptisol. Due to the impact of human activities and limitation of soil conditions, deciduous broad-leaved forest, swamp vegetation (e.g., Reed) and halophytes (e.g., green bristlegrass, seepweed, goosegrass, tamarix) are the main natural vegetation in this area, based on literature investigations (Song et al, 2008; Kong, 2016). Although larger wild animals are not common in SLOA, birds (magpies, swallows, sparrows) and invertebrates (grossshppers, mantises, spiders) are common. Domestic animals, such as pigs and chicken, are common in the village gardens (Hekou District Local History Compilation Committee, 2016). Reed (*Phragmites australis*) usually contains elevated MeHg concentrations and higher mean site-specific bioaccumulation factor (BAFs) for MeHg due to the anoxic conditions favorable for methylation formed by seepage water in ditches (Tong et al., 2013). Moreover, reed communities and barnyard grass are widely distributed in low-lying areas of river floodplains and coastal marshes of the study area (Wang et al., 2015). The habitats of the communities generally have seasonal water accumulation, which is favorable for bioaccumulation of total mercury (THg) and methylmercury (MeHg) from soils.

Field surveys were conducted to further identify the local plant and animal species. Based on the field surveys and literature investigations, reed (*Phragmites australis*), barnyard grass (*Echinochloa crusgalli*), green bristlegrass (*Setaria viridis*), and goosegrass (*Eleusine indica*) were chosen as the representative plant species, and grubs, grasshoppers, mantises, magpies, and swallows were chosen as the representative animal species. A conceptual model based on the network structure was established based on the relationship between these predators and captured predators (Zheng et al., 2008; Zhang et al., 2010). The conceptual exposure pathways of Hg transfer in the terrestrial ecosystems of SLOA are shown in Figure 2. The transfer of Hg from lower to higher positions in the food web occurs through the predator-prey relationships.

### *2.2 Sampling and Analysis*

An extensive sampling campaign was conducted in 2017 for this study. Samples were collected in eight areas of SLOA: YanWo, ChenZhuang, TingLuo, LiuHe, HeKou, XianHe, GuDao and DongYing port. The sampling was conducted in the three surface water bodies in the following order: Lijin Section of the Yellow River (A1—A8), Caoqiao ditch (B1—B8), and Shenxian ditch (C1—C8). The distance gradients from land to sea can illustrate the effects of soil salinization and river deposition on pollution levels (Figure 1). Gudao forest farm, which is an ecological redline area in Dongying without any significant local sources of Hg, was selected as the reference site. Table A1 summarizes the sampling locations and number of samples collected. To reflect the local food web structure, soils, plants, worms, grasshoppers, mantises and birds were collected in the study.

A total of 44 surface soils samples (0-5 cm depth) were collected. Each soil sample was a representative of five subsamples that were collected from an area of 2 m × 2 m and mixed thoroughly. Moreover, 74 plants samples from 4 species and 198 animal samples from 5 species were collected. A total of 18 samples of oilfield produced water were collected from 9 production wells. All soil, plant, and animal samples were separately wrapped in sealed polyethylene bags and stored in ice for transport to laboratory, with subsequent cryopreservation at -80 °C. The produced water samples were filtered with a 0.45 μm filter membrane after oil and water separation and then kept at 4 °C before analysis.

Freeze drying was performed to soil, plant, and animal samples prior to the mercury analysis. After freeze drying, soil samples were crushed and sieved with a 100-mesh screen. In contrast, plant and animal samples were pulverized using ceramic scissors and a porcelain mortar. The Hg concentration in soils, plants, and produced water was measured by the MERX mercury analytical system (Brooks-Rand Instruments, Seattle, WA, USA), following a standard operating procedure by the U.S. Geological Survey (DeWild et al., 2004). The Hg concentration in animals was determined by a DMA-80 Direct Mercury Analyzer (Milestone Srl, Sorisole, BG, Italy), as described in the United States Environmental Protection Agency Method 7473 (USEPA, 1998). The standard reference materials GSS-9, TORT-3, and GSB-11 were used for quality control of the mercury measurements.

### 2.3 Reference Concentration

The risk analysis of this study is based on the Hg level of the object tissue and the Hg concentration in the prey and/or the living environment (i.e. soil). NOAEL ensures no observable adverse effects. The species-specific endpoints selection is discussed in the following sections. Table 1 summarizes the chosen benchmark values for all species.

#### 2.3.1 Plants and soils

A LOAEL of 3.333 mg $kg^{-1}$ dry weight (d.w.) has been reported for maize (Lipsey, 1975). Therefore, a benchmark value of 3.0 mg $kg^{-1}$ d.w. for plant tissue was established for the present study as no specific NOAEL was available in the literature.

