

Swimming in Chemicals

Perfluorinated chemicals,
alkylphenols and metals in
fish from the upper, middle
and lower sections of the
Yangtze River, China



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Summary

For many years there has been growing concern over the manufacture and use of hazardous chemicals, and over the presence of many of these chemicals in the environment as a result of their release from industrial sources or from products that the chemicals have been used to manufacture.

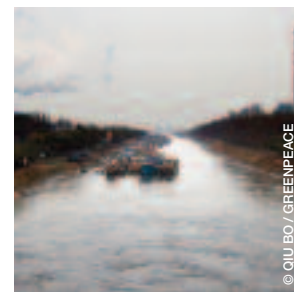
Some hazardous chemicals are highly persistent once released into the environment. They do not break down readily and can therefore remain as contaminants, sometimes far from where they were initially released, with the potential to cause harm over long periods of time. As a result of their continued production and use, many such chemicals have become widespread environmental contaminants. Furthermore, many are bioaccumulative, able to accumulate in the bodies of animals living in contaminated environments, and often pass along food chains.

Largely as a result of legislation, the manufacture and use of some of the most hazardous chemicals has greatly reduced in many countries and regions in recent years. However, the opposite trend is being seen in China for certain hazardous chemicals, where their manufacture and/or use has either continued largely unchanged or, in some instances, actually increased considerably in the last decade. For instance, while the manufacture and use of alkylphenols and perfluorinated chemicals has been greatly reduced in some other countries, there has been considerable recent growth in the amounts manufactured and used within China.

In addition to man-made organic chemicals, the use and release of metals can result in their presence in the environment at levels far exceeding natural background concentrations. This is of particular concern for metals that are highly toxic and able to bioaccumulate, with cadmium, lead and mercury being three such metals to have recently attracted attention. Within China, the production and use of lead and cadmium has increased in recent years, and China has become one of the largest producers and users of these metals, if not the largest. China also contributes a considerable fraction of total global atmospheric emissions of mercury, largely from metal smelting and the burning of coal.

This study was carried out to determine the concentrations of alkylphenols, perfluorinated chemicals and cadmium, lead and mercury in the tissues of wild fish collected from the Yangtze River in China, from January to March 2010. Information on these chemicals is given in the introduction of the main report, including information concerning their manufacture and use, their environmental distribution in fish and other organisms and the current status of regulation in some countries and regions.

A small fishing village in Jiangsu Province, downstream of the Yangtze River. Water and air in the area is severely polluted.



The Yangtze River, also known as the Chang Jiang ('Long River'), is the longest river in China, and the third longest river in the world. Samples of fish were collected from four locations along the course of the Yangtze River; Chongqing, Wuhan and Nanjing, the major cities on the upper, middle and lower sections of the Yangtze River respectively, as well as Ma'anshan, a large industrial city situated in the lower section between Wuhan and Nanjing. Two species of fish were included in the study, the southern catfish (*Silurus soldatovi meridionalis*) and the common carp (*Cyprinus carpio carpio*), both of which are widely distributed along the Yangtze River and are also commonly eaten in China. No catfish were collected from Ma'anshan, due to their scarce availability here during the sampling period. The concentrations of all chemicals were determined in the livers of the fish, and the concentrations of cadmium, lead and mercury were also determined in the fish muscle (flesh).

For the catfish, a single composite (pooled) liver sample of four fish from each location was analysed. However, due to difficulties in isolating the livers from some carp, individual livers from two of the four carp collected at each location were analysed, other than for the Wuhan carp, from which it was only possible to isolate the liver from one individual. Although the data provide average liver concentrations for a smaller number of carp compared to the catfish, they nonetheless do provide an indication of the extent to which liver concentrations vary between similar individual carp from the same location. A single composite (pooled) sample was also prepared from the muscle of four individuals collected from each location, for both carp and catfish, for the quantification of the metals.

Alkylphenols were detected in samples of both species from all sites. Nonylphenol (NP) was by far the most predominant alkylphenol present in all samples (constituting over 95% in all carp samples, and over 85% in all catfish samples). NP was detected in all but one liver sample, with concentrations in the range 9.20-85.0 µg/kg wet weight (ww) for individual carp livers, and 23.9-60.6 µg/kg ww for the composite catfish livers. 4-*tert*-octylphenol (t-OP) was detected in all but two liver samples, in the range 0.37-2.74 µg/kg ww (carp liver) and 1.98-3.37 µg/kg ww (composite catfish liver). In general, for fish of both species, liver samples from specimens collected at Wuhan and Nanjing contained higher NP and t-OP concentrations than those from the other locations.

Catfish from Nanjing contained the highest NP concentration, followed by catfish from Wuhan. In contrast, the Chongqing sample contained the highest t-OP concentration. Catfish was not collected from Ma'anshan. For carp, the sample from Wuhan had the highest NP concentration, followed by the Nanjing average. Carp from these two locations yielded very similar t-OP concentrations, higher than those from other locations. Carp collected at Ma'anshan contained the lowest concentrations of both NP and t-OP.

Overall, alkylphenol levels did not vary greatly between the three locations from where both species were collected, with the differences between the highest and lowest concentrations being 3 to 4 times for NP, and 2 to 3 times for t-OP. However, far lower levels of alkylphenols were found in carp collected at Ma'anshan, with average concentrations of NP and t-OP being 14 times and 7 times lower, respectively, than the highest carp levels from other locations.

The ranges of NP and t-OP concentrations found in this study are comparable with the ranges of concentrations previously reported for freshwater fish from other countries, including for common carp.

Perfluorinated chemicals (PFCs) were detected in all liver samples except for the carp collected from Chongqing. Where PFCs were detected, all samples contained perfluorooctanesulfonate acid (PFOS) and one or more longer-chain perfluorocarboxylic acids (PFCAs). PFOS accounted for between 45% and 99% of the total PFC concentrations (*i.e.* the sum of all PFC chemicals quantified in this study) in all liver samples for both species, with concentrations in the range 1.8-41.6 µg/kg ww (individual carp livers) and 18.4-39.7 µg/kg ww (composite catfish livers). Total PFCA concentrations were 0.45-9 µg/kg ww (individual carp livers) and 2.7-16.8 µg/kg ww (composite catfish livers), with perfluoroundecanoic acid (PFUnA) as the predominant PFCA in all but one sample.

The variation in PFOS concentrations between locations was similar to that seen for the alkylphenols, with the highest levels generally being found for samples from either Wuhan or Nanjing. For catfish, however, the Chongqing sample had the second highest PFOS concentration, being slightly higher than that from Nanjing.

A somewhat different pattern was found for PFCAs. The highest total PFCA concentrations were found in samples of both species from Nanjing, including the highest level recorded for catfish by far in this study. After Nanjing the next highest total PFCA concentrations were found in samples from Ma'anshan and Chongqing, for carp and catfish respectively. The variations between locations for individual PFCAs identified followed the same patterns as those for the total PFCAs concentrations for both species.

The ranges of PFC concentrations between different locations were generally broader than those for the alkylphenols, and were very different between the two fish species. For PFOS, the difference between the highest and lowest concentrations was 20 times for the carp, but only 2 times for the catfish. The total PFCA concentrations differed by 5.8 and 6.2 times between the highest and lowest levels for the carp and catfish respectively.

The range of PFOS concentrations found in this study is comparable with the ranges of levels for freshwater fish livers and carp blood and muscle reported in previous studies of fish in other countries. However, levels found in this study are towards the lower end of these ranges. The range of total PFCA levels found in this study is comparable with the ranges of levels reported in previously published studies for freshwater fish livers and carp muscle in other countries, though relatively few data are available in total for PFCAs.

Of the three metals, **cadmium, lead and mercury**, quantified in this study, all muscle (fillet) samples contained detectable levels of mercury, in the range 0.034-0.13 mg/kg for carp and 0.083-0.19 mg/kg for catfish. Cadmium and lead were below limits of quantification in all composite muscle samples except for in catfish collected at Nanjing, which contained 0.02 mg/kg cadmium. The mercury concentrations in catfish generally increased in samples collected along the Yangtze from upstream (Chongqing) to downstream (Nanjing) locations. A similar trend was apparent for mercury in carp, although carp from Nanjing had the lowest concentration among all carp samples.

None of the muscle samples contained concentrations of the three metals above their respective maximum allowed concentrations for fish intended to be used for human consumption in China, with the highest mercury concentration being less than half the applicable limit.

Mercury was detected in all but one liver samples, at concentrations in the ranges 0.008 to 0.052 mg/kg (carp livers) and 0.043 to 0.11 mg/kg (catfish livers). For both species, between the different locations, the variation of mercury concentrations in the livers followed similar patterns to those seen in the muscle samples. In all cases, higher mercury concentrations were found in muscle samples than in liver samples, by between 2-6 times for the carp, and 2-3 times for the catfish.

Cadmium was found in all catfish liver samples, at between 0.15 – 0.34 mg/kg, with the highest level in the sample from Nanjing. The levels in the catfish livers were by far the highest cadmium concentrations among all the samples (liver and muscle) analysed in this study. Cadmium was detected in just over half of the carp liver samples, with the highest concentration of 0.05 mg/kg, again in the sample from Nanjing. For comparative purposes, the maximum concentration of cadmium allowed in fish muscle intended to be used for human consumption in China is 0.1 mg/kg, although this limit is not directly applicable to fish livers. Unlike mercury, higher cadmium concentrations were found in the liver samples compared to muscle, by up to 15 times. Similar patterns between these organs have been reported for mercury and cadmium in other studies.

For both alkylphenols and PFCs, some relatively large differences were found in the liver concentrations between two individual carp with similar weights and lengths from the same location. For the alkylphenols, individual liver concentrations differed by up to 2.4 times for NP, and over 3.4 times for t-OP, while even larger differences were seen for PFCs for one location, with the PFOS and total PFCA concentrations differing by 11 times and 15 times respectively. Similarly for mercury and cadmium, individual liver concentrations differed by up to 4 and over 5 times respectively for similar carp from the same location. However, in some instances, liver concentrations between two individual from the same location differed to a lesser extent for all three groups of chemicals.

