



Review

Pesticide levels and environmental risk in aquatic environments in China – A review



Merete Grung^{a,*}, Yan Lin^a, Hua Zhang^a, Anne Orderdalen Steen^a, Jun Huang^b, Gan Zhang^c, Thorjørn Larsen^a

^a NIVA (Norwegian Institute for Water Research), Gaustadalléen 21, 0342 Oslo, Norway

^b School of Environment, Tsinghua University, Beijing, China

^c State Key Laboratory of Organic Geochemistry, Guangzhou Institute for Geochemistry, Chinese Academy of Sciences, China

ARTICLE INFO

Article history:

Received 19 February 2015

Received in revised form 28 April 2015

Accepted 29 April 2015

Available online 25 May 2015

Keywords:

Pesticides

China

Aquatic environment

Environmental risk

DDT

HCH

ABSTRACT

China is one of the largest producers and consumers of pesticides in the world today. Along with the widespread use of pesticides and industrialization, there is a growing concern for water quality. The present review aims to provide an overview of studies on pesticides in aquatic environments in China. The levels in the water, sediment and biota were scored according to a detailed environmental classification system based on ecotoxicological effect, which is therefore a useful tool for assessing the risk these compounds pose to the aquatic ecosystem. Our review reveals that the most studied areas in China are the most populated and the most developed economically and that the most frequently studied pesticides are DDT and HCH. We show maps of where studies have been conducted and show the ecotoxicological risk the pesticides pose in each of the matrices. Our review pinpoints the need for biota samples to assess the risk. A large fraction of the results from the studies are given an environmental classification of “very bad” based on levels in biota. In general, the risk is higher for DDT than HCH. A few food web studies have also been conducted, and we encourage further study of this important information from this region.

The review reveals that many of the most important agricultural provinces (e.g., Henan, Hubei and Hunan) with the largest pesticide use have been the subject of few studies on the environmental levels of pesticides. We consider this to be a major knowledge gap for understanding the status of pesticide contamination and related risk in China. Furthermore, there is also a lack of studies in remote Chinese environments, which is also an important knowledge gap. The compounds analyzed and reported in the studies represent a serious bias because a great deal of attention is given to DDT and HCH, whereas the organophosphate insecticides dominating current use are less frequently investigated. For the future, we point to the need for an organized monitoring plan designed according to the knowledge gaps in terms of geographical distribution, compounds included, and risks.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

1.	Introduction	88
2.	Pesticide production and use in China	88
3.	Methodology	88
3.1.	Selection criteria	88
3.2.	Data treatment	89
3.3.	Environmental risk assessment	89
4.	Pesticides in aquatic environment in China	89
4.1.	Regional distribution of field studies and types of pesticides analyzed	89
4.2.	Water	89
4.3.	Sediment	91
4.4.	Aquatic biota	94
4.5.	Food web studies	94

Abbreviations: AA, annual average; BCF, bio concentration factor; DDT, dichlorodiphenyl trichloroethane; EQS, environmental quality standard; HCH, hexachloro cyclohexane; MAC, maximum allowable concentration; OCP, organochlorine pesticides.

* Corresponding author.

E-mail address: mgr@niva.no (M. Grung).

5. Discussion	94
6. Future perspectives	95
7. Conclusions	96
References	96

1. Introduction

Pesticides have been widely applied to protect agricultural crops since the 1940s, and since then, their use has increased steadily. The organochlorine pesticides (OCPs) became the dominant pesticides after the Second World War. With the publishing of “Silent Spring” by Rachel Carson in 1962 (Carson, 2002), a wider audience was warned of the environmental effects of the widespread use of pesticides. As a result, DDT was banned for agricultural use ten years later in the US, and the regulation of chemical pesticide use was strengthened. Most organo-pesticides characterized as persistent in the environment can bioaccumulate through the food web and can be transported long distances (Sheng et al., 2013; Shen et al., 2005), as evidenced by the accumulation in arctic wildlife (Dietz et al., 2004).

China's environmental challenge associated with the use of pesticides has attracted a great deal of attention from both the public and the scientific community (Gao et al., 2008; Wang et al., 2005). As in many other developing countries, the use of pesticides to increase agricultural yields has been highly encouraged in China in the past. At the same time, the high levels of pesticide residues are one of the most urgent food safety concerns in China (Hamburger, 2002).

Water quality has become a great concern in China. It has been reported that “only 58% of freshwater meets the quality criteria for safe drinking water” (Bao et al., 2012). China's National water quality assessment criteria are mostly related to traditional pollutants, such as organic matter (BOD, COD), nutrient loading (N, P) and certain heavy metals. Little emphasis has been given to organic micropollutants, such as pesticides.

Pesticide production and usage in China has been increasing at a rapid pace in the past 30 years (Fig. 1), China is one of the largest producers and consumers of pesticides in the world today. High levels of DDT in human breast milk were found in several large Chinese cities (Wong et al., 2005). South China (Pearl River Delta) has been identified as one of the areas in China that has high environmental concentration of pesticides (Guo et al., 2009; Li et al., 2014b; Wang et al., 2005). Site-specific studies measuring pesticide (mostly DDT and HCH) concentrations in China have begun to emerge. To date, the existing large number of site-specific studies has given people knowledge of pesticide contamination status at a few hot spot areas, but large parts of China have still not been assessed. The environmental exposure level and associated risks remain largely unknown. It is therefore hard to gain any insights into the occurrences and risks of pesticides in the Chinese environment at the national level.

This study aims to review the overall occurrence of DDT and HCH in the Chinese environment by screening the existing literature and addresses the blind spots of studies to date. As part of the efforts to reveal what has been done and what remains an urgent need on pesticide pollution problems in China, this paper focuses on these two pesticide levels and the environmental risks in aquatic environments in China.

2. Pesticide production and use in China

The historical production and use of pesticides in China are shown in Fig. 1. Because OCPs accounted for 80% of the total pesticides before 1982, the first regulation of OCPs in China in 1982 (Wang et al., 2005) resulted in a sharp decrease in the production of total pesticides for five years. After that, the production of total pesticides (mostly non-OCPs) increased again (Fig. 1).

Interestingly, there are some conflicts in the data between production and use as the amount of use is considerably different from the amount of production when imports and exports are accounted for. This gap may be related to the different statistical materials available (e.g., production and import/export amounts were issued by the China Economic Yearbook (NBSC (National Bureau of Statistics of China), 2012) and the amount used was issued by the China Rural Statistical Yearbook (NBSC (National Bureau of Statistics of China), 2011)) and/or different statistical standards (on the basis of the amount of the pure and original pesticides or secondary processed products).

3. Methodology

3.1. Selection criteria

The present review aimed to provide an overview of studies on pesticides in the Chinese environment. The literature cited in the present study was extracted from the ISI Web of Knowledge citation index and search service (www.isiknowledge.com) using the following

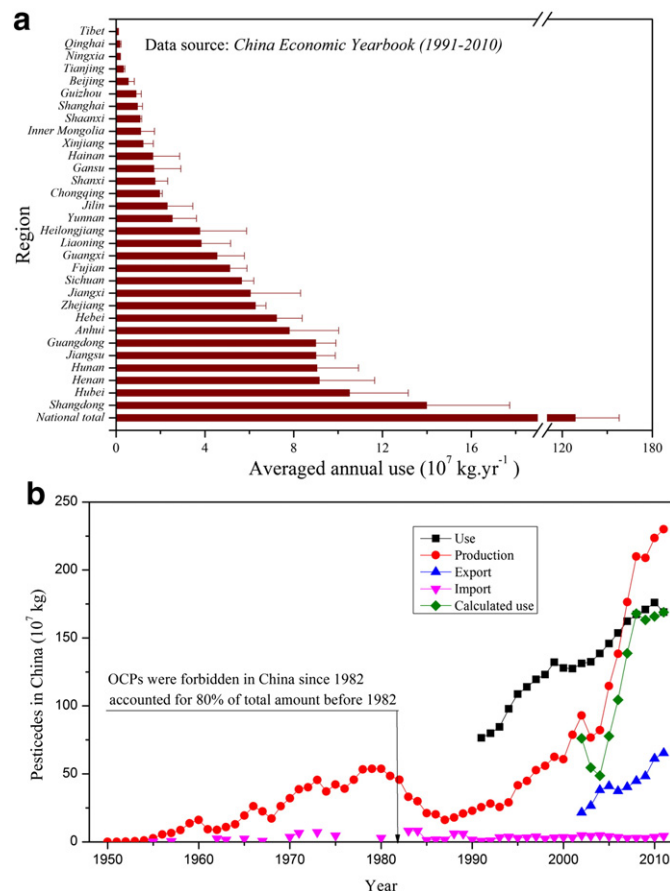


Fig. 1. a) Historical production, use, export and import amounts of all pesticides in China. “Use” in the figure is compiled from the China Rural statistical Yearbook (NBSC (National Bureau of Statistics of China), 2011), whereas the “calculated use” is calculated from the production, export and import from the China Economic Yearbook (NBSC (National Bureau of Statistics of China), 2012). b) Annual average pesticide use for the period 1991–2010 per province.