The LOAEL of Hg in soil that results in decreased growth of grass species has been reported as 25 mg $kg^{-1}$ d.w. (Weaver et al., 1984), whereas another study reported NOAEL for grass species in flooded plain conditions to be 11 mg $kg^{-1}$ d.w. (Cocking et al., 1995). Therefore, a benchmark concentration of 10 mg $kg^{-1}$ d.w. was set for this study.

#### 2.3.2 Invertebrates

The benchmark value of plants for herbivorous birds (0.1 mg $kg^{-1}$ d.w.) was used as the benchmark of plants for insects. Calabrese and Baldwin (1993) recommend that the lowest effect level of 30 mg $kg^{-1}$ should be divided by an uncertainty factor of 5, to go from a lethal endpoint to a chronic NOAEL. Hence, the resulting benchmark value was 6 mg $kg^{-1}$ w.w.

Based on Abbasi and Soni (1983), a NOAEL of 1 mg $kg^{-1}$ was proposed for the soil in which worms live. The corresponding NOAEL for earthworm tissue was reported as 27 mg $kg^{-1}$ w.w. Therefore, a benchmark value of 27 mg $kg^{-1}$ w.w. was established for worms.

#### 2.3.3 Birds

The NOAEL value selected for birds was 4 mg $kg^{-1}$ w.w. (in muscle tissue), which was based on a long-term observation of the North American loon (Evers et al., 2004). The main bird prey in SLOA are invertebrates, and the MeHg to total Hg ratio in invertebrates are unknown. Therefore, we chose a conservative NOAEL of 0.08 mg kg$^{-1}$ w.w. for bird preys, as suggested by Scheulhammer et al. (2007). Due to lack of test data, we used the same NOAEL (0.08 mg kg$^{-1}$ w.w.) for caryopses, which are eaten by herbivorous birds. Assuming a 20% moisture content in caryopses, the benchmark value for plants was 0.1 mg kg$^{-1}$ upon conversion of w.w. into d.w.

### *2.4 Risk Categorization*

To compare the sample and benchmark concentrations, a representative concentration for the sample population must be established. USEPA recommends using the 95% upper confidence limit (UCL) of the mean to estimate exposure. However, due to the limited amount of data for exposure areas, the arithmetic mean was used as the concentration term for quantitative risk characterization (USEPA, 1992).

The level of risk posed by diet through the food web was determined by comparing the Hg concentrations in a species and the NOAEL for tissue and prey concentrations. The risk was evaluated by using Hazard Quotients (HQs) (USEPA, 1992). HQs were calculated by dividing the mean (Table 2) by benchmark values (Table 1). An HQ less than 1 indicates low risk, and HQ greater than 1 indicates potential high levels of risk. Based on the HQs, we developed a set of criteria to establish the final risk for each of the species in the food web as follows.

Level 1 (background): If both HQ values based on tissue and prey concentrations are smaller than 1, and the means are smaller than the reference site values, the species is considered to be living under a similar condition as the background site.

Level 2 (minimal risk): If both HQ values based on tissue and prey concentrations are smaller than 1, but the means are larger than the reference site values, the species is considered at minimal risk.

Level 3 (moderate risk): If the HQ based on tissue concentration is smaller than 1, but the HQ based on prey concentration is larger than 1, the Hg levels in the species has not reached risky level, but the given diet presents a risky level of Hg. The species is then considered at moderate risk.

Level 4 (high risk): If both HQ values based on tissue and prey concentrations are larger than 1, the species has a risky diet and also has accumulated significant Hg in its body. The species is then considered at high risk.

## 3. Results and discussion

### *3.1. Hg concentrations in ecosystem compartments*

Oil extraction and smelting is likely the major source of Hg in the study area. Accordingly, all concentration values showed an increasing trend from the northeast coast to the southwest inland, with higher levels in the Lijin Section of the Yellow River and Caoqiao ditch area compared to the Shenxian ditch area. Frequent human inputs (from oil extraction and chemical production) may have led to those higher Hg levels. Mercury in oil extraction and smelting can escape to the environment by several pathways (wastewater, solid waste streams, and air emissions) (Wilhelm and Kirchgessner, 2001) and bioaccumulate in food chain (webs), then adversely affecting the biota of oilfield ecosystems.

