Which persistent organic pollutants in the rivers of the Bohai Region of China represent the greatest risk to the local ecosystem?

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HIGHLIGHTS

- PAHs posed the highest risk to aquatic organisms in rivers of Bohai Region.
- Risk from p,p'-DDE may be magnified due to being highly bioaccumulative.
- Fish was the most sensitive species group to the POPs.
- Hotspots with the highest risks were associated with big cities.

ABSTRACT

Freshwater aquatic organisms can be exposed to hundreds of persistent organic pollutants (POPs) discharged by natural and anthropogenic activities. Given our limited resources it is necessary to identify, from the existing evidence, which is the greatest threat so that control measures can be targeted wisely. The focus of this study was to rank POPs according to the relative risk they represent for aquatic organisms in rivers in the Bohai Region, China. A list of 14 POPs was compiled based on the available data on their presence in these rivers and ecotoxicological data. Those that were widely detected were benzo[a]pyrene, p,p'-DDE, p,p'-DDT, endrin, fluoranthene, heptachlor, hexabromocyclododecane, hexachlorobenzene, α-hexachlorocyclohexane, γ-hexachlorocyclohexane, naphthalene, perfluorooctanoic acid, perfluorooctane sulfonate and phenanthrene. Effect concentrations were compiled for Chinese relevant and standard test species and compared with river aqueous concentrations. Only bed-sediment concentrations were available so water levels were calculated based on the known local sediment organic carbon concentration and the Koc. The POPs were ranked on the ratio between the median river and median effect concentrations. Of the POPs studied, fluoranthene was ranked as the highest threat, followed by phenanthrene, naphthalene and p,p'-DDE. The risk from p,p'-DDE may be magnified due to being highly bioaccumulative. However, the greatest overlap between river concentrations and effect levels was for lindane. Overall, fish was the most sensitive species group to the risks from POPs. Hotspots with the highest concentrations and hence risk were mainly associated with watercourses draining in Tianjin, the biggest city in the Bohai Region.
1. Introduction

Persistent organic pollutants (POPs) are of concern globally due to their persistence, long-range transportation, bioaccumulation and toxicity to wildlife. Perhaps the best example of the potentially devastating impact of POPs was that of DDT and the associated DDE on birds of prey (Ratcliffe, 1967). Consequently, many POPs are now subject to a great deal of monitoring to assess the exposure and risks from such chemicals (Wong et al., 2005; Doney, 2010; Letcher et al., 2010; Covaci et al., 2011; Elliott and Elliott, 2013). Many POPs which are extremely persistent, such as PCBs and lindane, have been banned or restricted by international conventions, so some decrease in environmental exposure is starting to occur (Lohmann et al., 2007). However, human society still needs stable organic molecules with properties such as fire resistance (e.g. HBCDs), non-reactivity (e.g. PFOS) and plasticising properties (short chain chlorinated paraffins), so the environment will continue to be exposed to such chemicals, but just how much of a risk do they represent?

The Bohai coastal region, located to the east of Beijing is one of the China’s most important manufacturing areas. It includes the provinces of Shandong, Tianjin, Hebei and Liaoning which have benefitted from rapid industrialisation since the late 1970’s. Apart from its industrial base, the region has a combined population of 231 million people (National Bureau of Statistics (2014)). There are more than 40 rivers flowing into the Bohai Sea, a semi-enclosed sea, and they convey many chemical pollutants to the Bohai Sea (Wang et al., 2014, 2015b). With the Chinese rush for growth there have been concerns about a resultant chemical pollution of the environment, such as pesticides (Zhang et al., 2009), polycyclic aromatic hydrocarbons (Wang et al., 2015a), polychlorinated biphenyls (Zhao et al., 2005), perfluorooalkyl and polyfluoroalkyl substances (Wang et al., 2014) and hexabromocyclododecanes (Zhang et al., 2016) in the Bohai region. China is now taking steps to ban many of the most persistent organic pollutants (POPs) as indicated by the Stockholm Convention. Whilst some pollutants may no longer be discharged and could be considered a legacy of the past, others may still be generated, for example from combustion processes.