keywords: pesticide (OR pesticides) and China. In addition, cited references within this first set of publications were also included. Thus, only publications in English and in international peer reviewed journals were included in the present study. Publications in the last two decades, until December 2013, were selected in the present study. Following the criteria above, we reviewed a total of almost 500 publications. However, the publications that are presented in this review are selected results from this set.

3.2. Data treatment

The data presented in the present study were converted to a uniform format of units: water: ng L^{-1} , sediment: ng g^{-1} ($=\mu\text{g kg}^{-1}$) dry weight, and biota: ng g^{-1} ($=\mu\text{g kg}^{-1}$) wet weight. With the exception of the units for water, these are the same units utilized in the environmental quality standards (EQS) defined in Bakke et al. (2010) and Molvær et al. (1997) for water and sediment and biota, respectively. For ease of reading the tables, we have given all numbers two significant digits because analytical variability makes further precision superfluous. We reviewed the pesticides' distribution and occurrence in various environmental components in China: water, sediment, biota and the food web (Tables S1–S4). The values are colored in accordance with the EQS risk categories (Bakke et al., 2010; Molvær et al., 1997). Three values for each study location were summarized in the tables, including the maximum, mean and minimum values of the dataset wherever available.

3.3. Environmental risk assessment

Environmental classifications of the concentrations of pesticides have been made for different environmental compartments. Different classification systems for assessing the environmental risk exist, and a more elaborate comparison of such systems is given in the supporting material. The conclusion of this comparison was that the Norwegian classification system (Bakke et al., 2010; Molvær et al., 1997) was the most comprehensive regarding environmental quality standards. The Norwegian system was therefore chosen for the risk assessment and categorization of pesticides in aquatic environments in the present study.

Both Norwegian guidelines divide different matrices into five pollution classes based on ecotoxicological effect. Within the classification system, class I is considered to represent background conditions in pristine areas (in Norway). The upper limits for classes II and III are based on the predicted no effect concentrations (PNEC) for chronic and acute exposures to that compound, respectively. The upper limit of class IV is defined as concentrations between two and five times the PNEC (depending on the compound), with class V representing concentrations above this level.

Within the Norwegian classification system for DDT, the risk assessment is for the DDTs (ΣDDT , the sum of DDT and the degradation products DDE and DDD). Our data are presented accordingly unless otherwise stated. However, the risk categories for HCH are different depending on the matrix. The risks in water and sediment are based on concentrations of lindane (the γ -isomer of HCH), whereas the risk in biota is based on the sum of all HCH isomers. Again, our data are presented accordingly, which means that for water and sediment, we focus on the occurrence of lindane, and for biota, we focus on the sum of all HCH isomers. However, in the supporting information on biota (Table S3), the concentration of lindane is also presented whenever available.

4. Pesticides in aquatic environment in China

4.1. Regional distribution of field studies and types of pesticides analyzed

Fig. 2a shows the locations of all of the studies that have been reviewed in this article. Four areas clearly show up on the map as having

most of the studies: Beijing-Tianjin, Shanghai/Yangtze River Delta, Xiamen/Fujian coast, and Guangzhou/Pearl River Delta. These areas are among the most populated in China and the most developed economically. Most study sites are located in coastal areas and the deltas of the major rivers.

The studies covered a wide range of samples, including water, sediment and various types of biological samples. Most of the studies focused on conventional OCPs, mainly DDT and HCHs. For example, there were 44 papers reporting DDT and 42 papers reporting HCH in sediments, whereas only 4 included chlordanes and 8 HCB (Fig. 2c).

Organophosphates, pyrethroid and carbamate are the most common currently used pesticides in China. Although studies on the environmental occurrence and ecotoxicological risk of these pesticides are scarce in China (Li et al., 2013), studies have confirmed the occurrence of these currently used pesticides in the water, sediment and air in China (Gao et al., 2009; Li et al., 2014a; Wang et al., 2012). This has already drawn the attention of both academia and the public; poisoning events associated with organophosphate insecticides and carbamates are frequently reported (Li et al., 2014c). However, due to the large-scale use in agriculture in the past and their persistence, DDT and HCH have become ubiquitous in the environment. To do an extensive risk assessment for the environment in China that can cover most of the territory of China, the risks from DDT and γ -HCH (lindane) were assessed according to the EQS given by Bakke et al. (2010) and Molvær et al. (1997).

In the following sections, we summarize data for the two groups of OCPs included in the most studies, i.e., HCH and DDT. We search the published studies for the different compartments/matrices (water, sediment and biota) of aquatic environments. The results are separately summarized as risk levels for each matrix (Figs. 3–5). The risk assessments are based on the Norwegian guidelines for all the matrices because this guidance is the most comprehensive. The figures are based on data presented in Tables 1–3 in the supplementary information. Both the figures and the tables are colored according to the Norwegian risk guidelines as described in Bakke et al. (2010) and Molvær et al. (1997). This way of presenting data is more convenient than just reporting levels of concentrations, because the assessment is effect based. We tend to present all of the results in each study instead of an average value.

4.2. Water

An overview of the risk levels of DDTs and lindane in surface water is shown in Fig. 3a (DDTs) and Fig. 3b (lindane) based on more than 30 studies for each parameter. Detailed values and references are listed in Table S1 in the supplementary material. The Norwegian classification system (Bakke et al., 2010) contains no information about background levels (class I) for DDTs and lindane in water. Hence, only four environmental classes have been utilized for the water phase. In Table S1, studies of pore water are also shown, which, in general, show higher concentrations in this environmental matrix. However, these studies are not included in Fig. 3.

For DDT, most of the lakes and rivers that were investigated reached class II or III (i.e., good, $<1 \text{ ng L}^{-1}$ or moderate, $1\text{--}25 \text{ ng L}^{-1}$) with a few sites (approximately 25%) in some areas displaying class IV (e.g., $25\text{--}250 \text{ ng L}^{-1}$). The highest elevated concentration levels exceeding 250 ng L^{-1} (i.e., class V, very bad) were found in several areas located in the Haihe River Basin, the Huaihe River Basin, the Taihu Basin, and the Pearl River Basin (Fig. 3a). For lindane the majority of lakes and rivers reached class II (Fig. 3b). Generally, the risk levels for lindane in water were lower than for DDT. The highest concentrations of lindane were also found in the Haihe River Basin and the Pearl River Basin (Fig. 3b). There was also high risk identified in one study in Yunnan, probably due to illegal usage or discharge, which has been a problem in many areas in China (Yang et al., 2007).