### *3.1.1. Hg concentrations in oilfield produced water*

Oilfield produced water is the largest waste stream in the oil mining and smelting industry (Liu, 2016; Wilhelm and Kirchgessner, 2001; Zhu et al., 2016). We collected oilfield produced water samples from nine wells (No. 1-9) with Hg concentrations ranging from 0.03 to 0.29 μg $kg^{-1}$. The Hg levels are different from previously reported values for produced water in oilfeilds due to the different geological conditions and stage of oilfield exploitation, e.g., 3.7-147.3 μg $kg^{-1}$ (Manfra et al., 2007), 0.007-27μg $kg^{-1}$ (Meinhold et al., 1995), < 0.01-0.2 μg

$kg^{-1}$ (Trefry et al., 1996). However, the Hg levels of the produced water were similar to those of the surface water (0.02-0.31 μg $kg^{-1}$) in the Wuchuan mercury mining area of Guizhou, which presents a widespread Hg contamination of the aqueous system (Qiu et al., 2006). The level of Hg in the oilfield produced water was lower than the pollution emission standards for petroleum refining industry (0.005 mg $L^{-1}$) developed by the Standardization Administration of the People's Republic of China (CHNEPA, 2015). However, considering rainfall runoff pollution, inadequate management of mining, ecological effects, and human health concerns, the Hg concentrations were compared with environmental quality secondary standards for surface water (0.00005 mg $L^{-1}$) (CHNEPA, 2002). This standard is mainly applicable to first-grade protected zones for centralized drinking water and surface water sources, habitats of rare aquatic organisms, spawning grounds for fish and shrimp, and bait grounds for juvenile and young fish. The results showed that the level of Hg in the oilfield produced water was 0.66-5.88-fold higher than the standards for surface water. As Hg enters the surrounding water body and soil, it gradually bioaccumulates and is biomagnified through the food chain. Consequently, with increasing Hg levels in the environment, organisms at higher trophic levels will be at higher risks. For instance, the mean Hg concentration in bird feathers and mantis tissues were 3.33 and 9.04 times the Hg concentration in soils. Figure 3 summarizes the Hg concentrations in the oilfield produced water.

### *3.1.2. Hg concentrations in soils and plants*

Soil samples showed a clear trend of higher Hg concentrations from the northeast coast to the southwest inland, with higher levels in the Lijin Section of the Yellow River (mean ± one standard deviation, 30.83 ± 13.30 μg $kg^{-1}$) compared to the Caoqiao ditch and Shenxian ditch areas (24.56 ± 9.90 and 12.94 ± 2.98 μg $kg^{-1}$, respectively). The high Hg concentrations in the Lijin Section of the Yellow River were in good agreement with frequent anthropogenic inputs (oil extraction, chemical production) and sedimentation of highly contaminated sediment particles from the Yellow River. The soil Hg concentrations were similar to the previously reported values for SLOA, e.g., 10-41 μg $kg^{-1}$ (Lin et al., 2016), 20-100 μg $kg^{-1}$ (Cheng et al., 2017), and 8-106 μg $kg^{-1}$ (Ge et al., 2019). The average Hg concentration in the Lijin Section of the Yellow River and Caoqiao ditch area was 1.62 and 1.29 times the background value of Shandong Province, respectively. The Hg level observed in Shenxian ditch area was similar to the concentrations of Hg in the background level of Shandong Province (19 μg $kg^{-1}$) (CHNEPA, 1990). Figure 3 shows the summary of Hg concentrations for all the soil samples. Compared to oilfields in the Niger Delta (380 ± 320 μg $kg^{-1}$) (kIwegbue et al., 2006) and Serbia (35.6 ± 69.2 mg $kg^{-1}$) (Relic et al., 2019), the Hg concentration in the SLOA was relatively low, and it was classified within the range of uncontaminated soils worldwide (10-500 μg $kg^{-1}$) (Trefry et al., 1996). Although soil Hg concentration in SLOA was considerably high, farmland, waters, and organisms surrounding these oilfield mining and smelting facilities may still be at risk of mercury pollution due to the high bioaccumulation and biomagnification through food webs.

The concentrations of Hg in the four analyzed plants showed a similar pattern to that of soils, with Hg levels being slightly higher in the southwest of the study area (the Lijin Section of the Yellow River, and the Caoqiao ditch area) compared to the northeast (the Shenxian ditch area). The mercury concentration in plant tissues in the areas surrounding sampling sites A1, A6, and B5 was higher than those of other areas, which may have been caused by the surrounding oil extraction operations and chemical production. However, no significant correlation was observed between soil and plant Hg concentration, which is consistent with previous reports on mercury accumulation in plants (Blanton et al., 1975; Siegel et al., 1987). The soil mercury concentration is an important factor affecting plant Hg accumulation. However, the absorption of mercury by plants also depends on plant species, air pollution, and soil properties such as pH, redox potential, and organic matter content. The salinization of the soils in the study area may have led to changes in soil properties which then affected the bioavailability of Hg to plants in the soil (Turull et al., 2019).