There is now an increasing appreciation for the need to better protect the natural environment in China, such as the Water Pollution Control Action Plan in 2015 and the Soil Pollution Control Action Plan in 2016 issued by the State Council. However, with so many kinds of chemical contaminants being discovered and monitored, it is important to find some ways for identifying which represent the greatest risk. This is a problem for the whole world and not just China. In Europe, as part of the Water Framework Directive chemicals were identified as being of special concern (priority and hazardous substances) on the basis of several properties including persistence and different toxic properties. However, a recent approach has been proposed which argues that only two factors are critical, toxicity and exposure, and that relative risk can be assessed from the proximity of the median exposure and toxicity concentrations (Donnachie et al., 2014, 2015). In this study the ecotox dataset typically comprised 8 to 90 entries (see SI).

2. Method

2.1. Approach to risk ranking

The risk ranking approach, which compares levels of chemicals in the environments and effect concentrations in ecotoxicological tests, has been applied in the UK for metals and pharmaceuticals (Donnachie et al., 2014, 2015). To obtain measured environmental data for the Bohai region, literature from both English and Chinese sources were reviewed. For toxicity information, the US EPA ECO-TOX Database, as well as a wider literature review was used. With environmental data and effect data collected, the final risk ranking compared the proximity of the medians of both datasets. In this study the ecotox dataset typically comprised 8 to 90 entries (see SI). So the median was considered a robust (or fair) comparator of relative risk between chemicals. It is important to note that this approach is different from traditional risk assessment, where something like the 5% percentile toxicity concentration, or lowest observable ecotoxicity concentration (LOEC) or predicted no effect concentration (PNEC) is used as a comparator. These methods often put great weight on only a few data points and the danger is that some of these studies may be weak and unrepeatable (Harris et al., 2014). It should be acknowledged that where the median ecotoxic value is quite similar between chemicals, the ranking should not be seen as absolute, and that the output is a relative ranking rather than an absolute risk probability.

2.2. Chemicals selected for this study

The selection of chemicals was determined both by their presence in the rivers of Bohai region (the availability and quality of measured data) and by the degree of concern expressed in the literature over their toxicity, persistence or potential to accumulate. The persistent organic pollutants considered in this research included industrial chemicals, pesticides and by-products of human activity. Fourteen chemicals were selected from more than 20 groups of chemicals on the basis monitoring data availability. The criteria used included having recent monitored data (2010—2015), abundant freshwater sampling sites and a sufficient geographic spread across the Bohai Region (Table 1 and Fig. 1). Lakes and reservoirs were not considered due to lack of sufficient measurements.

2.3. Estimation of POPs concentration in water

Whilst it may not be entirely appropriate for POPs, most available ecotoxicity information for these chemicals is based on exposure through the water column. However, most POPs, being moderately to highly hydrophobic, partition strongly to river sediment. Due to the virtual absence of water column measurements or sediment-based toxicity data, predictions for the aqueous concentrations had to be made from Bohai region river sediment values. Measured concentrations in the Bohai Region were searched from the literature in the Web of Science™ database for English publications and CNKI database for Chinese publications. The partition theory can be used to estimate water concentrations from measured sediment concentration. $K_{oc}$, the organic carbon-water partition coefficient is defined as

$$K_{oc} = \frac{\text{Concentration}_{in\ organic\ carbon}}{\text{Concentration}_{in\ water}} = \frac{\text{Mass}_{chemical}/\text{Mass}_{organic\ carbon}}{\text{Concentration}_{water}}. \quad (1)$$

And the mass of organic carbon in Equation (1) can be expressed as

$$\text{Mass}_{organic\ carbon} = \text{TOC} \cdot \text{Mass}_{sediment}. \quad (2)$$

So the chemical concentration in water can be expressed as

$$\text{Concentration}_{in\ water} = \frac{\text{Concentration}_{in\ sediment}}{\text{TOC} \times K_{oc}}. \quad (3)$$
In this study, prediction of water concentration was conducted for all chemicals except PFOS and PFOA, which had sufficient water measurements. The partition theory assumes equilibrium status on the surface of sediment. So the estimated water concentration was close to the pore water concentration, which was likely to be several times higher than the surface water concentration. The data collected in the previous studies (Zhou et al., 2006; Tan et al., 2009) was used to test the deviation between the predicted values and measured values. Compared with the pore water concentrations, the relative deviations were 0.53 for α-HCH, 0.48 for γ-HCH, 0.04 for p,p’-DDE, 0.02 for p,p’-DDT, 0.02 for heptachlor and 4.1 for endrin. In comparison with the surface concentrations, the relative deviations were 7.7 for α-HCH, 8.0 for γ-HCH, 4.4 for p,p’-DDE, −0.1 for p,p’-DDT, 1.2 for heptachlor and 3.9 for endrin. Thus, predicted concentrations may over-estimate water column levels, however, it could be considered better to err on the precautionary side.