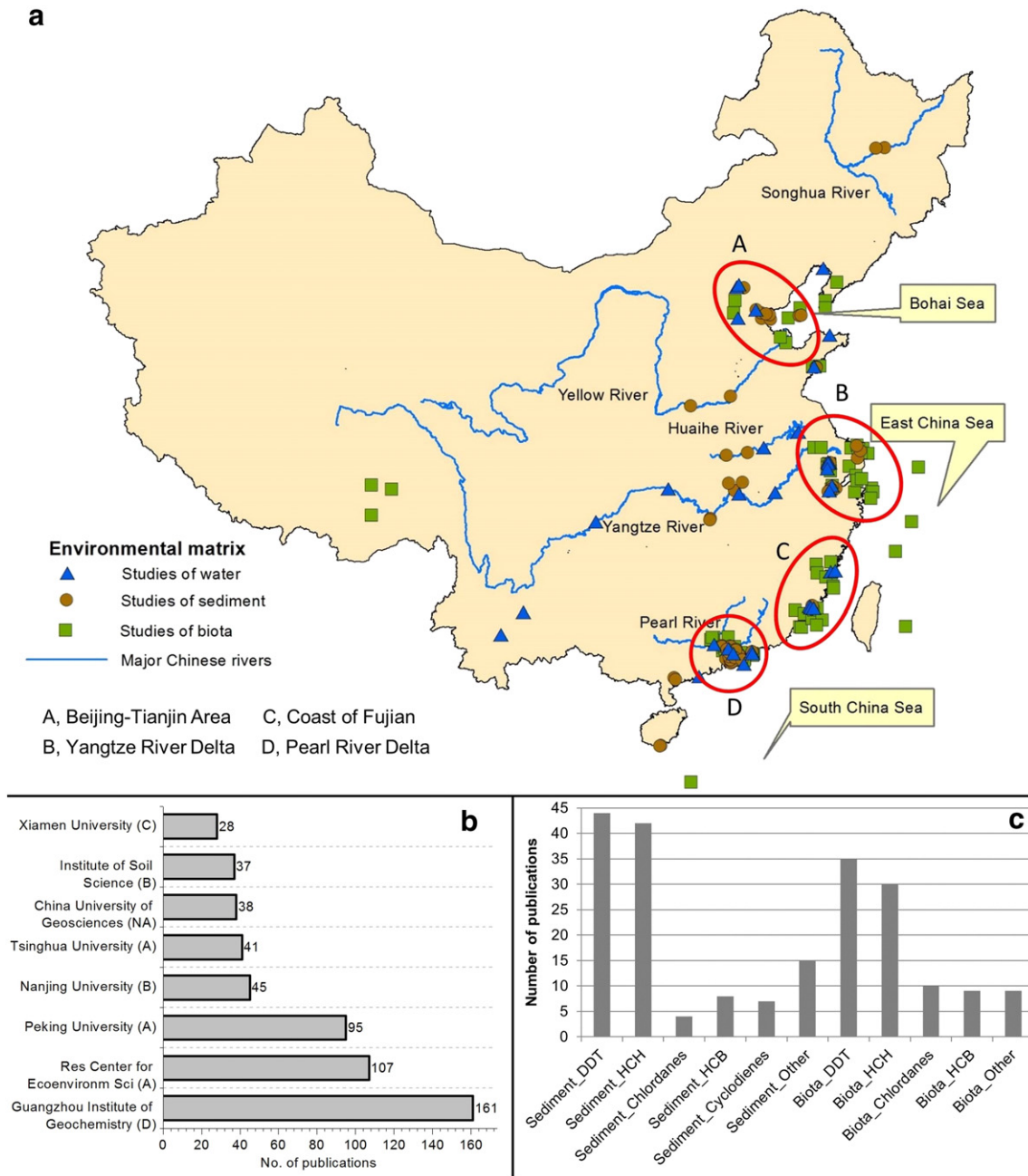


Fig. 2. a) Geographic locations of studies in this review (upper). b) The number of publications by the most-publishing institutions (letter in brackets indicates its geographic location corresponding to Fig. 2a) (lower left). c) The number of publications for each type of pesticide for sediments and biota (lower right).

The Haihe River is the largest river in the Beijing-Tianjin area and the economic center of northern China. It is considered the most polluted river among the largest rivers in China (Wang et al., 2010). The river converges near Tianjin, an important chemical industry city in China that has produced large amounts of OCPs, such as DDT and lindane.

The Huaihe River Basin was strongly polluted with pp-DDT. The high frequency of detection of pp-DDT was explained by the historical use of DDT in agriculture, in addition to the widely used dicofol, which contains up to 20% pp-DDT as an impurity, on cotton and fruit crops. The Huaihe River, in addition to the Yellow River and the Yangtze River basins are important and large agricultural areas. However, due to the dilution by the generally high annual runoff from the Yellow River and Yangtze River, the risks in these two large rivers are not as high as in the Huaihe River.

The Pearl River Delta is one of the seriously contaminated areas in China, especially for DDT in water (Fig. 3a). The delta is a heavily

industrialized area that mainly consists of three mega cities – Hong Kong, Shenzhen and Guangzhou, as well as some smaller cities. The delta area has many busy shipping routes and large ports. Many of the ships use an antifouling paint containing DDT. Therefore, this area suffers a great deal from DDT contamination from the shipping industry. According to Guo et al. (2008), the amount of dicofol used in China was almost 9000 tons between 1988 and 2002, and in 2003, an average of more than 14 tons of dicofol was applied in the Pearl River Delta.

In general, water is not considered a good matrix for monitoring the levels and risks of DDT and lindane, due to their strong lipophilic properties. The recommended matrices for assessment of DDT contamination according to the European Commission (European Commission, 2010) are sediment and biota. For lindane, water and sediment are optional matrices, but biota is the preferred matrix (European Commission, 2010).