These differences highlight the potential for a relatively high degree of variability in concentrations for similar fish from a single location. Although limited, these data suggest that fish size may not be a primary factor influencing differences in liver concentrations, an observation that has been previously reported for alkylphenol and PFCs in fish tissues in other studies. Caution is therefore required in making any firm conclusions on the ranking of locations by the concentrations of alkylphenols, PFCs, cadmium or mercury in the fish livers, where the differences in concentrations between locations are relatively small. Because of this underlying specimen-to-specimen variation in contaminant concentrations, data for the composite catfish samples, prepared from 4 individuals, are likely to provide a better measure for comparison than the average carp values (from 1 or 2 individuals).

As a whole, and irrespective of any apparent trends along the course of the river, this study has demonstrated the widespread presence of certain hazardous chemicals within wild fish from the upper, middle and lower sections of the Yangtze River. The data not only provide information on the levels of the hazardous chemicals investigated within the bodies of the fish, but also provide an indication of the levels of exposure to the fish for these hazardous chemicals, and therefore of the extent to which the Yangtze River itself is contaminated at the locations investigated. Furthermore, although chemicals entering to the Yangtze River, either from point sources or due to diffuse inputs, will to some extent move along the river with the flow of water and sediments within it, this study also provides some indications of differences in the quantities and composition of the local sources of the substances investigated at the four locations.

Ongoing releases of hazardous chemicals to the Yangtze River, and further afield in China, are likely to lead to ever-increasing levels in the receiving environment, which are likely to persist for some time even after any controls on their release have been introduced. Although some regulations apply to the release of the three metals within China under certain circumstances, these do not prohibit all releases that derive from human activities. Furthermore, the manufacture, use and release of alkylphenols and PFCs are currently not specifically regulated within China and this situation also applies to the majority of other hazardous chemicals currently used and released within China.

There is an urgent need for the development of a more sustainable approach to the management of chemicals within China, including developing an understanding of the current uses of hazardous substances for as wide a range of substances as possible, as well as of their release to the aquatic and wider environment. Regulations seeking to address impacts arising from the release of hazardous chemicals into the environment, by setting either acceptable levels of release or acceptable levels in the receiving environment, are, however, unable to address the serious and potentially irreversible consequences arising from ongoing releases of persistent pollutants to the environment, particularly those able to bioaccumulate. The most effective measures to address hazardous substances are those that seek alternatives to their use in manufacturing processes, progressively replacing them with less hazardous and preferably non-hazardous alternatives, in order to bring about rapid reductions and ultimate cessation in their discharges, emissions and losses. This approach can lead to a more sustainable industry, eliminating both the waste of resources and the pervasive threats to the environment and human health which the ongoing use and release of hazardous chemicals entails.

Introduction

In recent years there has been growing concern over the manufacture and use of hazardous chemicals and their release into the environment. Some of these are man-made organic chemicals that are persistent (they do not break down readily in the environment), bioaccumulative (able to accumulate in organisms) and have toxic properties, including being capable of disrupting endocrine (hormone) systems. As a result of their persistent and bioaccumulative properties, following their release many hazardous organic chemicals can accumulate in the environment, including in the bodies of organisms. In addition, the use and release of toxic metals can result in their presence in the environment at levels that far exceed natural background concentrations.

For many hazardous chemicals it is difficult, if not impossible, to remove them, or control the risks they present, once they have been released into the environment. The more environmentally-persistent chemicals can cause harm over a long period of time and over wide areas, even far from their point of release and long after any controls have been introduced. As a result, many such chemicals have become widespread environmental contaminants. Furthermore, many cannot be contained or destroyed effectively using traditional 'end-of-pipe' measures to treat industrial wastes, such as biological wastewater treatment plants.

In the current study, we have investigated the levels of two groups of persistent, bioaccumulative organic chemicals - alkylphenols and perfluorinated chemicals - as well as three toxic metals - cadmium, lead and mercury - in the tissues of fish collected from the Yangtze River in China. The Yangtze River, also known as the Chang Jiang ('Long River'), is the longest river in China, and the third longest river in the world. Some previous studies have demonstrated the contamination of the Yangtze River with a range of hazardous chemicals, including heavy metals, and many of these studies are summarised below within the sections describing the relevant chemicals to this study.

Samples of fish were collected from four locations along the course of the Yangtze River. These included Chongqing, Wuhan and Nanjing, the major cities located in the upper, middle and lower sections of the Yangtze River, respectively. In addition, to extend the scope of the study, samples were also collected from the city of Ma'anshan, a relatively large industrial city situated in the lower section between Wuhan and Nanjing (Figure 1). Two species of fish were collected, the southern catfish (*Silurus soldatovi meridionalis*) and the common carp (*Cyprinus carpio carpio*), both of which are commonly eaten in China. Common carp has been widely used as a biomonitor for the evaluation of pollutants in aquatic ecosystems, in part due to its widespread distribution and also its use as a human food source in many countries (Ye *et al.* 2008).

Figure 1. Sketch maps showing the Yangtze River basin within China (left), and locations from which the fish were collected along the Yangtze River (right).





Information on the chemicals tested

This study involved the quantification of alkylphenols (APs), perfluorinated chemicals (PFCs) and three metals (cadmium, lead and mercury) in the livers of the fish, as well as the quantification of the metals in the fish muscle. Information on these groups of chemicals is summarised below.

Alkylphenols

Four alkylphenols were quantified in this study: nonylphenol (NP), 4-n-nonylphenol (n-NP), 4-*tert*-octylphenol (t-OP) and 4-n-octylphenol (n-OP).

Production and use

Alkylphenols (APs), which include nonylphenols (NP) and octylphenols (OP), are manufactured almost exclusively to produce alkylphenol ethoxylates (APEs), chemicals used as non-ionic surfactants. NPs are used to manufacture nonylphenol ethoxylates (NPEs). OPs are used to manufacture octylphenol ethoxylates (OPEs).

'Nonylphenol' and 'octylphenol' are themselves groups of related (isomeric) compounds. 4-nonylphenol is the main NP in use, while 4-*tert*-octylphenol (t-OP) is the most commercially important isomer of OP (OSPAR 2004b, 2006b). NPEs and OPEs are used as surfactants, emulsifiers, dispersants and wetting agents in a variety of industrial and consumer applications, including the manufacture of textiles. The largest amounts are used in industrial and institutional cleaning products (detergents), with smaller amounts used as emulsifiers, textile and leather finishers and as components of pesticide formulations and other agricultural products, as well as water-based paints (OSPAR 2004b & 2006b, Guenther *et al.* 2002). Within China, the production of APEs (primarily NPEs) was estimated to be about 50,000 tons in 1998 (Huang 1998), and the use of APEs (primarily NPEs) is also thought to have increased substantially in recent years (Feng 2005). Exact levels of current production and consumption are not known.

Following release to the environment, APEs can degrade back to the AP from which they were produced (NPE to NP, and OPE to OP), and these APs are persistent, bioaccumulative and toxic to aquatic life.

Environmental distribution

Both APEs and APs (especially NP and its derivatives) are widely distributed in fresh and marine waters, particularly in sediments, in which these persistent compounds accumulate (see e.g. Fu *et al.* 2008, Soares *et al.* 2008, Shue *et al.* 2009, David *et al.* 2009). Because of their releases to wastewaters, APEs and APs are also common components of sewage effluents and sludge (Micic & Hofmann 2009, Ying *et al.* 2009, Yu *et al.* 2009), including that applied to land. NP has also been detected in rain and snow in Europe (Fries & Püttmann 2004, Peters *et al.* 2008), while residues of both NP and OP have been reported as contaminants in house dust (Butte & Heinzow 2002, Rudel *et al.* 2003) and indoor air (Rudel *et al.* 2003, Saito *et al.* 2004). In China, NPs have been identified in river water and sediment in many areas, as well as drinking water derived from contaminated river waters (Shao *et al.* 2005, Xu *et al.* 2006, Yu *et al.* 2009), including Yangtze

River water and drinking water in the area of Chongqing (Shao *et al.* 2005), and in river water and sediment from the Yangtze River estuary, with concentrations at some locations in the Yangtze estuary exceeding those reported for the Rhine River estuary in the Netherlands and the Elbe estuary in Germany (Fu *et al.* 2008).

Both NP and OP are known to accumulate in the tissues of fish and other organisms, and to biomagnify through the food chain (OSPAR 2004 & 2006). Alkylphenols, particularly NP, have frequently been reported as contaminants in aquatic organisms, especially in fish, from many locations around the world, with significant levels in invertebrates and fish in the vicinity of sites of manufacture and/or use of APEs and close to sewer outfalls (Lye *et al.* 1999, Rice *et al.* 2003, Mayer *et al.* 2007). More recently, the presence of APs as contaminants in human tissues has also been reported (Lopez-Espinosa *et al.* 2008). Many of the previous reports of APs in freshwater fish from various countries are summarised in Table 5, in the results and discussion section below.

Hazards

Both NP and OP are known hormone-disrupting chemicals (endocrine disruptors) as a result of their estrogenic activity, *i.e.* their ability to mimic natural estrogen hormones. This can lead to altered sexual development in some organisms, most notably the feminisation of fish (Jobling *et al.* 1995, 1996). Atienzar *et al.* (2002) described direct effects of NP on DNA structure and function in barnacle larvae, a mechanism that may be responsible for the hormone disruption effects seen in whole organisms. In rodents, exposure to OP caused adverse effects on male and female reproductive systems, including lower sperm production and increased sperm abnormalities (Blake *et al.* 2004). Chitra *et al.* (2002) and Adeoya-Osiguwa *et al.* (2003) describe effects on mammalian sperm function, while DNA damage in human lymphocytes has also been documented (Harreus *et al.* 2002), although the significance of these findings has been challenged by some. Impacts on immune system cells *in vitro* have also been described (Iwata *et al.* 2004).

Regulation

The manufacture, use and release of APs, including NP and OP, are not currently regulated in China. However, in some other regions, such regulations do apply to these chemicals.

More than 10 years ago, the Ministerial Meeting under the OSPAR Convention agreed on the target of cessation of discharges, emissions and losses of hazardous substances to the marine environment of the north-east Atlantic by 2020, and included NP/NPEs on the first list of chemicals for priority action towards this target (OSPAR 1998). Subsequently, t-OP was also listed under this category in 2000 (OSPAR 2006b).