### 2.4. Effect data collection and selection

Literature giving effect data for the selected POPs was largely obtained from the US EPA ECOTOX database, and when the dataset was not sufficient more literature was obtained using the Web of Science™ database and searched for via a series of key words (Donnachie et al., 2014, 2015). Ecotoxicity data for Chinese local freshwater species and standard test species were selected for each chemical. A range of effect measurements were present in the literature including LOEC, EC50, LC50, acute and chronic toxicity and all of these were collected. Where several studies reported effect concentrations using the same end-point for one species then in this case only the lowest effect concentration for a single species was used. Thus, the...
final ecotoxicity dataset allocated a single value for a single species for a particular end-point. Alternative approaches might have been to use the median of the ecotoxicity dataset points for a single species, or simply used all the data, regardless of whether several of the points are for the same species/end-point. When a comparison was made to look at the overall median ecotoxicity value for a chemical it was found that these choices made very little difference. The value of only plotting one data point per end-point and species is it reveals clearly to the viewer the number of different species available for analysis and does not give undue weight to commonly studied species.

2.5. Risk analysis

Once the datasets for ecotoxicology and river measurements were considered sufficient, the information included in them could be plotted and the medians noted. The difference between these medians can be described as a risk ratio, which can be used to rank concern; the larger the value, the greater the concern (Equation (4)).

\[ \text{Risk} = \frac{m_W}{m_T} \]  

Where \( m_W \) is the median river water concentration (\( \mu g/L \)) and \( m_T \) is the median effect concentration (\( \mu g/L \)).

3. Results and discussion

3.1. Risk ranking: which chemicals posed the greatest threat to wildlife?

The approach used was able to rank the 14 chemicals considered on the basis of risk (Figs. 2 and 3). The risk ratios ranged from \( 1 \times 10^{-3} \) to \( 1 \times 10^{-2} \), so this method suggests most wildlife would not be suffering unacceptable direct toxic effects via water exposure in rivers in the Bohai Region. Based on the median risk ratio, the PAHs group tended to be the POPs of greatest concern for the Bohai Region, with Flu, Phe, Nap and \( \beta[a]P \) ranking 1st, 2nd, 3rd and 5th. These were followed in terms of risk by traditional pesticides including \( p,p'-DDE \) and \( \gamma\text{-HCH} \) ranking 4th and 6th. The novel POPs including PFOA, HBCD and PFOS were further down ranking 7th, 9th and 12th. The other selected POPs including endrin, \( \alpha\text{-HCH} \), heptachlor and HCB had the lowest relative risk.

It is noted that for some of these chemicals there is an overlap, with some estimated/measured water values exceeding some of the levels where effects have been reported (Fig. 2). These include phenanthrene, DDE, benzo[a]pyrene, lindane, HBCD and PFOS. Lindane (\( \gamma\text{-HCH} \)) had the largest overlap according to the number of species involved. The insects/spiders were the most sensitive category, as well as crustaceans and fish (Fig. 4). Thus, from the available ecotoxicity information the possibility exists for lethal effects on insects such as mosquito (\( Culex sitiens \)) (Oh et al., 2013). Some crustaceans, such as ostracod (\( Cypris subglobosa \)), might receive adverse effects such as immobility (Cheng et al., 2011). Fish, such as walking catfish (\( Clarias batrachus \)) and pool barb (\( Puntius sophore \)) may also experience lethal effects.

The effects data can be disaggregated into algae, fish, insects/spiders and invertebrates/molluscs/crustaceans to examine their different sensitivities to these POPs. Generally, fish were the most sensitive group of species to this group of POPs. Insects/spiders and molluscs/crustaceans/invertebrates were less sensitive to POPs with algae being the least sensitive to these POPs (Fig. 5).