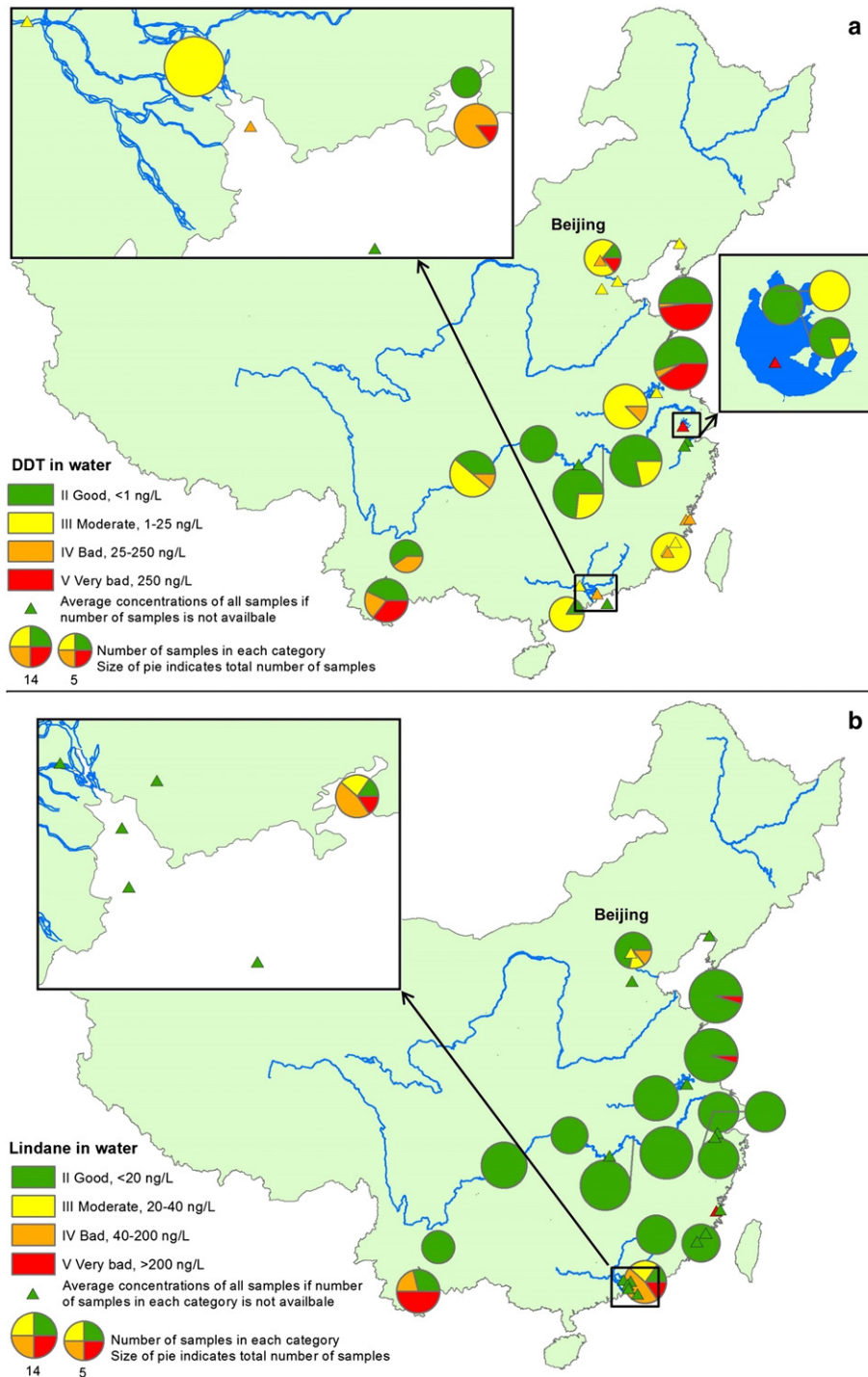


Fig. 3. a) Risk levels of water from DDTs (upper). b) Risk levels of water from lindane (lower). The fraction of the pie in each location indicates the percentage of samples in each risk category. The size of the pie indicates the number of samples. A dot with the risk corresponding to the average concentration is used at locations where the number of samples is not available.

4.3. Sediment

An overview of the risk levels of DDTs and lindane in sediment is shown in Fig. 4. Detailed values and references are listed in Table S2 in the supplementary material, comprising more than 50 investigations for each compound. The study sites for OCPs in sediments cover a few more areas than for water and a slightly better geographical coverage. The levels of HCB (hexachloro benzene) have been assessed for risk, and the levels of other OCPs and pesticides are also given in Table S2.

Similar to OCPs in water, most of the lakes and rivers investigated obtain class II ($0.5\text{--}20\text{ ng g}^{-1}$ for DDTs and $<1.1\text{ ng g}^{-1}$ for lindane). The areas with the highest levels of DDTs differ from the areas with the highest levels of lindane. High levels of DDTs in sediment were found in the Huaihe River, the Pearl River Delta and Hainan, at classes III–IV.

The Pearl River Delta is one of the places that showed an explicit contrast between DDT and lindane contamination (Fig. 4a&b). The DDTs used in antifouling paint by a large number of ships are the main source of DDT input. This was also confirmed by another study in fishing

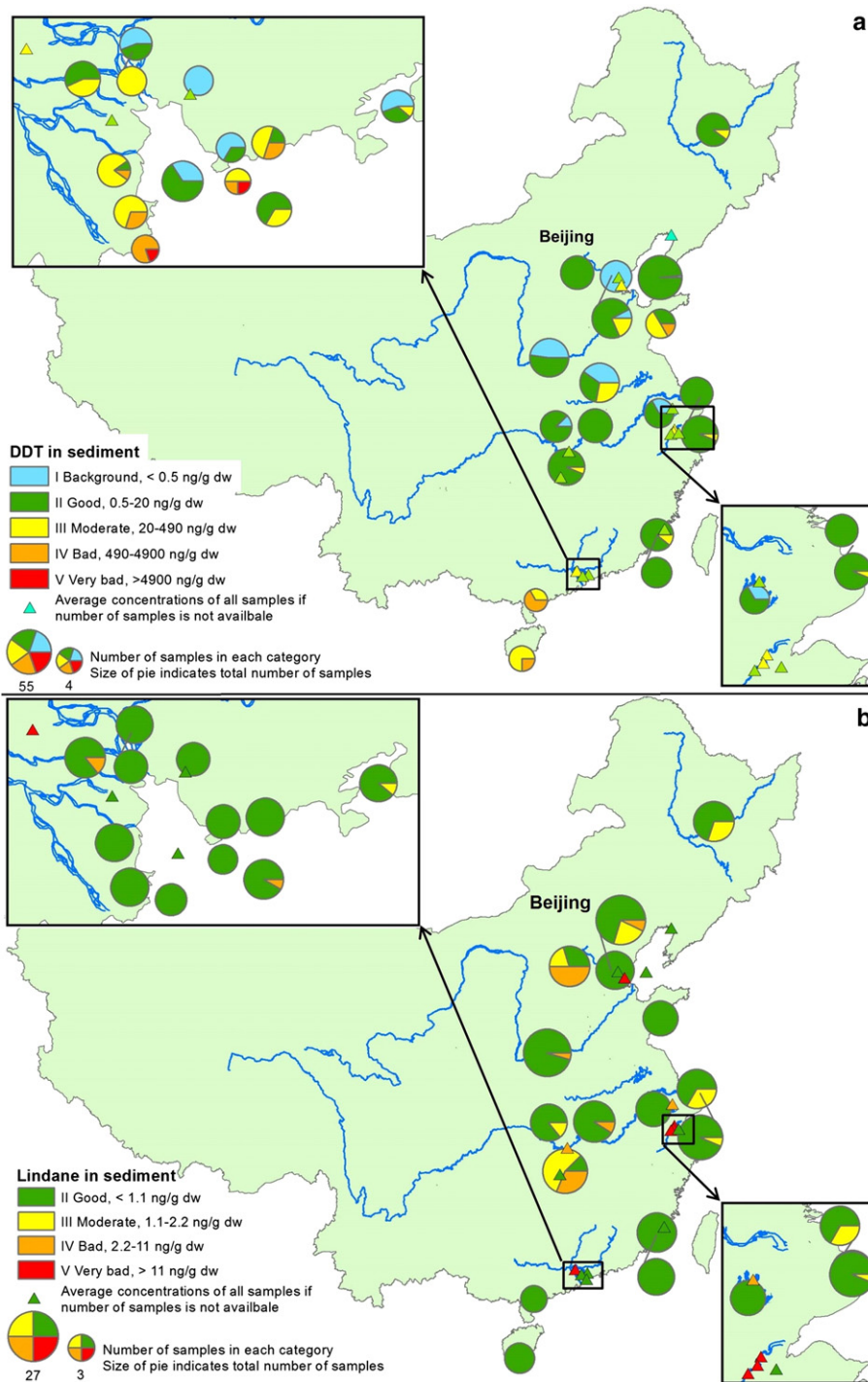


Fig. 4. a) Risk levels of sediment from DDTs (upper). b) Risk levels of sediment from lindane (lower).

harbors in China (Lin et al., 2009), which indicated that DDT risk levels had all reached class III–IV, whereas lindane risk levels were basically maintained at class I. Both Macao and Hong Kong harbors exceeded the level for “very bad” (4900 ng g⁻¹), where severe acute toxic effects can be expected. The authors of this study ascribed the high levels to the new local input of antifouling paint within the fishing harbors. More investigations like this one on coastal sediments are therefore warranted, along with proper management. The lowest levels of DDT in the study of Lin et al. (2009) (21–68 ng g⁻¹) were observed in Guangzhou harbor, which is located in the inner estuary. Even these levels are considered moderately polluted (Bakke et al., 2010), which shows that DDT pollution in the region represents a serious environmental problem. The

levels were confirmed in another study (Mai et al., 2002), where the levels in the Macao harbor were somewhat lower (1629 ng g⁻¹) and the levels near Guangzhou were 91 ng g⁻¹. In a third study of levels of DDT near Guangzhou, the levels were reported to be between nd and 11.9 ng g⁻¹ (Li et al., 2011b). In one study of fishpond sediments in the Pearl River estuary (Li et al., 2011a), an environmental risk assessment for DDT was performed, based on Long et al. (1995). Only 27% of the investigated samples had DDT concentrations that could be characterized as non-polluted, whereas 9% were medium polluted.