Since then, NP has been included as a 'priority hazardous substance' under the European Union (EU) Water Framework Directive, such that action to prevent releases to water will be required throughout Europe within 20 years of adoption of the regulation (EU 2001). In 2008, the Water Framework Directive was amended, laying down environmental quality standards (EQS) for a number of priority substances (EU 2008). Both NP and OP have been designated as a 'priority substance' by this Directive, which aims to combat the pollution of surface waters by 33 priority chemical substances. Already, however, the widely recognised environmental hazards presented by AP/APEs have led to some long-standing restrictions on their use in many countries. Of particular note in the European context is the Recommendation agreed by the Paris Commission (now part of the OSPAR Commission) in 1992, which required the phase-out of NPEs from domestic cleaning agents by 1995 and industrial cleaning agents by the year 2000 (PARCOM 1992). However, the precise extent to which this measure was effective is unclear.

The EU risk assessment for NP identified significant risks to the aquatic environment, to the soil and to higher organisms through secondary poisoning arising through numerous uses of NPEs (EU 2002b). According to Directive 2003/53/EC, after January 2005 products containing greater than 0.1% NP or NPEs may no longer be placed on the market within Europe, with some minor exceptions principally for 'closed-loop' industrial systems (EU 2003). At the same time, very little information exists regarding the ongoing uses of OP and its derivatives in consumer products within Europe.

Perfluorinated chemicals (PFCs)

A range of perfluorinated chemicals (PFCs) were quantified in this study, including:

- 5 perfluoroalkyl sulfonates (PFASs), including perfluorooctane sulfonate (PFOS)
- 11 perfluorinated carboxylic acids (PFCAs)
- 1 perfluorinated amide (PFA), perfluorooctane sulfonamide (PFOSA)

The group of PFCAs is commonly split into two subgroups; shorter chain PFCAs, *i.e.* those with a carbon chain length of 6-10 carbons,

and longer chain PFCAs, *i.e.* those with a carbon chain length of more than 11 carbons (Peng *et al.* 2010).

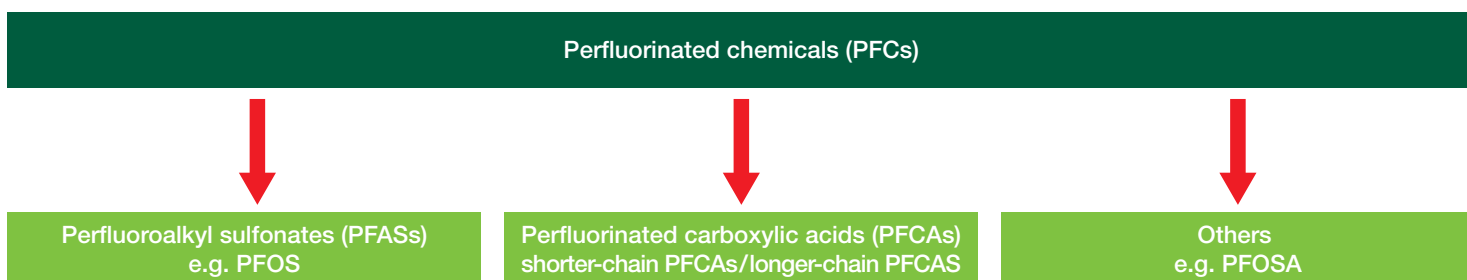
PFCs, their production and use

PFCs are man-made chemicals in which all the carbon-hydrogen bonds present in the organic chemical backbone have been replaced by carbon-fluorine bonds. These chemicals are not produced by natural processes and hence never occur in nature other than as a result of human activity. The direct chemical bond between carbon and fluorine is very strong, making it highly resistant to chemical, biological and thermal degradation (So *et al.* 2004). Many PFCs also have relatively low solubility in both water and oils, unique properties that have underpinned their development and widespread use as water, grease and stain-repellent finishes on textile and paper products, as well as for specialised solvents and surfactants used in industry and as components of cosmetics and plastic products (OECD 2002, Hekster *et al.* 2003). Their resistance to breakdown even at high temperatures has also led to their use in firefighting foams and in lubricants for high temperature applications (OSPAR 2006). However, the properties of this group of chemicals also result in one of their major environmental down-sides of PFCs, namely their long persistence in the environment once they are released, whether from manufacturing or disposal operations or during the useful lifetime of a product (Key *et al.* 1997).

The PFCs that have been manufactured over the past 60 years fall into four broad categories; PFASs, PFCAs, fluoropolymers (the best known being PTFE, marketed as Teflon and widely used for 'non-stick' cookware) and fluorotelomer alcohols (FTOH) (Dinglasan *et al.* 2004).

Until 2000, the most widely used PFASs globally were those based on PFOS. At that time, the annual production of all PFOS-related chemicals in the USA alone was 3,000 tonnes (Stock *et al.* 2004). Although there were a large number of different PFOS-related chemicals in use, designed to optimise specific properties conferred on different products, the majority share the common property of eventual degradation back to PFOS itself, a compound so resistant to further degradation that it is expected to persist for very long periods in the environment (Kannan *et al.* 2002a).

Since 2000, global production of PFOS and equivalent chemicals has



fallen sharply, and is currently estimated to be below 1,000 tonnes per annum (Paul *et al.* 2009). In contrast, production within China has increased in recent years. It has been reported that large-scale production of PFOS in China began in 2003, with total production before 2004 of 50 tonnes, increasing to over 200 tonnes per annum in 2006, of which approximately half was exported to the EU, Japan and Brazil (Bao *et al.* 2010).

Perfluorooctanoic acid (PFOA) is the most well-known of the PFCAs, being used as a polymerisation aid in the manufacture of the fluorinated polymer PTFE. It has been reported that PFOA is not currently manufactured in China, but is imported to produce PFC-related formulations (FECO/MEP 2009). Other than through deliberate production, PFOA (along with other shorter and longer-chain PFCAs) can also be generated as an unintended by-product in the manufacture of perfluorinated telomer alcohols, or FTOHs (Poulsen & Jensen 2005).

Environmental distribution

PFASs (especially PFOS) and PFCAs (especially PFOA) have been reported as contaminants in almost all environmental media, including freshwater, groundwater and seawater sediments and soils. Within China, PFCs including PFOS and PFOA have been reported in various environmental media including waters from many river systems (So *et al.* 2007, Jin *et al.* 2009, Lien 2007 cited in Kunacheva *et al.* 2009). A range of PFCs - particularly PFOA, but also PFOS and, to a lesser extent, PFOSA and some other PFCAs (including perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA) and perfluorodecanoic acid (PFDA)) - have been detected in river water from locations along the course of the Yangtze River, including at Chongqing, Nanjing and Shanghai, (So *et al.* 2007).

The highest concentrations were generally found in samples from near Shanghai, with samples from Chongqing being the second most contaminated. Others have reported the presence of PFOS and PFOA in all Yangtze River water samples collected in 2003 along the course of the river between Chongqing and Wuhan. In addition, PFOA, PFOS and other PFCs have been reported in the sediments of various rivers in China, including sediment collected from the Huangpu River, a tributary to the lower Yangtze River, which contained PFOA at levels higher than those generally reported in rivers worldwide (Bao *et al.* 2010). Sediments collected from the Yangtze River Estuary have yielded some of the highest PFOS concentrations ever recorded (Pan & You 2010). Furthermore, the presence of PFOS and PFOA has also been reported in tap water in many cities in China, including Chongqing, Wuhan and Nanjing. Some of the highest concentrations of PFOS and PFOA were found in tap waters from Shanghai, Wuhan and Nanjing on the Yangtze River, as well as in Guangzhou and Shenzhen on the Pearl River Delta (Jin *et al.* 2009, Mak *et al.* 2009).

Unlike many persistent organic pollutants, PFOS accumulates in the bodies of animals by binding to proteins in the blood, thereby building up to particularly high levels in liver tissue (Giesy & Kannan 2001,

Martin *et al.* 2003a, b). Numerous studies have reported the presence of PFCs in tissues of aquatic invertebrates, amphibians, fish, birds and mammals (from mice to far larger mammals including whales and polar bears) (Giesy & Kannan 2001, Houde *et al.* 2006). PFOS and PFOA have also been reported in red and giant pandas from zoos and wildlife parks within China (Dai *et al.* 2006). PFOS is generally the predominant PFC reported in the tissues analysed (Giesy & Kannan 2001, Kannan *et al.* 2005, Houde *et al.* 2006). PFOA and perfluorononanoic acid (PFNA) – or, occasionally perfluoro-n-undecanoic acid (PFUnDA) - have generally been the most abundant PFCAs reported in animal tissues, particularly in top predators (Martin *et al.* 2004, Smithwick *et al.* 2005). In the aquatic environment, PFCs have been reported in organisms at all levels of food webs (Houde *et al.* 2006). Many of the previous reports of PFCs in freshwater fish from various countries are summarised in Table 6, in the results and discussion section below.

Within China, PFOS, PFCAs and also PFOSA have been previously reported in the blood of fish, including in common carp and leather catfish from Gaobeidan Lake near Beijing (Li *et al.* 2008). PFOS and some PFCAs have also been reported in seafood from Zhoushan and Guangzhou (Gulkowska *et al.* 2006). A recent study also reported PFOS and other PFCs, including both short and long-chain PFCAs, in wild Chinese sturgeon captured from the Yangtze River (Peng *et al.* 2010). PFOS was the predominant PFC recorded in these studies, accounting for almost half the total PFC concentration in the sturgeon livers. While collection locations are not given, it should be kept in mind that sturgeon are diadromous fish (*i.e.* they migrate between the Yangtze and the marine environment).

Human exposure to perfluorinated chemicals

PFOS and other perfluorinated chemicals have been found in human blood and human breast milk sampled from people living in many countries around the world, even in remote areas such as the Canadian Arctic. PFOS is the most predominant PFC to be found in human blood, with PFOA often being the next most abundant (Kannan *et al.* 2004, Toms *et al.* 2009, Rylander *et al.* 2010, Dallaire *et al.* 2009).

In China, a study on people from nine different cities showed that PFOS was the dominant PFC detected in blood samples, with perfluorohexansulfonate (PFHxS) being the next most abundant (Yeung *et al.* 2006). Two other studies in China have also found PFCs in the blood of people from several different regions (Yeung *et al.* 2008 and Liu *et al.* 2009). In addition, other PFCs have been detected in human blood, including longer-chain PFCAs and PFOSA (Kannan *et al.* 2004, Yeung *et al.* 2008).

In the US, average concentrations of PFOS, PFOA and PFHxS in blood samples have reduced in recent years, which may be as a result of the discontinuation of industrial production of PFOS and related chemicals in the US in 2002 (Calafat *et al.* 2007). Conversely, in Shenyang, China, levels of PFOS and PFOA levels in human blood increased between 1987 and 2002 (Jin *et al.* 2007).