The average concentration of Hg in reeds, green bristlegrass, goose grass, and barnyard grass was 8.88 ± 3.30, 4.19 ± 1.18, 5.09 ± 2.14 and 3.17 ± 0.97 μg kg$^{-1}$, respectively. The Hg concentrations of the four plants in SLOA were lower than those in the rice samples from Wuchuan mining areas of Guizhou (26.8 μg kg$^{-1}$), but higher than that of market purchased rice (2.8 μg kg$^{-1}$) (Li et al., 2008). The Hg concentration in reeds was approximately 2-3 times those of other terrestrial plants (green bristlegrass, goose grass, and barnyard grass). In addition, reeds presented a higher bioaccumulation factor (0.21-0.89) than the other three plants (goose grass: 0.11-0.39; green bristlegrass: 0.09-0.59; barnyard grass: 0.08-0.24). The concentrations recorded for reeds were higher because more mercury is deposited in water sediments through discharge of chemical waste and oil extraction. Figure 3 shows the summary of Hg concentrations for all plants samples.

### *3.1.3. Hg concentrations in invertebrates and birds*

Earthworms are commonly used as biomarkers of soil pollution (Calisi et al., 2013). Grubs and earthworms have similar living habits. Both of them live underground and are saprophagous worms that feed on organic matter, such as rotten leaves and plant rhizomes, and are prey of birds. Therefore, we used grubs as substitutes for earthworms to conduct the ecological risk assessment in the study area. Grubs showed extremely high Hg concentrations (57.60 ± 12.94 μg kg$^{-1}$) in their tissues, mainly due to the high Hg concentration in the soil (50.26 ± 21.11 μg kg$^{-1}$). Additionally, the habitats of grubs include high organic matter content, which can enhance the environmental risk of Hg by accelerating methylation processes and increasing mercury bioavailability (He et al., 2019), thereby increasing the health risks of birds that feed on grubs.

Hg concentrations in tissues showed a significant biomagnification effect from grasshoppers to mantises. Their average Hg concentrations were 16.98 ± 11.32 and 83.85 ± 36.88 μg kg$^{-1}$, respectively. Similar to plants, the mercury concentration in tissues of grasshoppers and mantises in the area around sampling sites A1, A6, and B5 were higher than those in other areas (except for sampling site C2). The high mercury concentration in grasshopper tissues at sampling site C2 may be related to the dominant species status of barnyard grass in the area, as the barnyard grass presented higher Hg concentration compared to other plants. Even at the reference site, a biomagnification effect was observed: from 34.0235 to 53.2524 μg kg$^{-1}$ from grasshoppers to mantises. The average Hg concentration in grasshoppers and mantises in the SLOA is comparable to those of previous reports on serious mercury pollution in Huludao city; average Hg concentrations of 43.00 and 87.00 μg kg$^{-1}$ in grasshoppers and mantises, respectively, have been reported (Zheng et al., 2008; Zhang et al., 2010). Similar Hg biomagnification was observed from the secondary trophic level of the food chain, thus posing higher ecological risk for organisms at higher trophic levels. Figure 3 shows the summary of Hg concentrations for all invertebrate samples.

The Hg concentration in bird feathers was higher than the concentrations observed in other species: 139.26 ±193.24 μg kg$^{-1}$. The Hg concentrations in the feathers of omnivorous and carnivorous birds were 248.39 ± 248.57 (49.96-711.53) and 84.70 ± 127.23 (21.29-480.12) μg kg$^{-1}$, respectively. These birds mainly feed on grubs, grasshoppers, and mantises. The results show that omnivorous birds (magpie) accumulate 66% more mercury than carnivorous birds (swallow) likely due to their different eating habits (frequency and amount). The Hg levels of birds in this study were lower than those of birds in the Caohai wetland of Guizhou (40-5058 μg kg$^{-1}$) (Peng et al., 2018). This difference might be attributed to different dietary structures of birds and higher levels of Hg pollution in Caohai wetland. Moreover, the birds of Caohai wetland feed on fish, whereas the studied birds mainly feed on invertebrates and plants. The standard deviation of Hg concentration in this study is large because birds are not restricted to the relatively small study area. Therefore, birds have a much more complicated diet. They may eat invertebrates or plants from other areas with less Hg contamination.

### *3.2. Hg concentrations in different species of the food web*

Levels of Hg in species tissues differ throughout different trophic levels. As the trophic level increases, the Hg concentrations also increases, which demonstrates a bioaccumulation effect of Hg through SLOA terrestrial food webs. In the study area, Hg concentration in plants were the lowest in the terrestrial food web and showed the following pattern: reed> goosegrass > green bristlegrass > barnyard grass. This result indicates that reed is a candidate plant for remediation of mercury pollution in oilfield due to its excellent performance to enrich mercury from soils. Compared to plants, invertebrates (grubs) showed extremely high Hg concentrations in their tissues mainly because they lived in a soil with high Hg concentration and high organic matter content. In addition, they had a high Hg uptake rate through their exoskeletons or other body coverings (Gall et al., 2015). Hg concentrations in tissues of grasshoppers and mantises also demonstrated the biomagnification effect. The Hg concentration in birds was measured as feather concentration. Therefore, it was not possible to directly compare them to the tissue concentration of grasshoppers and mantises. Nevertheless, the Hg concentration in bird feathers (magpies and swallows) was higher than in grasshoppers' and mantises' tissues. The SLOA terrestrial food web is not as obvious as the aquatic food web in terms of biomagnification (Cui et al., 2011), but it still shows a significant food chain accumulation effect. Figure 4 summarizes the Hg concentrations for all evaluated species in the terrestrial food web.