High levels of lindane were found in the Beijing-Tianjin area, Qiantang River and central Yangtze River with classes III–IV and even V. These samples were therefore very different from the water samples

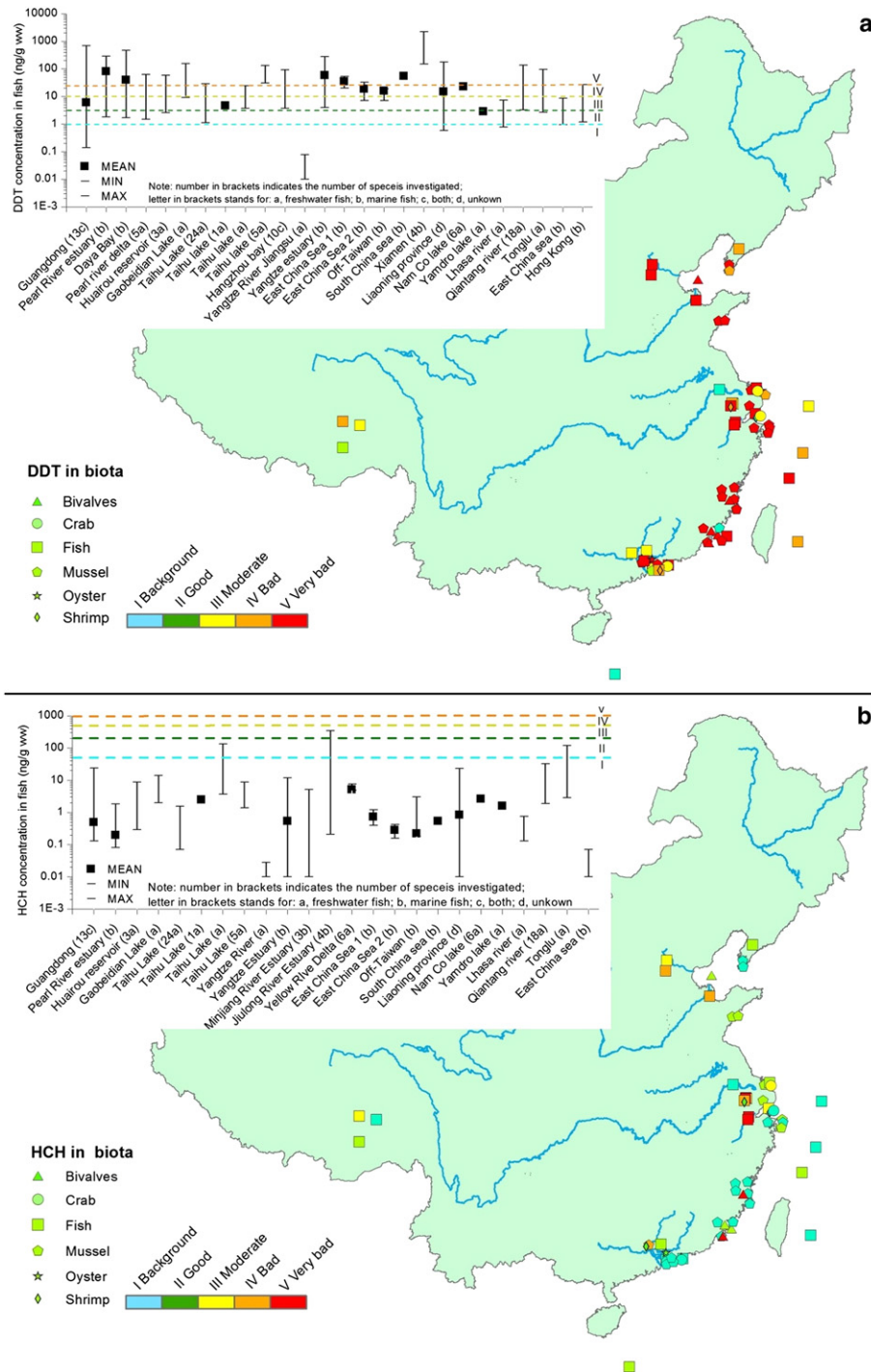


Fig. 5. a) Risk levels of biota from DDTs (upper). b) Risk levels of biota from all HCH isomers (HCHs) (lower).

where the risk level of lindane was generally lower than that of DDT. The geographic distribution of risks of DDT and lindane in sediment samples did not show a clear relationship. A site with a very high level of DDT in the sediments was found near Tianjin and was also found to have high levels of DDT and lindane in the water phase (Tao et al., 2007). The input was described as recent and was ascribed to large chemical companies and small-scale pesticide manufacturers. The highest levels of lindane were reported in the Haihe River (L. Zhao et al., 2010); in addition, in the estuary, some of the levels of lindane were still above 10 ng g⁻¹. The authors claimed that the Haihe River Basin is one of the most POP-contaminated basins in China. The

production of lindane and HCH in the area was not stopped until 2000 and 2003, respectively.

The Qiantang River was one of the sites that showed a serious risk level of lindane and a moderate risk level of DDT. The dominance of lindane in most sediment samples reflected the recent use of lindane. The high concentration of biological metabolites p,p'-DDD from the parent DDTs indicated that DDT contamination was mainly from the aged and weathered agricultural soils, which had been retained under anaerobic conditions in the sediment (Zhou et al., 2006).

Taihu Lake is also a site that has attracted investigations of pesticide occurrence. A study by Z. Zhao et al. (2010) investigated the mutagenic

potential of sediment extracts and revealed poor correlations between the OCP content and the exception of endosulfans. The levels of DDT varied from 0.06–5.8 ng g⁻¹ dw sediment. This means that the pollution of DDT in the sediment is not very severe and that no toxic effect following chronic exposure is expected.

One study covered the Songhua River, which is the biggest river by runoff volume in northeast China. HCH was the dominant pollutant, and there was still fresh HCH input from agriculture at the time the study was conducted (He et al., 2008).

The contrast of the occurrence of DDT and lindane in the environment shows a clear pattern of use of these two different types of OCPs. HCH is preferred more in recent agricultural activities, and the DDT occurrence in these agricultural areas is usually from residues of previous use. The use of DDT in the interior of the country has declined over time, whereas HCH continues to have fresh input. The DDT risk levels in these agricultural areas are therefore generally lower than lindane risk levels. DDT in coastal areas shows the opposite story, where ships use large amount of DDT containing antifouling paint. The risk levels of DDT in these areas are therefore much higher than the lindane risk levels.

4.4. Aquatic biota

An overview of the risk levels of DDTs and HCHs in various types of biota is shown in Fig. 5a (DDT) and Fig. 5b (HCH). Detailed values and references are listed in Table S3 in the supplementary material, and additional pesticides were also assessed for risk (HCB) and referenced (other OCPs and pesticides). The study sites for OCPs in biota are generally scattered along the east coast of China, where aquatic biota are present in large rivers, estuaries and the sea. There were very few studies presenting data from inland waters and major rivers. Only one study with three locations was conducted in Tibet, which was the only study in the entire western part of the country.

The risk levels in Fig. 5 are based on the average concentrations of OCPs in each type of biota. This is different from Figs. 3 & 4 which showed the number of samples in each risk category. The HCH risk assessment in biota is based on the total concentration of all HCH isomers (Norwegian guidelines (Molvær et al., 1997)).

In general, the environmental risk of DDT is much higher than that of HCH in biota (Fig. 5) and most of the biota samples showed a risk level of V for DDT. The HCH in biota has only a few places with a risk level of V, often corresponding to the sites identified for HCH (lindane) in sediment (Fig. 4b). The majority of high DDT levels were detected along the Chinese coast, some at the outflow of major rivers. High levels were detected in mussels, suggesting the present usage of DDTs and HCH near coastal waters (Monirith et al., 2003). The majority of the Chinese sites investigated were of industrial or agricultural origin. The study revealed that the levels of DDT probably have ecotoxicological effects (risk level V according to Norwegian guidelines), but the levels of HCH in the same locations showed lower effects (risk levels I and II).

High levels of DDT in fish were observed in consumer fish, both from freshwater cultured fish and marine cultured fish, as well as in fish purchased from markets. One of the most investigated sites was near the Pearl River estuary, where several species have been investigated. Many of the investigations showed that DDT is likely to have an ecotoxicological effect in this area and that the risk of HCH is lower. Again, the investigations point to antifouling paints on boats as the source of the high DDT levels in the area, especially because production takes place in this region.