3.2. Hot-spots: in which areas of the Bohai Region might POPs have the greatest impacts?

The Dagu Drainage River featured as a hot-spot where 5 chemicals were found at their highest concentrations (Fig. 6). It is
68 km long and is the primary drainage canal for Tianjin City, which is one of the four municipalities directly under the National Central Government and is an important industrial centre, with a population of 11 million. The Dagu Drainage River, receives 0.8 million m³/day effluent from municipal wastewater treatment plants and industrial and agricultural wastewaters along its way to Bohai Sea (Li et al., 2011). In order to improve water quality, local government dredged the contaminated sediment in this water body in 2008 and 2009, but clearly the POPs have not been eliminated. The Yongding New River, had the highest concentrations of p,p'-DDE and p,p'- DDT, is a similar artificial river located in Tianjin, which receives the river flows from Haihe River Basin and municipal and industrial wastewater along its way to Bohai Bay as well.

3.3. Bioconcentration factor (BCF) ranking of POPs

Whether a chemical is bioaccumulative has been a traditional concern of chemicals in risk assessment. A judgement on whether a chemical could be considered bioaccumulative has been linked to the bioconcentration factor, which is the partitioning of a chemical between the water phase and an aquatic organism. According to the European standard, a BCF value above 2000 is considered to be bioaccumulative and 5000 is considered very bioaccumulative (EC, 2006).

The median BCF value of each POP was examined, using data from the US EPA Ecotox Database and additional literature (Fig. 7). Of the top ranked POPs in this study (Figs. 2 and 3) only p,p'-DDE would be considered bioaccumulative. This could be an argument for raising our concern over this chemical within the top five ranked POPs in the rivers of the Bohai region.

3.4. Local source of the PAHs

PAHs can be introduced into the environment from both natural and anthropogenic processes including biomass burning, fossil fuel combustion, transportation emissions, and petroleum industries (Yunker et al., 2002). As for the individual research in the Bohai Region, the sources of PAHs in the environment were usually attributed by their characteristic isomer ratios, such as InP/ (InP + BghiP), Flu/(Flu + Pyr), An/(An + Phe) and BaA/(BaA + Chr) (InP for indeno[1,2,3-cd]pyrene, BghiP for benzo[ghi]perylene, Flu

**Fig. 5.** Risk ranking of chemicals for different groups of species. (a) algae, (b) fish, (c) insects/spiders, (d) molluscs/crustaceans/invertebrates. X means not enough ecotoxic data available for this chemical.
for fluoranthene, Pyr for pyrene, An for anthracene, Phe for phenanthrene, BaA for benzo[a]anthracene and Chr for chrysene). The ratios, as well as their sources represented, varied in locations in these investigations, and even varied in sampling sites in individual campaign. For the rivers involved, biomass and coal combustion was the main source of PAHs in the rivers in the north of the Bohai Region such as the Dagu Drainage River (He et al., 2011), Yongdingxinhe River (Wang et al., 2015a) and Daliao River (Zheng et al., 2016). But in the south of the Bohai Region, the main source of PAHs was petroleum and its combustion in the watersheds such as the Yellow River (Wang et al., 2015a) and the Tuhai-Maja River (Liu et al., 2012). Previous studies on PAHs in the Bohai Rim indicated that their origin was a mix of combustion and petroleum production (Zhang et al., 2009; Jiao, 2012; Jiao et al., 2013). Rapid industrialization and urbanization in the Bohai Region increased the fossil fuel consumption due to power generation, heating supply, industrial and commercial activities and residents. In 2014, energy consumption in these four provinces was 932-milion-ton standard coal equivalent including coal, petroleum and natural gas (Hebei Government, 2015; Liaoning Statistical Bureau, 2015; Shandong Statistical Bureau, 2015; Tianjin Statistical Bureau, 2015), which amounted to 22% of the total energy consumption of China. In addition to biomass and coal combustion, the petroleum industry may also be a direct source of PAHs from oilfield operations such as in Shengli Oilfield, Jinzhou Oilfield and other oilfield drilling platforms in the Bohai Region.