### *3.3. Risk categorization for different biota in the food web*

The risk of each species in the SLOA was rated based on the abovementhioned methods. Plants were exposed to minimal risk due to the low concentrations of Hg in the soils. The risks showed an increasing trend as the distance from the northeast coast increased. As expected, relatively high HQ values were observed at the Caoqiao ditch area and Lijin Section of the Yellow River (sampling sites: A1, A6, and B5).

The risks for invertebrates showed significantly different patterns compared to plants. Their HQ values showed the same trend of higher Hg levels at the Caoqiao ditch area and Lijin Section of the Yellow River compared to the Shenxian ditch area. HQ values of grasshoppers were lower than that of the reference site, so we considered they were living under similar conditions as the background site. HQ values of grubs based on their tissue concentration were smaller than 1, and combined with the high mercury concentration in the soil in which they live, they were considered at minimal risk (higher than background). Mantises, which are predators of insects, were exposed to higher risks than grasshoppers based on their tissue concentration of Hg. Mantises have a slightly higher tissue concentration compared to the reference value, but they are still exposed to minimal risk due to the low concentration of Hg in the grasshoppers (Table 3).

The Hg concentration in birds was measured in their feathers. The NOAEL of birds in the literature is commonly given as blood concentration. Thus, the bird feather concentrations were converted to blood concentration for the risk assessment (method described in SI text 2). Birds with different diets showed different risk levels. Herbivorous birds were mostly at minimal risk for all the locations. Omnivorous and carnivorous birds showed minimal risk in the Shenxian ditch area, but moderate risk for Caoqiao ditch area and Lijin Section of the Yellow River due to the migration and prey distribution of birds. As expected, the risks increase for species at higher positions in the food web. This demonstrates the effect of Hg bioaccumulation through the food web.

Geographically, the biota in the Caoqiao ditch area and Lijin Section of the Yellow River showed predominantly higher risk levels than in the Shenxian ditch area. This result may be attributed to the longer history of oil extraction and smelting, and fluvial deposits in the Caoqiao ditch area and Lijin Section of the Yellow River. Additionally, this result can also be related to the lack of strict supervision of pollution emissions (petrochemical industry, salt chemical industry, and chlor-alkali plants). The results show minimal risks of Hg exposure for predators in SLOA, except for carnivorous and omnivorous birds. Carnivorous and omnivorous birds are mostly at moderate risk for Hg exposure. Herbivorous insects, grubs, and birds showed low or minimal risk for Hg exposure.

The risk assessment results suggest that reducing the Hg concentration in predators' diet is important to protect them, as they are at moderate risk. Therefore, we propose some measures that can be useful for the development of a risk management plan:

(1) Strengthen the treatment and management of oilfield wastewater (from drilling and oilfield processing), solid waste (drilling waste mud and drilling cuttings), and pollutants from petroleum chemical treatment (process wastewater, polluted rainwater, and chemical waste). There should be a focus on lowering the content of pollutants in the discharged waste. Moreover, a total emission control system for oilfield pollutants should be implemented to minimize pollution loads.

(2) Improvement of processes, equipment, and operation technology within the oilfield development and chemical production, by adopting pollution-free or less-polluting production technology and implementing full-process control of the pollution and production processes.

(3) Consider feeding chickens in a poultry house. Free-range chickens can potentially eat various invertebrates from the nearby environment, which would lead to a risk similar to that of omnivorous birds. Moreover, this risk could be further transferred to humans through the food chain.

This study also identified a dilemma which should be considered when developing a remediation plan. There have been several studies showing the phytoremediation potential of Hg-hyperaccumulating plants at contaminated sites (Wang et al., 2011b; Wang et al., 2014). However, one has to be overly cautious when selecting plants for this purpose because hyperaccumulating plants can be eaten by invertebrates or birds. Therefore, Hg bioaccumulation could easily be magnified through the food web, as the Hg concentration in the tissue of those plants were exceedingly high. Consequently, top predators would still be at risk.

## 5. Conclusions

The study developed a risk assessment conceptual model based on the food web structure. The case study demonstrated the usefulness of the model in identifying potential risks related to the food chain (especially for predators) which could be overlooked if only Hg concentrations are compared. The results indicate increasing risks for the biota higher in the food web hierarchy. Grasshoppers were mostly at no risk throughout the study area, whereas grubs at the Lijin Section of the Yellow River and Caoqiao ditch area were at minimal risk due to the high Hg concentrations in the soil. Mantis, an insect predator, were also at minimal risks. Herbivorous birds were at no risk, whereas omnivorous and carnivorous birds were at moderate risks. The outcomes of the risk assessment can be used as references when developing a risk control strategy.