One of the lakes that showed high levels of DDT in biota was Taihu. The lake has had several investigations of biota, and the organisms investigated range from bivalves, shrimp and fish to bird eggs (eggs are not included in the figure). In general, the highest levels were observed in bird eggs (up to 5 800 ng g⁻¹) (Dong et al., 2004) and birds (Nakata et al., 2005). For the investigation of bird eggs, the significant differences in levels between different species could be attributed to the variation in prey and habitat. Both investigations studied fish and bivalves in the same lake at the same time, both of which had lower levels of DDT.

This can possibly be ascribed to the fact that birds are often on top of the food chain and their trophic level can often be as high as 4 in China (Cui et al., 2011; Wan et al., 2008). We therefore encourage the use of birds and bird eggs in studies of environmental risk. The same investigations also reported levels of HCH in the bird eggs; however, the risk of this pesticide was lower but still in risk category V in one of the studies (Nakata et al., 2005). Additionally, in bird eggs from Hong Kong, elevated levels of DDT were detected (Connell et al., 2003).

Aquatic living organisms are suitable for assessing the environmental quality of their environment. Many older pesticides, as well as some of the new pesticides, have a quite high log Kow and will therefore accumulate in biological tissue. Some of the aquatic organisms will also constitute human food and thereby a potential impact on human health. For environmental monitoring purposes, the use of organisms high in the food chain is essential. We therefore encourage future monitoring campaigns to focus on analyses of biota for lipophilic compounds. It would also be beneficial to include analyses of nitrogen (and carbon) isotopes to facilitate the measurement of the trophic level of the organisms analyzed.

4.5. Food web studies

The major portion of the studies reported in the previous chapters has focused on one matrix for the analysis of the level of pesticides. However, some investigations have chosen to study the food web, which may include diverse matrices, such as water, plants, biota and sediment. These studies are very useful because the environmental risk as well as the risk for human health can then be assessed to a certain extent. Whether pesticides accumulate in the local food web and to what extent is always of importance. A true study of bioaccumulation is always best performed in the same study because different studies will invariably have different timing, locations and analyses of the compounds. Food web investigations are shown in Fig. 6 and in Table S4 in the supporting material. One of the few places in China where the food web has been studied is the Qiantang River, which flows through an agricultural area (Zhou et al., 2008). Thirteen OCPs were determined in different biota (crab, clam, shrimp and fish) as well as aquatic plants, water and sediments. The conclusion of the study was that almost half of the edible aquatic animals had higher levels than those recommended for human consumption by the US EPA. The log BCF (bio concentration factor) was calculated in the different sampling sites and for all biota and ranged from 2.9–6.3 for fish, 3.8–6.2 for shrimp and 3.1–5.4 for clams. The highest BCF values were observed for p,p'-DDE. The analyzed pesticides were distributed differently than the aquatic matrices. The percentage of \sum DDTs (sum pesticides analyzed) was higher in the sediment and biota than in the water and plants, whereas the opposite was observed for the \sum OCPs, other than the DDTs and HCHs analyzed. This demonstrates the importance of analyzing more than one matrix when performing environmental risk assessments and choosing the best matrix for analyses based on the inherent properties of the pesticide in question.

DDT and HCH in the food web of Baiyangdian Lake was studied by Hu et al. (2010). A range of biota, including zooplankton, shrimp, crab, snail, mussels, different fish, turtle and duck, were analyzed, as well as water and sediment samples. Stable isotope analyses were performed on the biological matrices, allowing the trophic level of the organisms to be determined. The correlations between these analyses allowed for the determination of the biomagnification in the food web, which were determined to be 1.6 and 1.7 for α -HCH and p,p'-DDT, respectively. The compositional profiles for DDT and HCH varied substantially among different biota.

5. Discussion

The information reviewed and summarized here obviously does not represent a statistically good sampling design with representative sampling. The geographic distribution of the studies is probably

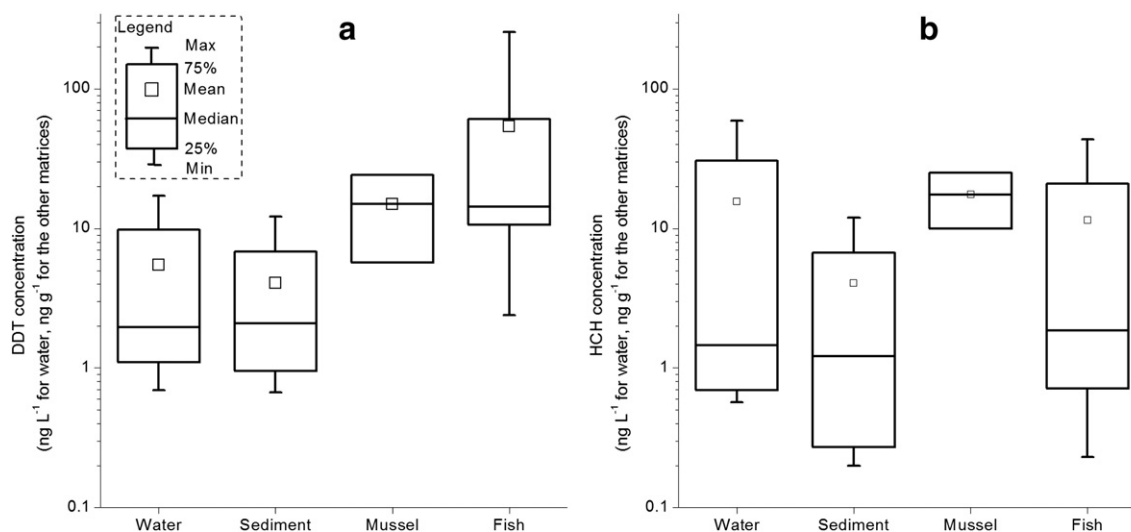


Fig. 6. Pesticide bioaccumulation through the food web. A straight line inside the box indicates the median of the values, while a square indicates the mean; the box indicates the 25% and 75% cut of the values; the whiskers indicates the maximum and minimum of the values.

not representative of the real occurrence of the problem. The studies tend to be geographically concentrated around cities because they are the base of a few institutes and universities with the competence to analyze organic pollutants. Fig. 1b shows the eight institutes and universities in China that have the most publications related to pesticides in aquatic environments in China. All of the institutes are located in the four areas where most studies are carried out, with only one exception (China University of Geosciences in Wuhan). This bias towards more studies in the most developed areas of China may relate to

- the availability of funding (more funding available for environmental studies in the most developed areas);
- local environmental awareness (the general population as well as policy makers in developed areas may be more concerned about environmental issues);
- the sampling of local “hot spots” where elevated concentrations may be expected and the local pollution situation is of particular interest;
- the convenience of sampling (most of the studies have had scientific goals other than to provide a geographic distribution of pesticides in the environment, hence sampling close to “home” is convenient).

Many of the most important agricultural provinces and the provinces with the largest pesticide use (Fig. 1b) have few studies. For example, the central Chinese provinces of Henan, Hubei and Hunan are important grain (wheat and rice) production areas with high pesticide use, where very few studies of pesticides in the environment have been published. We consider this lack of studies from the areas using the most pesticides to be a major knowledge gap for the status of pesticide contamination in China.

Additionally, there is a lack of studies in remote environments in China; there were merely three studies on the Tibetan Plateau, two on the Yunnan Plateau and none in the entire northwest and the upper and middle Yellow River Basin. Given the importance of the occurrence of pesticides in remote environments on a global scale, the lack of data from remote regions in China is striking and another important knowledge gap identified by this review.

Another uncertainty in our compiled dataset and risk maps is the data quality. Because the collated data are from the international peer-reviewed literature, a reasonable QA/QC scheme must be expected,

and hence, the analytical quality should be acceptable for the current purpose. In addition, the standard OCPs should be relatively easy to analyze. However, sampling procedures and sample representativeness may be a weakness and may be difficult to assess.

Many of the reviewed publications have a limited scope in terms of discussing the data in a wider context. Often the discussion is limited to a comparison with reported concentrations from other studies and other countries and to some extent, a comparison with EQS values. In general, the data presented in different publications are used for risk assessments to a limited extent.