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PFOS has also been found to be the most abundant PFC in breast milk from women around the world. The level of PFOS, PFOA and PFHxS in breast milk samples from countries in Asia are reported to be at similar levels to those detected in Sweden, Germany and the United States (Tao *et al.* 2008). In China, PFOS and PFOA were the predominant PFCs found in breast milk samples taken from women from 12 provinces in 2007 (Liu *et al.* 2010). PFOS and PFOA have also been found in blood samples taken from the umbilical cord at birth, indicating the transfer of PFCs from the mother's blood across the placenta to the developing infant in the womb (Monroy *et al.* 2008, Tao *et al.* 2008).

Research shows that food intake is the major route for exposure to PFCs in the general population (Fromme *et al.* 2009, Vestergren and Cousins 2009, Zhang *et al.* 2010a), though additional exposure may occur in populations living near PFC production facilities (Fromme *et al.* 2009). Within China, PFOS and PFCAs have been reported in various foods (meat and eggs) (Zhang *et al.* 2010a), as well as in seafood from Zhoushan and Guangzhou (Gulkowska *et al.* 2006). It has been suggested that marine fish and other seafood may account for the majority of human exposure in China (Zhang *et al.* 2010).

Health impacts

Studies of laboratory animals indicate that PFCs can cause adverse impacts during development and during adulthood. PFOS and PFOA have both been reported to have adverse effects on the liver in rodents and monkeys (Kawashima *et al.* 1995, Adinezhadeh *et al.* 1999, Berthiaume & Wallace 2002, Lau *et al.* 2007). PFCs have also been shown to act as hormone (endocrine) disruptors (Jensen and Leffers 2008). Some examples of the effects PFCs have on endocrine systems include decreasing testosterone levels and increasing estradiol levels in adult rats, which can result in changes in the cells of the testis (Jensen and Leffers 2008), as well as the birth of offspring to laboratory rodents that were exposed to PFOS when pregnant that had changes in thyroid hormone levels and growth deficits (Lau *et al.* 2007, Yu *et al.* 2009). Studies have also investigated impacts of PFCs on the immune system, including the developing immune system of mice following prenatal exposure to PFOS (Keil *et al.* 2008) and on the immune system of adult laboratory rodents (Yang *et al.* 2002, Lau *et al.* 2007, DeWitt *et al.* 2008, Peden-Adams *et al.* 2008).

PFCs also appear to have impacts on the hormone system in humans. In the US, higher PFOA and PFOS concentrations in blood have been found to be associated with thyroid disease (and being on thyroid-related medication) in the general adult population (Melzer *et al.* 2010). High combined levels of PFOA and PFOS in men's blood in Denmark were found to be associated with having fewer normal sperm (Joensen *et al.* 2009). Furthermore, women in Denmark with higher blood levels of PFOA and PFOS took longer to become pregnant than those with lower levels (Fei *et al.* 2009). Elevated levels of PFC exposure may also affect foetal growth and development, though there are inconsistencies between different studies (Fei *et al.* 2008 & 2009, Olsen *et al.* 2009).

No consistent associations have been found between adverse health effects and the levels of PFCs in blood as a result of occupational exposure in the workplace (Lau *et al.* 2007). One study based on a limited number of cases did find a statistically significant increase in the number of deaths from bladder cancer in workers who were highly exposed to PFOS (Alexander *et al.* 2003); however, a subsequent update of the study offered "little support for an association between bladder cancer and PFOS exposure" (Alexander & Olsen 2007). The European Food Safety Authority has noted that "Epidemiological studies in PFOS exposed workers have not shown convincing evidence of increased cancer risk" (EFSA 2008). The possibility remains of a small increased risk in highly-exposed workers, but the limited size of the study population prohibits a conclusive answer. Regarding workplace exposure to PFOA, one study found a statistically significant link between prostate cancer and employment duration; however, an update to the study found no evidence of an increase in this and other types of cancer (Lau *et al.* 2007, DuPont 2006).

Regulation

Within China there are currently no regulations of the manufacture and use of PFOS, or other PFCs. However, PFOS has recently been included among the persistent organic pollutants (POPs) regulated under the Stockholm Convention, a global treaty to protect human health and the environment. Under the terms of the Convention, contracting parties must take measures to restrict the production and use of PFOS, although a wide range of uses are currently exempt, including uses in the semiconductor and photographic industries, metal plating operations, aviation hydraulics, fire-fighting foams, and certain pesticides (UNEP 2009).

The marketing and use of PFOS has been prohibited within the EU for certain uses since 2008, although many similar exemptions exist to those under the Stockholm Convention (EU 2006). The manufacture and use of PFOS has also been prohibited in Canada, though again with certain exemptions (CEPA 2008).

The above regulations do not apply to PFCAs and other PFCs. Furthermore, even when all uses are discontinued, the high persistence of PFOS and other PFCs will inevitably mean that they will continue to be environmental contaminants for a long period.



Metals: cadmium, lead and mercury

The metals quantified in this study (cadmium, lead and mercury) are found naturally at some level in uncontaminated environmental samples, such as sediments and surface waters, though generally at low concentrations. Inputs from point sources such as industrial discharges, as well as diffuse inputs including atmospheric deposition and run-off from land, can result in levels that far exceed natural background concentrations. A very wide range of levels of cadmium, lead and mercury has been reported in rivers and other surface water systems around the world, ranging from natural background concentrations to levels that far exceed them by many thousands of times (Salomons & Forstner 1984, ATSDR 1999, 2007, 2008).

For the middle and lower sections of the Yangtze River, from below the Three Gorges Dam to the river estuary, levels of dissolved cadmium, lead and mercury have recently been reported to be generally comparable with, or lower than, those found in other major rivers around the world. However, suspended particles in the river were found to contain levels of cadmium and particularly mercury above world river averages. Furthermore, markedly higher dissolved and particulate concentrations of cadmium, lead and mercury were found at certain locations along the Yangtze River (Müller *et al.* 2008).

Cadmium (Cd)

Cadmium is a rare metal, found naturally in the environment at very low concentrations (ATSDR 2008). When released to aquatic environments cadmium is generally more mobile than most other metals (ECB 2007). Cadmium has many uses, including within electrical and electronic products and rechargeable batteries, in pigments for glass and plastic, as stabilisers in polyvinyl chloride (PVC), in metal alloys and for metal plating processes (ATSDR 2008, Hawkins *et al.* 2006). In recent years China has become one of the major producers of cadmium metal, and also of portable nickel-cadmium batteries, the manufacture of which constitutes the largest use of cadmium globally (UNEP 2006a). Cadmium compounds are also present as trace components in bulk raw materials, including coal, and phosphate ores used to produce fertilisers. Use of these materials can result in substantial releases of cadmium to the environment, including to surface waters, through run-off from land and deposition of atmospheric cadmium emissions (OSPAR 2004a, Pacyna *et al.* 2009).

Cadmium has no known biochemical or nutritional function and is highly toxic to a wide range of life forms, including aquatic organisms. Effects on fish and aquatic invertebrates can occur at levels as low as 1 µg/L, with effects being dependent on other water quality factors including the presence of other pollutants (ECB 2007). In addition, many aquatic organisms can bioaccumulate cadmium from water and sediments (Ankley *et al.* 1994, ECB 2007).

Cadmium is also toxic to humans and can accumulate in the body over time, with exposure for the general population being primarily through diet. Long-term exposure can cause damage to the kidneys and bone structure (ECB 2007, Hellstrom *et al.* 2001). Other health effects from

cadmium exposure include the development of hypertension (high blood pressure) and heart disease. Recent studies have indicated impacts due to cumulative long-term low-level exposure (Satarug & Moore 2004). Cadmium and its compounds are known human carcinogens, effective primarily through inhalation of contaminated fumes and dusts (DHSS 2005).

Lead (Pb)

Lead is a metal that is found naturally in the environment, though usually at very low concentrations unless at locations affected by inputs from human activities (ATSDR 2007). Following release to the environment, lead generally has low mobility compared to other metals.

Lead and its compounds have many uses, including in batteries and electronics products, in metal alloys, pigments for glass and plastic, and as stabilisers in PVC formulations (ATSDR 2007, Matthews 1996). Historically, lead compounds have been used as an anti-knock additive in petrol, which has contributed to current levels of environmental contamination (Pacyna *et al.* 2009). In addition to inputs from point sources, run-off from land and deposition of lead emitted to the atmosphere (including from lead and other metal smelters, and the burning of coal) can act as diffuse sources of lead to surface waters (Liang *et al.* 2010, Pacyna *et al.* 2009). China is currently the world's major producer and user of lead, with consumption more than doubling between 1998 and 2005 (UNEP 2006b).

Lead is highly toxic to humans as well as many animals and plants, having no known biochemical or nutritional function (ATSDR 2007, Adams & Chapman 2006, WHO 1989). Levels can build up in the body through repeated exposure and lead can have irreversible effects on the nervous system. This is of particular concern for the developing nervous system in young humans, with impacts occurring even at very low levels of exposure. Other effects in humans include damage to the blood system, and impacts on the kidneys and on reproduction (ATSDR 2007, Jusko *et al.* 2008, Sanders *et al.* 2009). Some studies have indicated that there may be no safe level of exposure, particularly in the developing central nervous system in humans (Canfield *et al.* 2003). Similar toxic effects are seen in animals, including aquatic organisms (WHO 1989, Sadiq 1992).

Mercury (Hg)

Mercury is generally found in the environment at extremely low levels. Mercury and its compounds have been used in numerous products and industrial processes, including in batteries, thermometers and other measuring and control instruments, as well as in dentistry, a use which is known to contribute directly to municipal wastewater inputs (ATSDR 1999, Danish EPA 2004, UNEP 2002). The main industrial processes that employ mercury are the chlor-alkali mercury cell process, and the use of mercury compounds as catalysts in the manufacture of certain polymers, both of which are employed in China (ATSDR 1999, UNEP 2002, Liu 2006). In addition to point source

inputs to surface waters, run-off from land and the deposition of mercury emitted to the atmosphere (including from metal smelters, incineration, cement production and particularly from the burning of coal) can act as diffuse sources of mercury to surface waters (Streets *et al.* 2005, Pirrone *et al.* 2010).