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## Abbreviations

The following abbreviations are used in this manuscript:

Hg: mercury
MeHg: methylmercury
THg: total mercury
BAFs: the mean site-specific bioaccumulation factor
SLOA: Shengli oilfield area
NOAEL: no observable adverse effect level
LOAEL: lowest observable adverse effect level
EC: specific effect concentrations
$LC_{50}$: lethal concentrations at which 50% of the population die
$LC_{5}$: lethal concentrations at which 5% of the population die
w.w.: wet weight
d.w.: dry weight
USEPA: United States Environmental Protection Agency
95%UCL: 95 % upper confidence limit
HQ: hazard quotient

## The Latin names for each species

Reed (*Phragmites australis*);
Barnyard grass (*Echinochloa crusgalli*);
Green bristlegrass (*Setaria viridis*);
Goosegrass (*Eleusine indica*);
Seepweed (*Suaeda glauca*);
Grub (*Larva Holotrichiae*);
Grossshpper (*Acrida chinensis*);
Mantis (*Paraten-odera sinensis*);
Typically loons (*Gavia Immer*)；

Magpie (*Pica pica*);

Swallow (*Swallow*).

Tamarix *(Tamarix chinensis Lour)*

## Appendix A, Supplementary Material

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## Figure legends

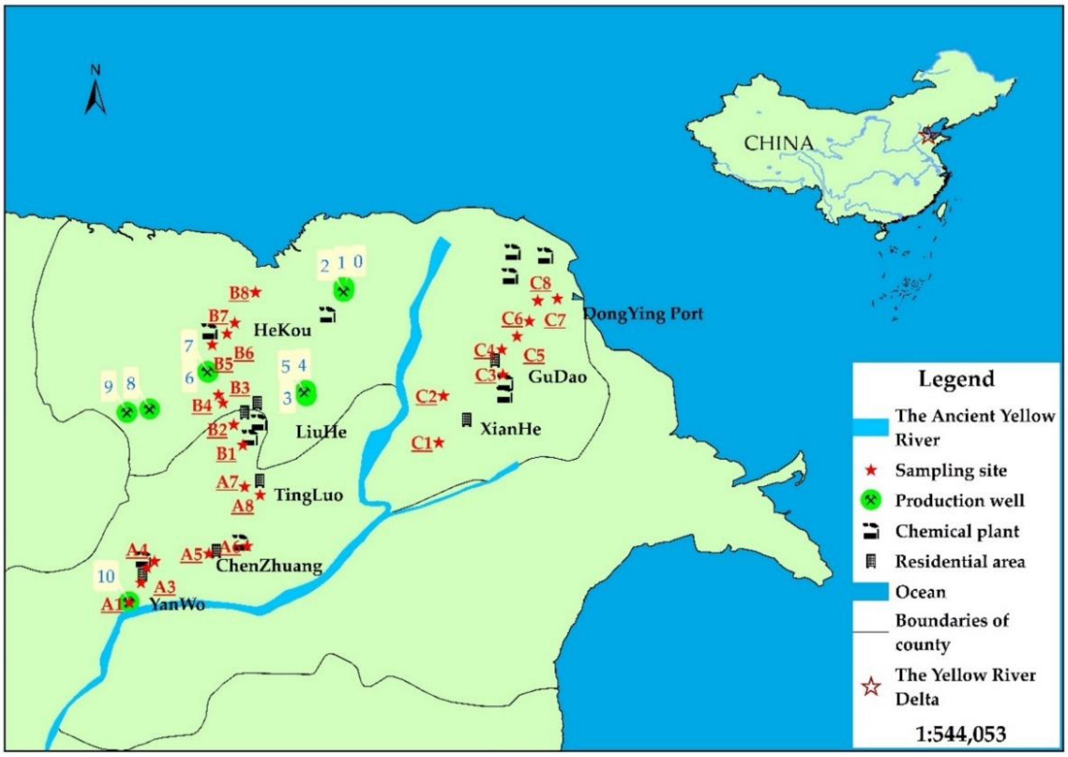
**Figure 1.** Map of case study area SLOA with sampling locations indicated by distance from the tailing.

**Figure 2.** Conceptual model of the terrestrial food web in SLOA. Shown are the approximate trophic levels of the species in the food web, including grubs (worms, Scarabs Larvae), grasshoppers, mantes and birds (including insectivorous and omnivorous birds).