The compounds selected for analysis in the different studies probably also represent a serious bias. Most studies focus on DDT and HCH. Whether this is reasonable from the perspective of these two (groups of) compounds being the most serious or whether they are selected because they are easy to analyze is not clear. China has banned the use of these two insecticides since 1983, and organophosphate insecticides have dominated China's insecticide market since then. Even so, fewer studies have been conducted on the pesticides that are currently used than on DDT and HCH (Li et al., 2014b).

We have chosen to assess the risk levels of DDTs and lindane (HCHs in biota) according to the Norwegian classification system. There are, of course, uncertainties related to the use of a risk classification system from a different part of the world. The species from China may exhibit a different sensitivity to the pesticides than the ones on which the classification system is based. Soil properties may give rise to different distribution patterns, and physical properties may differ significantly, such as climate (temperature), which is an important factor for degradation. However, because this is among the first attempts at assessing the overall risk of pesticides, we believe that the use of a coherent risk assessment classification system is valuable.

Despite the uncertainties and challenges discussed above, it is clear that the currently available (as peer-review published) information on OCPs in aquatic environments in China gives an incomplete picture of the contamination situation, both in terms of the spatial distribution and the compounds of concern, and possibly also regarding general risk levels.

6. Future perspectives

- There is a clear need for an organized monitoring plan, designed according to knowledge gaps in terms of geographical distribution, compounds included, as well as risks. This should target researchers as

well as environmental management and help focus research and strategic environmental planning.

- Regarding DDT, the manufacturing process for dicofol and DDT containing anti-fouling paint are the two main uses of DDT until recently. These uses have very recently been fully regulated and are therefore in the process of being phased out. Hence, the only intentional use of DDT in China should be against malaria in some limited regions. Changes in terms of reduced DDT contamination in the environment should be expected. Appropriate monitoring to follow and document these changes should be established. DDT will be present in the environment for decades after use is stopped and long term monitoring is important.
- Future studies should be designed to focus on the total environmental pressure, not only single matrices, such as sediment or water.
- In the reviewed publications, there are already many studies at “hot-spots” and contaminated sites. The focus on “hot-spots” should continue in parallel with general monitoring because they give relevant examples of high use and/or high production and the related impacts. Although such sites may have low significance area-wise, they may be important in terms of impacts.
- We therefore propose inventories of pesticide contamination in the environment as a combination of a statistical sampling design to capture the regional picture, combined with known hot spots.
- Little information exists about the environmental occurrence of new pesticides; hence, the risk they may pose to the environment is largely unknown. More investigations are needed based on gridded inventories as well as hot spot examples. In addition to the obvious issues related to the widespread use of pesticides, focus should also be on contamination related to the production of these pesticides.
- Only a few food web studies were reported from China, and consequently, there is a strong need for more investigations on this important aspect.

7. Conclusions

For DDT and HCH, the most relevant matrix for environmental risk assessment is biota. The concentrations in biota reveal that a large fraction of the results from the studies are classified as “very bad” for DDT. The risk in biota is much lower for HCH, for which the majority of the levels in biota can be classified as class I or II (background or good).

In many cases, the reported concentrations show lower risks in water and also, to some extent, sediment. Because biota is the matrix of concern, this illustrates the need to focus more on biota samples and less on water samples. More food web studies would be particularly useful.

Most studies are performed in the same few regions, and there are large regions where pesticide use is high with very little information on environmental levels and risks.

Reports were heavily biased toward DDT and HCH. Hence, these pesticides apparently pose the greatest risks. However, this may be biased due to a lack of data for other pesticides.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2015.04.013>.

References

- Bakke, T., Kallqvist, T., Ruus, A., Breedveld, G.D., Hylland, K., 2010. Development of sediment quality criteria in Norway. *J. Soils Sediments* 10, 172–178. <http://dx.doi.org/10.1007/s11368-009-0173-y>.
- Bao, L.-J., Maruya, K.A., Snyder, S.A., Zeng, E.Y., 2012. China's water pollution by persistent organic pollutants. *Environ. Pollut.* 163, 100–108. <http://dx.doi.org/10.1016/j.envpol.2011.12.022>.
- Carson, R., 2002. Silent Spring, 1st. Pub. Houghton Mifflin, 1962. Houghton Mifflin Harcourt.
- Connell, D., Fung, C., Minh, T., Tanabe, S., Lam, P.K., Wong, B.S., Lam, M.H., Wong, L., Wu, R.S., Richardson, B., 2003. Risk to breeding success of fish-eating Ardeids due to persistent organic contaminants in Hong Kong: evidence from organochlorine compounds in eggs. *Water Res.* 37, 459–467. [http://dx.doi.org/10.1016/S0043-1354\(02\)00294-4](http://dx.doi.org/10.1016/S0043-1354(02)00294-4).
- Cui, B., Zhang, Q., Zhang, K., Liu, X., Zhang, H., 2011. Analyzing trophic transfer of heavy metals for food webs in the newly-formed wetlands of the Yellow River Delta, China. *Environ. Pollut.* 159, 1297–1306. <http://dx.doi.org/10.1016/j.envpol.2011.01.024>.
- Dietz, R., Riget, F.F., Sonne, C., Letcher, R., Born, E.W., Muir, D.C.G., 2004. Seasonal and temporal trends in polychlorinated biphenyls and organochlorine pesticides in East Greenland polar bears (*Ursus maritimus*), 1990–2001. *Sci. Total Environ.* 331, 107–124. <http://dx.doi.org/10.1016/j.scitotenv.2004.03.025>.
- Dong, Y.H., Wang, H., An, Q., Ruiz, X., Fasola, M., Zhang, Y.M., 2004. Residues of organochlorinated pesticides in eggs of water birds from Tai Lake in China. *Environ. Geochem. Health* 26, 259–268. <http://dx.doi.org/10.1023/B:EGAH.0000039589.46698.2b>.
- European Commission, 2010. Common implementation strategy for the water framework directive (2000/60/EC). Guidance Document No. 25 on Chemical Monitoring of Sediment and Biota under the Water Framework Directive.
- Gao, J., Liu, L., Liu, X., Lu, J., Zhou, H., Huang, S., Wang, Z., Spear, P.A., 2008. Occurrence and distribution of organochlorine pesticides – lindane, p, p'-DDT, and heptachlor epoxide – in surface water of China. *Environ. Int.* 34, 1097–1103. <http://dx.doi.org/10.1016/j.envint.2008.03.011>.
- Gao, J., Liu, L., Liu, X., Zhou, H., Lu, J., Huang, S., Wang, Z., 2009. The occurrence and spatial distribution of organophosphorous pesticides in Chinese surface water. *Bull. Environ. Contam. Toxicol.* 82, 223–229. <http://dx.doi.org/10.1007/s00128-008-9618-z>.
- Guo, L., Qiu, Y., Zhang, G., Zheng, G.J., Lam, P.K.S., Li, X., 2008. Levels and bioaccumulation of organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in fishes from the Pearl River estuary and Daya Bay, South China. *Environ. Pollut.* 152, 604–611. <http://dx.doi.org/10.1016/j.envpol.2007.06.067>.
- Guo, Y., Yu, H.-Y., Zeng, E.Y., 2009. Occurrence, source diagnosis, and biological effect assessment of DDT and its metabolites in various environmental compartments of the Pearl River Delta, South China: a review. *Environ. Pollut.* 157, 1753–1763. <http://dx.doi.org/10.1016/j.envpol.2008.12.026>.
- Hamburger, J., 2002. Pesticides in China: a growing threat to food safety, public health and the environment. In: Turner, J.L. (Ed.), *China Environment Series*. Woodrow Wilson Center, Washington DC, pp. 29–44.
- He, M., Wang, H., Lin, C., Quan, X., Guo, W., Yang, Z., 2008. Distribution of persistent organochlorine residues in sediments from the Songhuajiang River, northeast China. *Environ. Technol.* 29, 303–314. <http://dx.doi.org/10.1080/09593330802099809>.
- Hu, G., Dai, J., Mai, B., Luo, X., Cao, H., Wang, J., Li, F., Xu, M., 2010. Concentrations and accumulation features of organochlorine pesticides in the Baiyangdian Lake freshwater food web of North China. *Arch. Environ. Contam. Toxicol.* 58, 700–710. <http://dx.doi.org/10.1007/s00244-009-9400-1>.
- Li, H., Ling, W., Lin, C., 2011a. Fishpond sediment-borne DDTs and HCHs in the Pearl River Delta: characteristics, environmental risk and fate following the use of the sediment as plant growth media. *J. Hazard. Mater.* 186, 1474–1480. <http://dx.doi.org/10.1016/j.jhazmat.2010.12.031>.
- Li, H., Tyler Mehler, W., Lydy, M.J., You, J., 2011b. Occurrence and distribution of sediment-associated insecticides in urban waterways in the Pearl River Delta, China. *Chemosphere* 82, 1373–1379. <http://dx.doi.org/10.1016/j.chemosphere.2010.11.074>.
- Li, H., Sun, B., Lydy, M.J., You, J., 2013. Sediment-associated pesticides in an urban stream in Guangzhou, China: implication of a shift in pesticide use patterns. *Environ. Toxicol. Chem.* 32, 1040–1047. <http://dx.doi.org/10.1002/etc.2147>.
- Li, H., Ma, H., Lydy, M.J., You, J., 2014a. Occurrence, seasonal variation and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides in an urban community in South China. *Chemosphere* 95, 363–369. <http://dx.doi.org/10.1016/j.chemosphere.2013.09.046>.
- Li, H., Zeng, E.Y., You, J., 2014b. Mitigating pesticide pollution in China requires law enforcement, farmer training, and technological innovation. *Environ. Toxicol. Chem.* 33, 963–971. <http://dx.doi.org/10.1002/etc.2549>.
- Li, H., Zeng, E.Y., You, J., 2014c. Mitigating pesticide pollution in China requires law enforcement, farmer training, and technological innovation. *Environ. Toxicol. Chem.* 33, 963–971. <http://dx.doi.org/10.1002/etc.2549>.
- Lin, T., Hu, Z., Zhang, G., Li, X., Xu, W., Tang, J., Li, J., 2009. Levels and mass burden of DDTs in sediments from fishing harbors: the importance of DDT-containing antifouling paint to the coastal environment of China. *Environ. Sci. Technol.* 43, 8033–8038. <http://dx.doi.org/10.1021/es901827b>.
- Long, E.R., Macdonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Manag.* 19, 81–97. <http://dx.doi.org/10.1007/BF02472006>.
- Mai, B.-X., Fu, J.-M., Sheng, G.-Y., Kang, Y.-H., Lin, Z., Zhang, G., Min, Y.-S., Zeng, E.Y., 2002. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environ. Pollut.* 117, 457–474. [http://dx.doi.org/10.1016/S0269-7491\(01\)00193-2](http://dx.doi.org/10.1016/S0269-7491(01)00193-2).
- Molvær, J., Knutzen, J., Magnusson, J., Rygg, B., Skei, J., Sørensen, J., 1997. *Classification of Environmental Quality in Fjords and Coastal Waters. A Guide*. (No. TA 1467/1997). NIVA.
- Monirith, I., Ueno, D., Takahashi, S., Nakata, H., Sudaryanto, A., Subramanian, A., Karuppiyah, S., Ismail, A., Muchtar, M., Zheng, J., Richardson, B.J., Prudente, M., Hue, N.D., Tana, T.S., Tkalin, A.V., Tanabe, S., 2003. Asia-Pacific mussel watch: monitoring contamination of persistent organochlorine compounds in coastal waters of Asian countries. *Mar. Pollut. Bull.* 46, 281–300. [http://dx.doi.org/10.1016/S0025-326X\(02\)00400-9](http://dx.doi.org/10.1016/S0025-326X(02)00400-9).
- Nakata, H., Hirakawa, Y., Kawazoe, M., Nakabo, T., Arizono, K., Abe, S.-I., Kitano, T., Shimada, H., Watanabe, I., Li, W., Ding, X., 2005. Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. *Environ. Pollut.* 133, 415–429. <http://dx.doi.org/10.1016/j.envpol.2004.07.003>.
- NBSC (National Bureau of Statistics of China), 2011. *China Rural Statistical Yearbook in 1991–2010* (Beijing).