Mercury and its compounds are highly toxic and have no known biochemical or nutritional function (UNEP 2002, Clarkson 2002). Following release to the environment, mercury can enter surface water bodies, either directly or following deposition, where it can be transformed into methyl mercury. Methylmercury is a highly toxic form that can bioaccumulate and biomagnify (progressively concentrate to high levels) in food chains, particularly in fish. Consumption of contaminated foods is the main route of exposure for the general public (UNEP 2002).

In humans, methylmercury can accumulate in the body and its main impact is damage to the nervous system. It can readily pass through the blood-brain barrier and also through the placental barrier, and can have adverse effects on the developing brain and central nervous system in children and fetuses, even at levels to which people are commonly exposed in some countries (Mahaffey *et al.* 2004, UNEP 2002). Recent research also indicates that exposure can increase cardiovascular and heart disease (Virtanen *et al.* 2005).

Regulation of cadmium, lead and mercury

Within China, the discharge of cadmium, lead and mercury in wastewater is regulated under the Integrated Wastewater Discharge

Standard (GB8978-1996), which sets maximum concentrations for these metals (MEP 1998). In other regions, cadmium, lead and mercury are covered under certain regional conventions, though China is not a contracting party to these. For example, the Aarhus Protocol on Heavy Metals, one of the eight protocols to the UNECE (United Nations Economic Commission for Europe) convention on Long-Range Transboundary Air Pollution (LRTAP), calls for contracting parties to the convention within the UNECE region to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. The Protocol includes specific provisions to reduce releases of cadmium, lead, and mercury, with the objective of cutting emissions from large, stationary sources, including industrial sources (e.g. iron and steel and non-ferrous metal production), combustion processes (e.g. power generation and road transport), and waste incineration (LRTAP 1998). In addition, the OSPAR and Helsinki Conventions also address releases of cadmium, lead and mercury to the marine environments of the north-east Atlantic and the Baltic Sea, respectively (OSPAR 1998). For mercury, the United Nations Environmental Protection Agency (UNEP) has recently initiated the Global Mercury Partnership, with the aim of protecting human health and the global environment from the release of mercury and its compounds by minimising and, where feasible, ultimately eliminating global anthropogenic mercury releases to air, water and land (UNEP 2009). Within Europe, cadmium, lead and mercury, and their compounds, have been selected as priority hazardous substances under the European Water Framework Directive, with the ultimate aim of the cessation of emissions, discharges and losses which derive from human activities into water (EU 2001).

Table 1. Collection dates and locations for the carp and catfish samples analysed.

City	Samples	Date	Location
Carp			
Chongqing	CQ1-4	19/01/2010	Mudong dock, 40km downstream of Chongqing
Wuhan	WH1-4	06/02/2010	Zhujiajiao river, a tributary to the Yangtze river, 16km downstream of central Wuhan
Ma'anshan	MAS1-4	12/03/2010	20km upstream of central Ma'anshan
Nanjing	NJ1-3	15-29/03/2010	Sanchahe gateway, central Nanjing
	NJ4	16/03/2010	Dadaohe catchment, 45km downstream of Nanjing
Catfish			
Chongqing	CQ5	19/01/2010	Mudong dock, 40km downstream of Chongqing
	CQ6-7	19/01/2010	Restaurant at Mudong dock selling locally caught fish from the Yangtze River in the vicinity of Mudong dock
	CQ8	19/01/2010	Tangjiatuo dock, Yangrenjie, 15km downstream of central Chongqing
Wuhan	WH5-8	06/02/2010	Near Tianxingzhou Bridge, 17km downstream of central Wuhan
Ma'anshan	-	-	-
Nanjing	NJ5-8	30/03/2010	Dadaohe catchment, 45km downstream of Nanjing

Sampling programme

From January to March 2010, samples of freshly caught common carp (*Cyprinus carpio carpio*) were obtained from four locations along the course of the Yangtze River (Chongqing, Wuhan, Ma'anshan and Nanjing), along with southern catfish (*Silurus soldatovi meridionalis*) from three of these locations (Chongqing, Wuhan and Nanjing). Due to the scarce availability of catfish in Ma'anshan during this period, it was not possible to collect this species from that location. A list of the collection locations and dates is given in Table 1, and the locations shown on a sketch map in Figure 1 (see page 6).

In all cases, the samples of freshly-caught fish were provided by local fishermen or retailers, who verified the precise catch locations. In order to avoid contamination or cross-contamination of the samples, the freshly-caught fish were wrapped individually in sheets of new, clean aluminium foil and placed inside transparent polyethylene bags. All samples were frozen as soon as possible after collection and stored in the dark. The frozen samples were transported by courier to the Greenpeace Research Laboratories, University of Exeter (UK), in insulated boxes packed with dry ice. All samples were verified as still being frozen on arrival at the laboratory, from which they were dispatched (again by courier) to an independent accredited laboratory in Germany for analysis.

Initially it was intended that a single composite (pooled) sample would be prepared from the livers of four individuals of each species for each of the

four locations, to be subsequently analysed for a range of substances; alkylphenols, PFOS and certain other PFCs, and for cadmium, lead and mercury. This approach was carried out for the catfish from each location. However, it was not possible to isolate the livers from all four individual carp collected at each location. As an alternative approach, livers were analysed individually from two carp collected from each location, with the exception of Wuhan, for which it was only possible to isolate the liver from one individual. Although this approach provides liver concentrations for a smaller number of carp from each location compared to the catfish, it does provide an indication of the extent to which liver concentrations vary between individual carp of similar weight and length collected from the same location.

In addition, a single composite (pooled) sample was prepared from the muscle of four individuals of each species collected from each location, for both carp and catfish. These composite samples were subsequently analysed for the three metals cadmium, lead and mercury.

A summary of the carp and catfish samples collected from each location, with the numbers of individuals in each composite sample prepared, their average lengths, total weights and muscle (edible flesh) weights is given in Table 2a. In addition, a summary of the carp samples from which individual liver samples were analysed, including their lengths and total weights, is given in Table 2b.

Table 2a. Sample codes and sample sizes (number of individuals in composite sample) for carp and catfish collected from each location, from which composite liver samples (catfish only) and composite fillet samples (carp and catfish) were prepared, including average lengths, total weights and muscle weights determined from individuals in each composite sample.

Location	Sample code (number in sample)	Average length, cm (range)	Average total weight, kg (range)	Average muscle weight, g (range)
Carp				
Chongqing	CQ1-4 (4)	46 (42-50)	1.60 (1.3-2.1)	391 (278-551)
Wuhan	WH1-4 (4)	53 (52-59)	2.13 (1.6-2.6)	640 (499-474)
Ma'anshan	MAS1-4 (4)	50 (49-52)	1.8 (1.7-2.0)	443 (360-521)
Nanjing	NJ1-4 (4)	42 (39-48)	1.15 (0.85-1.9)	333 (191-697)
Catfish				
Chongqing	CQ5-8 (4)	64 (61-66)	2.19 (1.9-2.6)	599 (513-664)
Wuhan	WH5-8 (4)	61 (46-73)	2.24 (1.0-3.9)	611 (250-1089)
Ma'anshan	-	-	-	-
Nanjing	NJ5-8 (4)	49 (46-52)	0.79 (0.70-0.85)	215 (182-244)

Analytical methods

Table 2b. Sample codes for carp collected from each location, from which individual liver samples were analysed, including lengths and total weights.

Location	Sample code	Length, cm	Total weight, kg
Chongqing	CQ2	40	1.3
	CQ3	39	1.5
Wuhan	WH4	47	1.6
Ma'anshan	MAS2	53	2.0
	MAS4	49	1.7
Nanjing	NJ2	40	0.85
	NJ3	39	1.0

Sample preparation

All fish were thawed, weighed and their lengths recorded. The fish were then gutted and the intact livers isolated. For catfish, the livers from all samples from each location were combined to obtain one composite sample. For carp, individual livers from specific fish were analysed separately. In addition, a composite muscle sample was prepared for each species from each location.

Sample analysis

For PFC and AP quantification, individual carp liver and pooled catfish liver samples were freeze-dried and subjected to ultrasonic extraction. All extracts were cleaned using hexane partitioning, followed by ENVI-Carb clean-up for PFC quantification, or trimethylsilyl derivatisation for AP quantification. Quantification of PFCs was carried out using high performance liquid chromatography-electrospray mass spectrometry (LC/ESI-MS-MS), and quantification of APs was carried out using gas chromatography-mass spectrometry (GC/MS). For the quantification of metals, freeze-dried homogenised samples underwent acid digestion, and the concentrations of cadmium and lead were determined in the sample extracts using inductively coupled plasma-mass spectrometry (ICP-MS). The concentrations of mercury were determined using cold vapour-atomic absorption spectroscopy (AAS). Full details of the methods employed in the preparation, extraction and analysis of the samples, along with quality assurance/quality control procedures, are provided in the Appendix.

Results and discussion

For both carp and catfish, the length of the individual fish increased with weight for each species (Figures 2a & b), though the relationship was somewhat less clear for the catfish, for which two distinct groupings of weights/length were apparent.

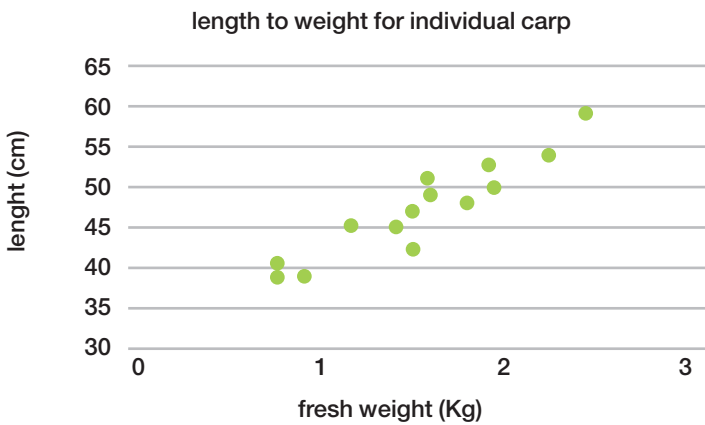


Figure 2a. Relationship of specimen length to specimen weight for all 16 carp individuals.