**Figure 3.** The summary of the Hg concentrations for all the samples (oilfield produced water, sediment plants and invertebrates)

**Figure 4.** Summary of Hg concentrations in different species in the food web. Boxes indicate the 25%-75% percentile values, whiskers indicate the 5%-95% percentile values. The Dk.blue short dash lines represent the average of each species. The black line represents the median value of each species. Dots on the up and down of the boxes indicate 5%/95% percentiles outliers in all the individual measurements.

## Figures



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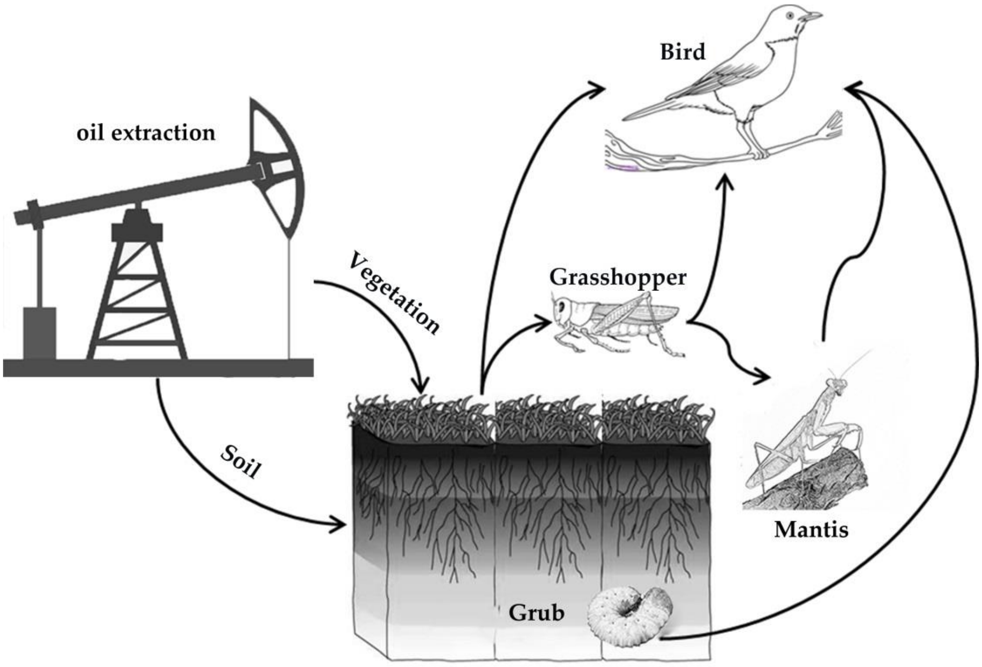

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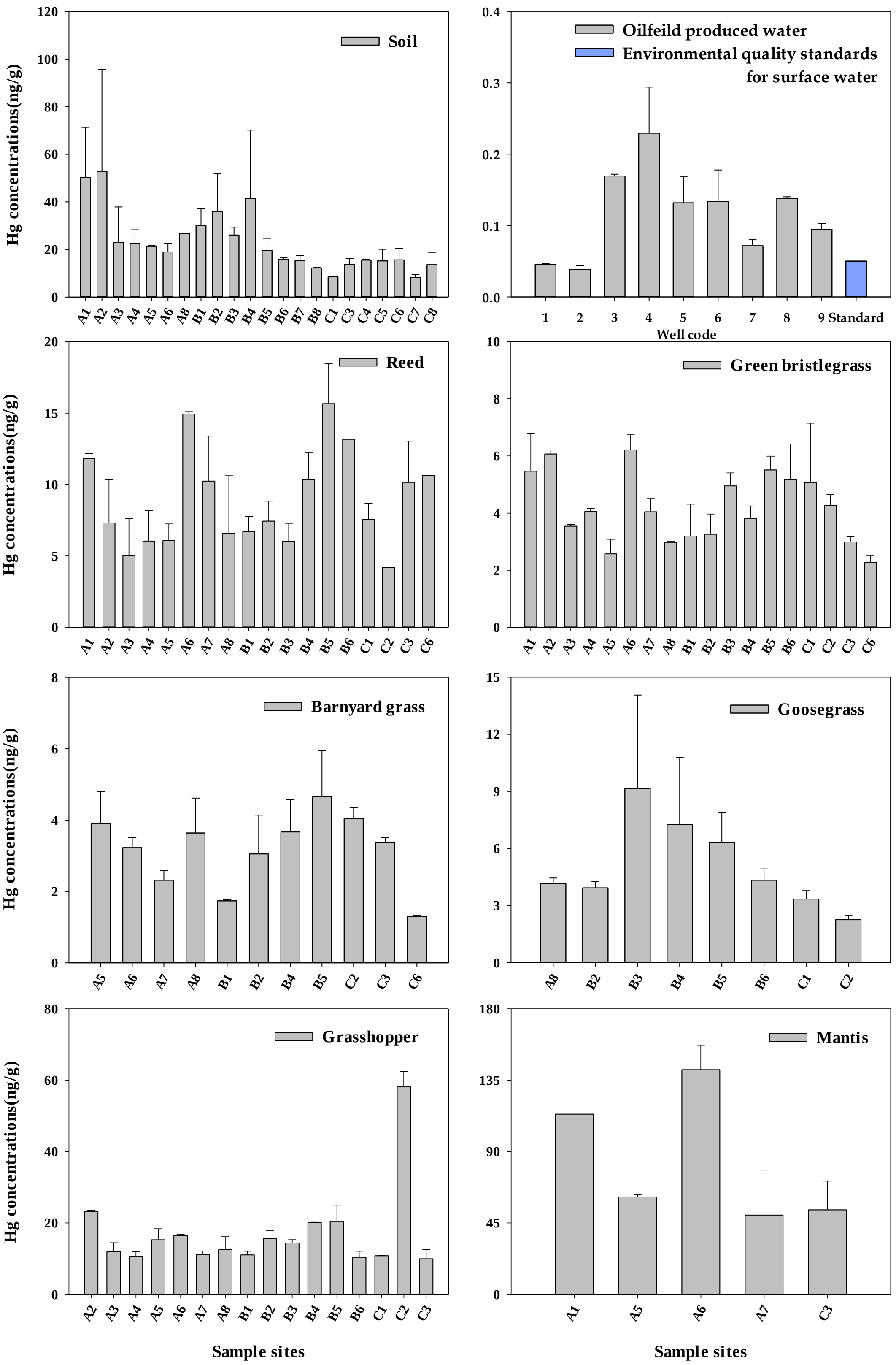