- NBSC (National Bureau of Statistics of China), 2012. *China Economic Yearbook in 1950–2011* (Beijing).
- Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., Bidleman, T.F., 2005. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. *Environ. Sci. Technol.* 39, 409–420. <http://dx.doi.org/10.1021/es049489c>.
- Sheng, J., Wang, X., Gong, P., Joswiak, D.R., Tian, L., Yao, T., Jones, K.C., 2013. Monsoon-driven transport of organochlorine pesticides and polychlorinated biphenyls to the Tibetan plateau: three year atmospheric monitoring study. *Environ. Sci. Technol.* 47, 3199–3208. <http://dx.doi.org/10.1021/es305201s>.
- Tao, S., Li, B.G., He, X.C., Liu, W.X., Shi, Z., 2007. Spatial and temporal variations and possible sources of dichlorodiphenyltrichloroethane (DDT) and its metabolites in rivers in Tianjin, China. *Chemosphere* 68, 10–16. <http://dx.doi.org/10.1016/j.chemosphere.2006.12.082>.
- Wan, Y., Hu, J., Zhang, K., An, L., 2008. Trophodynamics of polybrominated diphenyl ethers in the marine food web of Bohai Bay, North China. *Environ. Sci. Technol.* 42, 1078–1083. <http://dx.doi.org/10.1021/es0720560>.
- Wang, T., Lu, Y., Zhang, H., Shi, Y., 2005. Contamination of persistent organic pollutants (POPs) and relevant management in China. *Environ. Pollut.* 31, 813–821. <http://dx.doi.org/10.1016/j.envint.2005.05.043>.
- Wang, B., Yu, G., Huang, J., Wang, T., Hu, H., 2010. Probabilistic ecological risk assessment of OCPs, PCBs, and DLCs in the Haihe River, China. *Sci. World J.* 10, 1307–1317. <http://dx.doi.org/10.1100/tsw.2010.126>.
- Wang, J.-Z., Li, H.-Z., You, J., 2012. Distribution and toxicity of current-use insecticides in sediment of a lake receiving waters from areas in transition to urbanization. *Environ. Pollut.* 161, 128–133. <http://dx.doi.org/10.1016/j.envpol.2011.10.020>.
- Wong, M.H., Leung, A.O.W., Chan, J.K.Y., Choi, M.P.K., 2005. A review on the usage of POP pesticides in China, with emphasis on DDT loadings in human milk. *Chemosphere* 60, 740–752. <http://dx.doi.org/10.1016/j.chemosphere.2005.04.028>.
- Yang, J., Zhang, W., Shen, Y., Feng, W., Wang, X., 2007. Monitoring of organochlorine pesticides using PFU systems in Yunnan lakes and rivers, China. *Chemosphere* 66, 219–225. <http://dx.doi.org/10.1016/j.chemosphere.2006.05.055>.
- Zhao, L., Hou, H., Zhou, Y., Xue, N., Li, H., Li, F., 2010a. Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in surficial sediments from Haihe River and Haihe Estuary Area, China. *Chemosphere* 78, 1285–1293. <http://dx.doi.org/10.1016/j.chemosphere.2009.12.007>.
- Zhao, Z., Zhang, L., Wu, J., Fan, C., Shang, J., 2010b. Assessment of the potential mutagenicity of organochlorine pesticides (OCPs) in contaminated sediments from Taihu Lake, China. *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* 696, 62–68. <http://dx.doi.org/10.1016/j.mrgentox.2009.12.013>.
- Zhou, R., Zhu, L., Yang, K., Chen, Y., 2006. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. *J. Hazard. Mater.* 137, 68–75. <http://dx.doi.org/10.1016/j.jhazmat.2006.02.005>.
- Zhou, R., Zhu, L., Chen, Y., Kong, Q., 2008. Concentrations and characteristics of organochlorine pesticides in aquatic biota from Qiantang River in China. *Environ. Pollut.* 151, 190–199. <http://dx.doi.org/10.1016/j.envpol.2007.02.015>.