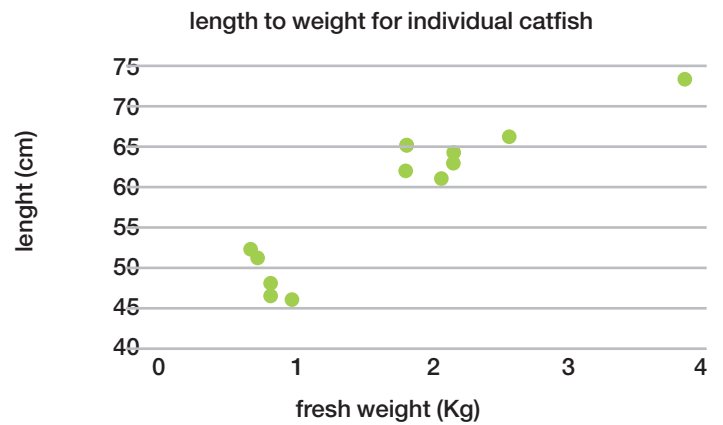


Figure 2b. Relationship of specimen length to specimen weight for all 12 catfish individuals.

The results of the analyses of the liver samples for alkylphenols, PFCs and the three metals are summarised in Table 3, and the results of the analyses of the muscle samples for the three metals are summarised in Table 4. All values are expressed as $\mu\text{g}/\text{kg}$ wet weight (ww) of liver (parts per billion, or ppb) for alkylphenols and PFCs, and as mg/kg ww of liver or muscle tissue (parts per million, or ppm) for the three metals; cadmium, lead and mercury.

For the liver samples, the dry residue percentage is also included (percentage of the mass of each sample remaining following freeze-drying), to enable comparison with data published on a dry-weight basis.

Liver samples

Table 3. Concentrations of alkylphenols ($\mu\text{g}/\text{kg}$ wet weight), perfluorinated substances ($\mu\text{g}/\text{kg}$ wet weight) and metals (mg/kg wet weight) in individual and composite liver samples.

Species	Carp						
Location	Chongqing			Wuhan	Ma'anshan		
Sample	CQ2	CQ3	CQav ^(b)	WH4	MAS2	MAS4	MASav ^(b)
Dry residue (%)	29.55	34.87	-	28.25	31.07	34.06	-
Alkylphenols ($\mu\text{g}/\text{kg}$)							
4-n-octylphenol (n-OP)	< 0.20	< 0.20	<0.20	< 0.20	< 0.20	< 0.20	< 0.20
4-tert-octylphenol (t-OP)	1.01	< 0.30	0.58	1.68	0.37	< 0.30	0.26
4-n-nonylphenol (n-NP)	< 0.20	< 0.20	<0.20	< 0.20	< 0.20	< 0.20	< 0.20
4-nonylphenol (NP)	19.0	27.4	23.2	85.0	9.20	< 5.0	5.9
Total alkylphenols	20.01	27.4	23.78	86.68	9.57	-	6.16
Perfluorinated chemicals ($\mu\text{g}/\text{kg}$)							
Perfluorooctane sulfonate (PFOS)	< 0.3	< 0.3	< 0.3	41.6	2.3	1.8	2.1
Perfluorooctanoic acid (PFOA)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Perfluorononanoic acid (PFNA)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Perfluorodecanoic acid (PFDA)	< 0.3	< 0.3	< 0.3	< 0.3	0.8	0.4	0.6
Perfluoroundecanoic acid (PFUnA)	< 0.3	< 0.3	< 0.3	0.6	1.0	0.8	0.9
Perfluorododecanoic acid (PFDoA)	< 0.3	< 0.3	< 0.3	< 0.3	0.3	< 0.3	< 0.3
Perfluorotridecanoic acid (PFTrA)	< 0.3	< 0.3	< 0.3	< 0.4	0.7	< 0.3	0.4
Total PFCAs	ND	ND	ND	0.6	2.8	1.2	1.9
Total PFC chemicals	ND	ND	ND	42.2	5.1	3.0	4.1
Metals (mg/kg)							
Cadmium (Cd)	0.01	<0.01	<0.01	0.02	0.01	<0.01	<0.01
Lead (Pb)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mercury (Hg)	0.009	<0.005	0.006	0.011	0.052	0.013	0.033

< indicates concentrations below the limit of quantification (LOQ).

ND – not determined as no congeners were above the LOQ.

(a) Composite sample.

(b) Average. Where individual values are below the LOQ, the average is calculated using half the LOQ.

(c) Maximum level allowed in fish muscle for consumption in China; the mercury limit is defined for methyl mercury (MHPRC 2005).

			Catfish			Fish muscle limit ^(c)	
Nanjing			Chong-qing	Wuhan	Ma'an-shan	Nanjing	
NJ2	NJ3	NJav ^(b)	CQ5-8 ^(a)	WH5-8 ^(a)	-	NJ5-8 ^(a)	
25.36	32.94	-	24.82	26.12	-	26.97	
< 0.20	< 0.20	<0.20	< 0.20	< 0.20	-	< 0.20	
2.74	0.85	1.80	3.37	2.67	-	1.98	
< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	-	< 0.20	
48.4	20.0	34.2	23.9	31.7	-	60.6	
51.14	20.85	36.00	27.27	34.37	-	62.58	
51.3	4.5	27.9	21.5	39.7	-	18.4	
< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	-	< 0.3	
0.9	< 0.3	0.5	< 0.3	< 0.3	-	< 0.3	
1.9	< 0.3	1.0	1.4	0.9	-	6.1	
1.5	0.4	1.0	2.2	1.8	-	7.1	
0.6	< 0.3	0.4	0.3	< 0.4	-	2.1	
1.0	< 0.4	0.6	0.7	< 0.4	-	1.5	
5.9	0.4	3.5	4.6	2.7	-	16.8	
57.2	4.8	31.0	26.1	42.4	-	35.3	
<0.01	0.05	0.03	0.15	0.15	-	0.34	0.1
<0.05	<0.05	<0.05	0.05	<0.05	-	0.07	0.5
0.02	0.008	0.014	0.046	0.043	-	0.11	0.5

Swimming in Chemicals

Perfluorinated chemicals, alkylphenols and metals in fish from the upper, middle and lower sections of the Yangtze River, China

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A photograph showing a riverbank. On the left, there are several large, grey, cylindrical cooling towers of an industrial plant, with white steam rising from them. The sky is overcast with grey clouds. In the foreground, there is a sandy bank with some sparse vegetation. On the right side of the river, a fishing village is visible, with many small boats docked along the shore. The water is calm and reflects the sky.

In 2008, the Yangtze River received more than 21 billion tonnes of water waste

There are 50 houses in the fishing village of Yanglingang in Jiangsu Province. Following the establishment since 2002 of chemical plants, power plants and paper mills in the area, water and air has become severely polluted.



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Catfish collected in Wuhan City, Hubei Province.



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Fishing season lasts from March to April in Jiangsu Province.



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Wuhan, Hubei Province. A rich selection of fish at a vegetable market.

Swimming in Chemicals

Perfluorinated chemicals, alkylphenols and metals in fish from the upper, middle and lower sections of the Yangtze River, China

Fillet Samples

None of the other PFCs included in this study were found in any of the samples at levels that could be quantified, including the perfluorocarboxylic acids PFBA, PFPeA, PFHxA, PFBA, PFHpA, PFOA and PFTA, the perfluorosulfonates PFBS, PFHxS, PFHpS and PFDS, and also the perfluorosulfonamide PFOSA. These chemicals are, therefore, not listed in Table 3.

Table 4. Concentrations of cadmium, lead and mercury in composite muscle (fillet) samples, in mg/kg wet weight.

Species	Carp				Catfish				Fish muscle limit ^(a)
	Chongqing	Wuhan	Ma'anshan	Nanjing	Chongqing	Wuhan	Ma'anshan	Nanjing	
Location	Chongqing	Wuhan	Ma'anshan	Nanjing	Chongqing	Wuhan	Ma'anshan	Nanjing	
Sample	CQ1-4	WH1-4	MAS1-4	NJ1-4	CQ5-8	WH5-8	-	NJ5-8	
Cadmium	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.02	0.1
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-	<0.05	0.5
Mercury	0.037	0.053	0.13	0.034	0.083	0.12	-	0.19	0.5

< indicates concentrations below the limit of quantification (LOQ).

(a) Maximum level allowed in fish muscle for consumption in China; the mercury limit is defined for methyl mercury (MHPRC 2005).



Sampling of a common carp in Ma'anshan City, Anhui Province.

Alkylphenols

APs were detected in samples of both species from all sites. NP was detected in all liver samples, other than for one carp liver from Ma'anshan (MAS4), at concentrations in the range 9.20-85.0 µg/kg ww (individual carp livers) and 23.9-60.6 µg/kg ww (composite catfish livers). In addition, t-OP was detected in all but one liver sample (CQ2, Chongqing), though at lower concentrations than NP in all samples (0.37-2.74 µg/kg ww for carp livers and 1.98-3.37 µg/kg ww for composite catfish livers). The concentrations of NP and t-OP for all locations are presented in Figure 3. The predominance of NPs over OPs seen in the fish livers has been commonly reported in other studies (see Table 5). The other two APs that were included in this study (4-n-nonylphenol and 4-n-octylphenol) were not found in any of the samples at levels which could be quantified (<0.20 µg/kg ww).

As a consequence of NP being by far the most predominant alkylphenol present in all samples (over 95% in all carp samples, and over 85% in all catfish samples), the relationships between the total concentrations of APs and the collection locations were the same as those for the NP concentrations, which are discussed below.

Among the composite catfish liver samples, the sample from fish collected at Nanjing contained the highest NP concentration, followed by the Wuhan sample, with the lowest NP concentrations in the Chongqing sample. No catfish were collected from Ma'anshan. For t-OP, present at far lower levels in all samples, the opposite pattern was observed, with the highest concentration in the Chongqing sample, and the lowest in that from Nanjing. The range of composite catfish liver concentrations was not large; the highest NP concentration was 2.5 times higher than the lowest level, while for t-OP, the highest concentration was 1.7 times the lowest level.