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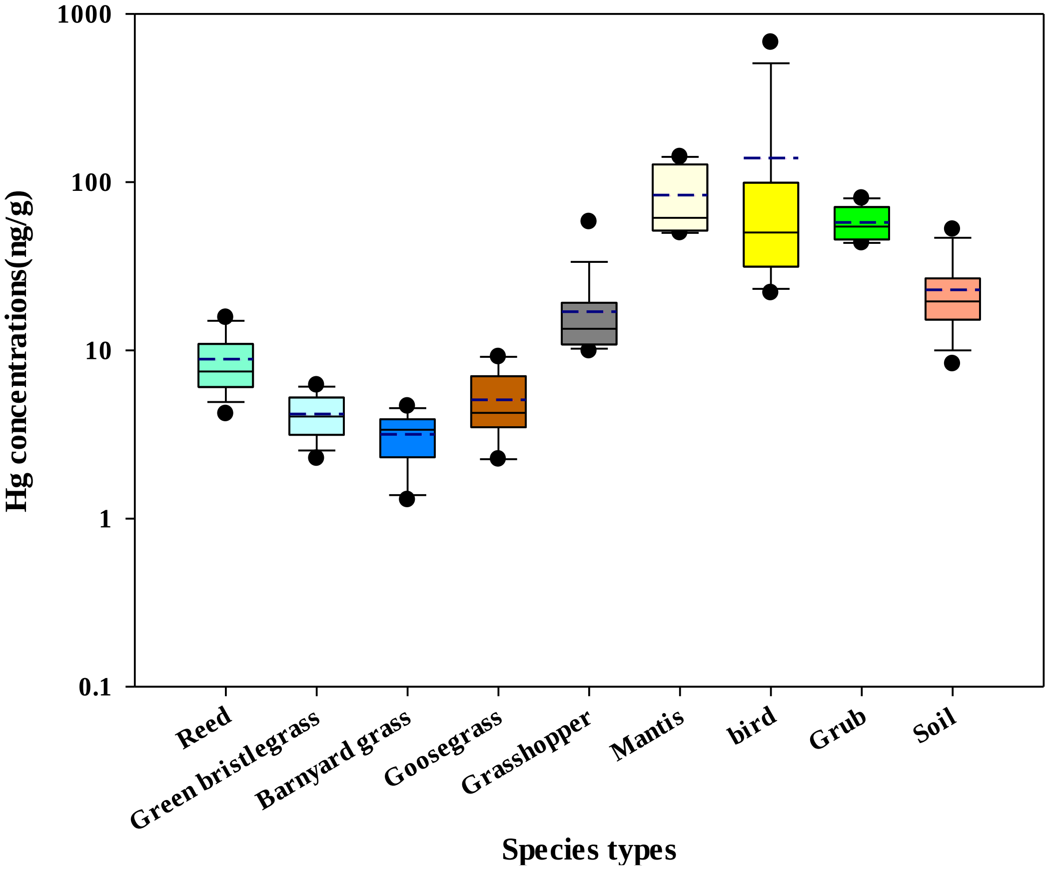

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