3.5. Local source of pesticides

The compound p,p'-DDE is a degradation product of DDT, a pesticide which had been widely used globally. DDTs had been produced in China since the 1950s, and despite the official ban in 1983 the use of DDTs in agriculture had not been stopped until 2000 due to the use of pesticide dicofol with high impurity of DDTs.
compounds (Tao et al., 2007; Liu et al., 2008). The ratios such as (DDE + DDD)/DDTs, o,p′-DDT/p,p′-DDE were usually used to distinguish the sources of DDTs. These ratios indicated that the DDTs in the rivers were the legacy from historical production and use (Li et al., 2013; Gao et al., 2015), especially the use of the technical DDT before 1987 and the use of dicofol after 1987 in the Daling River (Wang et al., 2013).

Two types of HCHs had been used in China as pesticides, technical HCHs and lindane. Technical HCHs (18% of 1990s. The ratio \( \delta \)-HCH/\( \gamma \)-HCH was used from the 1950s to 1983, while lindane (99.9% of \( \gamma \)-HCH) in the 1990s. The ratio \( \alpha \)-HCH/\( \gamma \)-HCH indicated the historical use of both technical HCHs and lindane in the Haihe River and the Daling River (Li et al., 2013; Wang et al., 2013).

3.6. Local sources of flame retardants and per-fluorinated compounds

HBCDs are used as flame retardant in extruded/expanded polystyrene insulation boards, textile, and electric/electronic products. Due to the limited effect data for the individual isomers for \( \alpha \)-, \( \beta \)- and \( \gamma \)-HBCD, they were considered as a whole technical mixture. PFOS and PFOA, known as PFASs are widely used in polymer, surfactants, lubricants for their surface activity and heat/acid resistance. The biggest HBCD and PFASs manufacturers in China are located in the Bohai Rim and support the whole industrial chain in this region. Spatial analysis of PFASs levels in the samples taken from the rivers and producers indicated that the fluoropolymer industries along the Xiaoeqing River and the Daling River were the major sources of PFOA and PFOS in the rivers in the Bohai Region (Wang et al., 2014; Meng et al., 2015; Zhu et al., 2015). The spatial analysis and isomer ratio of \( \gamma \)-HBCD/\( \alpha \)-HBCD indicated that the manufacturing was the major source of HBCD in the environment (Li et al., 2012; Zhang et al., 2016). Extremely high levels of HBCD and PFASs in the world had been found in the environment in the Bohai Region due to their high production and use.

Of the other chemicals examined, endrin, heptachlor and HCB presented much lower risks. Endrin has not been produced in China and the production of heptachlor and HCB and their application in agriculture were banned in 1983.

3.7. Uncertainties and limitations of the study

This study can only be as strong as the existing monitoring and ecotoxicity data allows it to be. It may be that some other POPs, so far not measured, may have a much higher risk ranking to the compounds studied here. Similarly, a wider, more systematic monitoring programme may reveal higher concentrations for some chemicals in the Bohai Region than reported so far. The ecotoxicity database is driven by water exposure studies, yet most POPs measurements are not from the water column but from the river bed-sediments. It is necessary to predict the water concentration and the method used is most likely to several times overestimate, rather than underestimate, this concentration.

Finally, for some POPs the ecotoxicity database is still not as wide or complete as would be desirable. For traditional POPs such as \( \gamma \)-HCH and p,p′-DDE, abundant effects data could be found in EPA ECOTOX database. But for novel POPs such as HBCD and PFOS/PFOA, very limited ecotoxicity data was available, especially for individual HBCD isomers.

4. Conclusions

From this group of POPs, the PAHs congeners posed the greatest risk for aquatic wildlife in rivers around the Bohai Sea, followed by p,p′-DDE and \( \gamma \)-HCH. However, there was still more than 3-orders of magnitude distance between the median ecotox and median environmental concentrations suggesting the risks to wildlife through water exposure were not large, although the potential for these chemicals to bioconcentrate must be acknowledged. It was observed that there were locations where some water concentrations, for example for lindane, exceeded effect levels for some of the aquatic wildlife. The greatest impacts of POPs on wildlife would be expected in the Dagu Drainage River in Tianjin. The results suggest that regarding threats from POPs to the environment in the Bohai Region the greatest efforts should be in reducing fossil fuel combustion (to lower PAHs). The highly bioaccumulative metabolite of DDT, p,p′-DDE, was also flagged up as high risk but has now been controlled by the Government, so its environmental concentrations are expected to reduce in future. It was somewhat encouraging that some of the emerging POPs such as PFOS, PFOA and HBCD were not posing the highest risks.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.02.137.

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