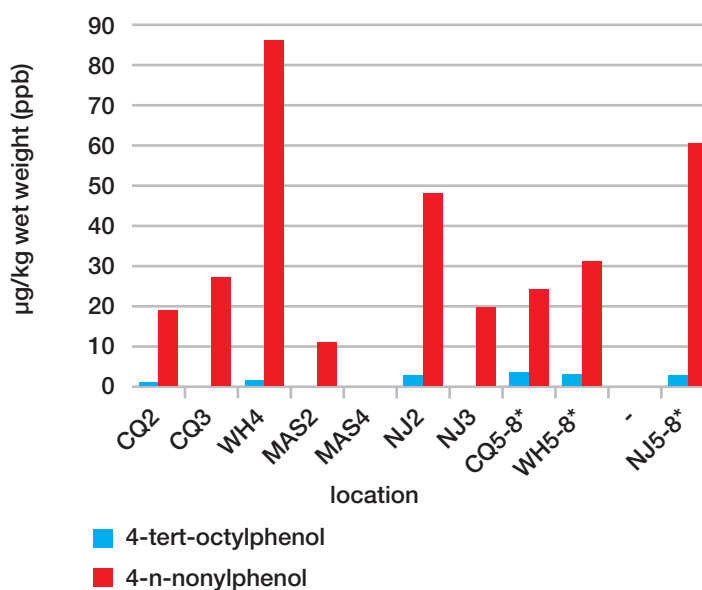
The lowest average concentrations of both NP and t-OP were found in the liver samples from carp collected at Ma'anshan. No catfish were collected from this location to enable comparison between species for this location. Comparing average carp liver concentrations for the three other locations (Chongqing, Wuhan and Nanjing), carp from Wuhan had the highest average NP concentration (85.0 µg/kg ww), followed by those from Nanjing (34.2 µg/kg ww). For t-OP, carp from Nanjing (1.80 µg/kg ww) and Wuhan (1.68 µg/kg ww) had similar average concentrations, considerably higher than average concentrations for the other two sites.

For these three locations, the lowest average concentrations of both NP and t-OP were found for carp collected at Chongqing. The lowest catfish liver concentration of NP was also found in the Chongqing sample. The NP concentrations were almost identical for the two fish species from Chongqing; 23.2 and 23.9 µg/kg ww for the carp (average) and catfish respectively. However, the t-OP liver concentration was considerably lower for the carp from Chongqing compared to the catfish.

The range of average carp liver concentrations was slightly broader than that for catfish. The highest NP concentration, in the sample from Wuhan, was 3.7 times the average level for Chongqing. The t-OP concentrations for Nanjing and Wuhan were both approximately 3 times the level for Chongqing. While no catfish were available from Ma'anshan to enable comparisons, the highest NP liver concentration for carp (from Wuhan) was 14 times higher than the average concentration for Ma'anshan. Similarly, the highest average t-OP carp liver concentration (from Nanjing) was 7 times higher than the average concentration for Ma'anshan.

Figure 3. Concentrations of alkylphenols detected in individual carp, and composite catfish (*) liver samples, by location from which the fish were collected (CQ-Chongqing; WH-Wuhan; MAS-Ma'anshan & NJ-Nanjing).

Concentrations of alkylphenols in liver samples



A summary of previously reported data for levels of alkylphenols in freshwater fish tissues is summarised in Table 5 below. The range of NP concentrations in this study are comparable with the ranges of concentrations previously reported for freshwater fish from other countries, including common carp. Far fewer data have been previously published for OP, though again the range of concentrations found in this study are comparable with previous levels where OP has been detected. Some studies have not detected OP in fish tissue, though for these the detection limits were above the levels of t-OP found in this study, and in other previously reported data (Lee *et al.* 1999).

Table 5. Concentrations of alkylphenols reported in studies of fish from many countries. All reported values have been converted to µg/kg wet weight (ww) for comparison.

Species	Location	Year	Tissue	AP	Concentration (µg/kg ww)	Source
Common carp (<i>n</i> = 7)	China, Yangtze River	2010	liver	NP	5.9-85*	This study
			liver	OP	0.58-1.80*	
Southern catfish (<i>n</i> = 12)			liver	NP	23.9-60.6*	
			liver	OP	1.98-3.37*	
Chub; roach; gudgeon (<i>n</i> = 5)	UK, River Ayre	1995	muscle	NP	200; 600; 800*	Blackburn <i>et al.</i> 1999
			muscle	OP	<100*	
Mature flounder (<i>n</i> = 6)	UK, Tyne estuary	1997	liver	NP	nd-30	Lye <i>et al.</i> 1999
Juvenile flounder (<i>n</i> = 11)	UK, Tees estuaries		whole	NP	nd-180	
			whole	OP	nd-7	
7 species (<i>n</i> = 183), including; Bluegill sunfish (<i>n</i> = 36) Smallmouth bass (<i>n</i> = 27) White sucker (<i>n</i> = 60) Rock bass (<i>n</i> = 49)	USA, Michigan	1999	digestive / excretory system	NP	4.0* (<3.3-29.1)	Keith <i>et al.</i> 2001
				NP	5.7 ± 5.2*	
				NP	5.8 ± 5.2*	
				NP	7.2 ± 5.2*	
				NP	8.1 ± 5.38	
Common carp (<i>n</i> = 1)	USA, Nevada	1999	centered cross-section	NP	184	Snyder <i>et al.</i> 2001
Common carp (<i>n</i> = 79)	USA, Ohio	2000	whole	NP	7-110*	Rice <i>et al.</i> 2003
Common carp (<i>n</i> = 8)			whole	OP	<20*	
Lake trout (<i>n</i> = 3)	USA, Great Lakes	-	whole	NP	248-1842	Datta <i>et al.</i> 2003
Coreius heterodon (<i>n</i> = ?)	China, Chongqing	2001	liver	NP	800	Shao <i>et al.</i> 2005
Rhinogobio ventralis (<i>n</i> = ?)			liver	NP	1900	
Goldfish <i>carassius auratus</i> (<i>n</i> = 12)	China	2001	muscle	NP	30-1510*	Jin <i>et al.</i> 2004

* indicates mean value or composite sample.

The data for individual carp livers provides an indication of the variation in concentrations between similar individuals from the sample location (see Table 2b). Where individual samples were quantified (for carp livers), the highest and lowest values for each location differ by up to 2.4 times for NP (NJ2 & NJ3), and over 3.4 times for t-OP (CQ2 & CQ3), highlighting the potential for a relatively high degree of variability in similar fish from a single location. Notwithstanding the small sample size in the current study, the size of the fish does not appear to have been a major factor influencing differences in NP and t-OP liver concentrations, an observation that has been previously reported for NP in fish tissues (whole carp) (Mitchellmore & Rice 2006).

Caution is therefore required in making any firm conclusions on the ranking of locations by the alkylphenol concentrations, where the differences in concentrations between locations are relatively small. This may be particularly the case for t-OP, for which the range of concentrations across the four locations was narrower than that of NP. The composite catfish data are average values for 4 individuals (as opposed to 1 or 2 individuals for carp), and therefore these may provide a better measure for comparison of AP levels between different locations.

Perfluorinated chemicals

PFOS and certain PFCAs were detected in all liver samples, other than from the two carp collected from Chongqing. PFOS was the predominant PFC present in all liver samples for both species, at concentrations in the range 1.8-41.6 µg/kg ww (individual carp livers) and 18.4-39.7 µg/kg ww (composite catfish livers), and accounting for between 45% and 99% of the total PFC concentrations.

In addition to PFOS, the other PFCs identified were longer-chain PFCAs. Total PFC concentrations were 0.45-9 µg/kg ww (individual carp livers) and 2.7-16.8 µg/kg ww (composite catfish livers). The predominant PFC in all but one sample was perfluoroundecanoic acid (PFUnA), which was detected in all PFC containing samples at 0.4-1.5 µg/kg ww (individual carp livers) and 1.8-7.1 µg/kg ww (composite catfish livers). The other PFCAs that were detected in many of these samples, in the same order of abundance for all but one sample, were PFDA, perfluorotridecane acid (PFTrA) and perfluorododecane acid (PFDoA). In addition, PFNA was detected in one sample, a carp liver from Nanjing.

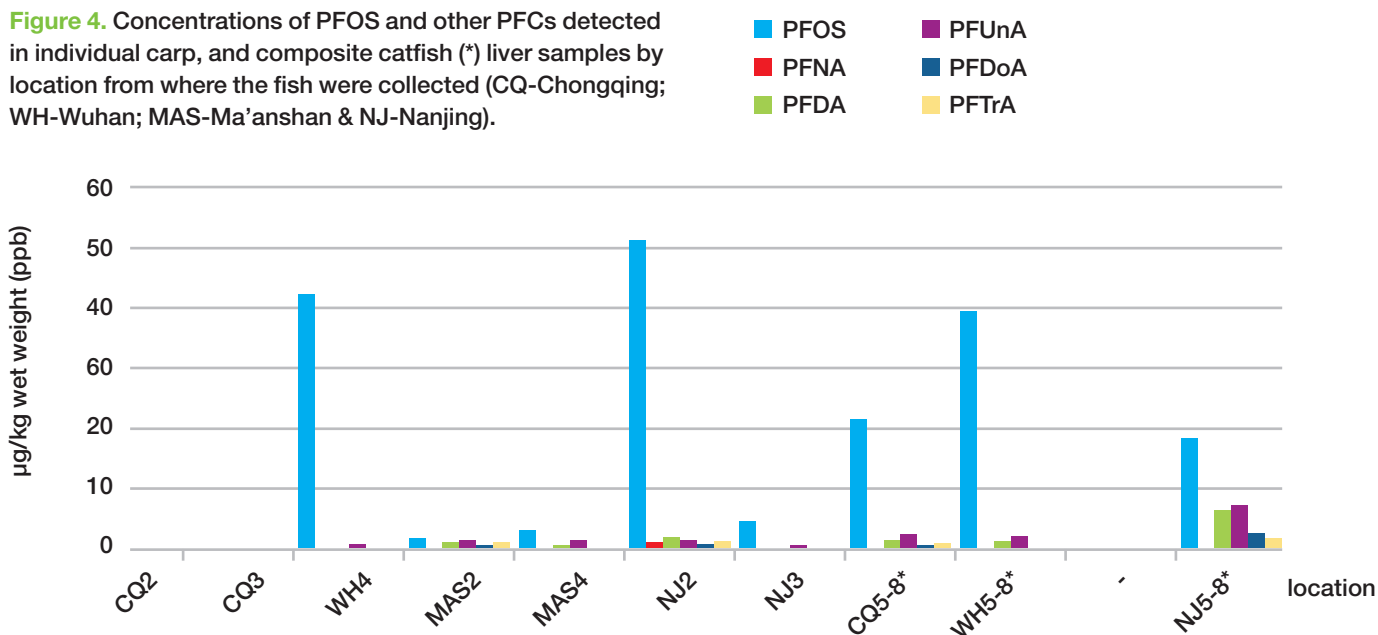
Similar distribution patterns of PFCAs have been previously reported in fish tissues from many locations, including carp muscle (Martin *et al.* 2004, Ye *et al.* 2008). The only previous study of fish collected from the Yangtze River (17-23 year old Chinese sturgeon) also found that PFOS and longer-chained PFCAs were the predominant PFCs in livers and other organs, though the relative contribution by some longer chained PFCAs were greater in the sturgeon, most likely due to their considerably higher age than the fish in this study (Peng *et al.* 2009, Martin *et al.* 2003).

In a similar way as to how NP dominated the total concentrations of APs, PFOS dominated the total concentrations of PFCs in the carp livers, and therefore the relationships between carp collection locations and the total concentrations of PFC were identical to the relationships with PFOS concentrations, as discussed below. This, however, was not the case for the catfish livers, due to the presence of certain PFCAs at appreciable concentrations, particularly in the composite sample from Nanjing (NJ5-8), as shown in Figure 4.

For PFOS, the variation in concentrations between locations was similar to that seen for the APs, with the highest levels generally being found for samples from Wuhan or Nanjing. The highest PFOS values were found for samples from Wuhan for both carp and catfish, with very similar levels for both species (41.6 µg/kg ww average for carp; 39.7 µg/kg ww for catfish). Similarly, the highest total PFC concentrations for both species were for samples from Wuhan (42.2 µg/kg ww average for carp; 42.4 µg/kg ww for catfish). However, one individual carp sample from Nanjing (NJ2) contained the highest PFOS and total PFC levels for all individual carp livers (51.3 µg/kg ww and 57.2 µg/kg ww respectively). As for Wuhan, the PFOS concentrations for samples from Nanjing were reasonably similar between the two species (27.9 µg/kg ww average for carp; 18.4 µg/kg ww for catfish).

Among the carp, the Nanjing samples had the second highest average concentration, with a far lower level for Ma'anshan (2.1 µg/kg ww). No PFOS was detected in the Chongqing samples. In contrast, the catfish from Chongqing had the second highest PFOS concentration, slightly higher than that for Nanjing (23.9 µg/kg ww).

Figure 4. Concentrations of PFOS and other PFCs detected in individual carp, and composite catfish (*) liver samples by location from where the fish were collected (CQ-Chongqing; WH-Wuhan; MAS-Ma'anshan & NJ-Nanjing).



For the PFCAs, a somewhat different pattern was found for the variation in concentrations between locations. For both species, the highest total PFCA concentration was found at Nanjing (3.5 µg/kg ww average for carp; 16.8 µg/kg ww for catfish). The Nanjing catfish had by far the highest total PFCA concentration found in this study. The highest individual carp level was also found in one sample from Nanjing (NJ2; 5.9 µg/kg ww). For carp, Ma'anshan had the second highest average total PFCA concentration, followed by Wuhan, with no PFCAs detected in carp from Chongqing. In contrast, the catfish from Chongqing had the second highest concentration followed by Wuhan. No catfish were collected from Ma'anshan.

For each of the individual PFCAs identified (PFUnA, PFDA, PFTrA, PFDoA, PFNA), the variation in concentrations by location followed the same patterns as the total PFCAs concentrations for both species, as described above. The highest concentration for each of these PFCAs was found in the composite catfish sample from Nanjing, other than PFNA which was only detected in one carp sample from Nanjing (NJ2).

The range of PFOS concentrations between locations was very different for the two species. For carp, the highest average level (Wuhan) was 20 times that of the lowest average level (Ma'anshan), while for the composite catfish samples, the highest level (Wuhan) was only 1.8 times the lowest (Chongqing). The range of total PFCA concentrations was similar for both species, with the highest levels (Nanjing for both) being 5.8 (carp) and 6.2 (catfish) times higher than the respective lowest levels (Wuhan for both).

As seen for the APs, there was no clear trend for which species had greater concentrations of PFCs for each of the locations. The catfish concentrations of PFCAs were considerably higher than the average carp concentrations for all locations. However, the pattern for PFOS is less clear, with the average carp concentrations being slightly higher for Wuhan and Nanjing, though far lower for Chongqing.

In some cases there were large differences between PFC concentrations for individual carp livers from the same location. For Ma'anshan, where only low levels of PFCs were found, the two individuals had similar concentrations of PFOS and PFCAs, differing by no more than 2 times. However, for Nanjing there was a very large difference in PFC concentrations between the two individuals, with the PFOS and total PFCA values differing by 11 times and 15 times respectively for fish with very similar weights and lengths (see Table 2b). No PFCs were detected in either sample from Chongqing.

The reasons for the large differences between the two individuals from Nanjing are not clear. As noted for APs, these data, although limited, highlight the potentially high degree of variability in similar fish from a single location. This in turn suggests that the size of the fish may not be a major factor influencing PFC liver concentrations. Previous studies have reported similar variations in concentrations of PFOS and PFCAs in both liver and blood between individual common carp collected from a single location (Hoff *et al.* 2005, Ye *et al.* 2008), with one study reporting that fish weight was not a significant factor in the concentrations of PFOS and PFCAs in carp muscle (Ye *et al.* 2008). A similar observation was reported for PFOS and shorter-chain PFCAs in Chinese sturgeon, although increasing levels of longer-chain PFCAs with age were reported, the latter being attributed to the relatively high age of the sturgeon (17-23 years) (Peng *et al.* 2010).

Therefore, as for the APs, caution is required in making any firm conclusions on the ranking of locations by the PFC concentrations where the differences are relatively small between locations. As mentioned above, the composite catfish samples prepared from four individuals are likely to provide a better measure for comparison of PFC levels between different locations than the average carp values.

For comparison, a summary of previously reported data for PFOS and PFCAs in freshwater fish tissues is summarised in Table 6 below. The levels of PFOS in this study are comparable with the range of levels for freshwater fish livers, and carp blood and muscle, reported in studies of fish from other countries, though levels found in this study are towards the lower end of the range. Considerably higher PFOS concentrations have been reported in some studies; in the livers of bluegill and largemouth bass from Lake Biwa in Japan and New York State in the US; however these species are carnivorous fish (Taniyasu *et al.* 2003, Sinclair *et al.* 2006). Higher concentrations have also been reported in European eel livers (Santillo *et al.* 2006), although in that study, samples from half the locations across Europe contained levels below 40 µg/kg ww.

Fewer data are available for a range of PFCAs, though again the total PFCA levels found in this study are comparable with the range of levels reported for freshwater fish livers and carp muscle from other countries. As for PFOS, higher concentrations of PFCAs have been reported in European eels, though PFCAs were not detected in composite samples from the majority of the locations across Europe (Santillo *et al.* 2006).



Table 6. Concentrations of PFOS, total PFCAs (Σ PFCA), and PFOSA in studies of fish from many countries. All reported values have been converted to $\mu\text{g}/\text{kg}$ wet weight (ww) for comparison.

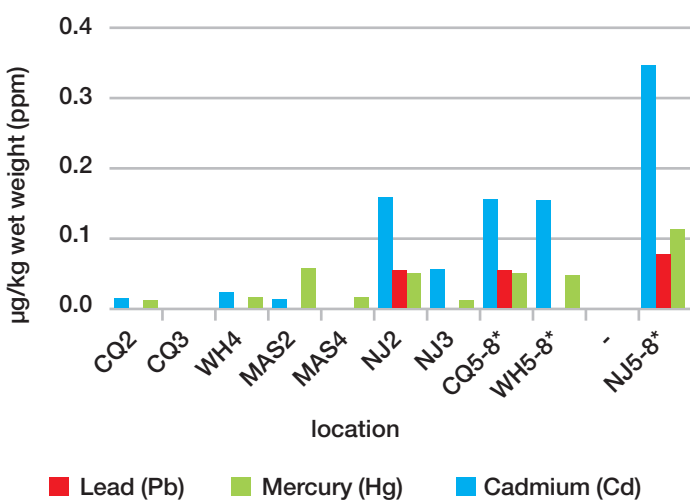
Species	Location	Year	Tissue	PFC	Concentration ($\mu\text{g}/\text{kg}$ ww)	Source
Common carp ($n=7$)	China, Yangtze River	2010	liver	PFOS	< 0.3-41.6*	This study
			liver	Σ PFCA		
Southern catfish ($n=12$)			liver	PFOS	18.4-39.7*	
			liver	Σ PFCA	4.6-16.8*	
Bluegill ($n=2$)	Japan, Lake Biwa	2002	liver	PFOS	282*	Taniyasu <i>et al.</i> 2003
Largemouth bass ($n=2$)			liver	PFOS	34*	
White sucker ($n=3$)	Canadian arctic lakes	2002	liver	PFOS	7.6* (6.5-8.6)	Martin <i>et al.</i> 2004
			liver	Σ PFCA	15*	
Brook trout ($n=2$)			liver	PFOS	39* (29-50)	
			liver	Σ PFCA	18*	
Lake whitefish ($n=2$)			liver	PFOS	12* (12)	
			liver	Σ PFCA	17*	
Chinook salmon ($n=6$)	USA, Great Lakes	1999-	liver	PFOS	100* (32-173)	Kannan <i>et al.</i> 2005
Lake whitefish ($n=5$)		2000	liver	PFOS	67* (33-81)	
Carp ($n=10$)			muscle	PFOS	124* (59-297)	
Smallmouth bass ($n=28$)	USA, New York State	2001-	liver	PFOS	22-93*	Sinclair <i>et al.</i> 2006
Largemouth bass ($n=38$)		2003	liver	PFOS	16-282*	
European eel ($n=2-5$)	EU, 11 countries	2005	liver	PFOS	<16 – 498*	Santillo <i>et al.</i> 2006
			liver	Σ PFCA	23-92*	
Crucian carp ($n=13$)	China, Beijing	2005-	blood	PFOS	64.2* (48.9-84.4)	Li <i>et al.</i> 2008
Common carp ($n=6$)		2007	blood	PFOS	32.2* (14.2-32.2)	
Common carp ($n=30$)	USA, Mississippi River	2006	muscle	PFOS	9.9-47*	Ye <i>et al.</i> 2008
			muscle	Σ PFCA	1.7-4.5*	
Sturgeon ($n=7$)	China, Yangtze River	2003-	liver	PFOS	5.8 \pm 3.2*	Peng <i>et al.</i> 2010
(17-25 years old)		2006	liver	Σ PFCA	7.6 \pm 5.8*	
			liver	PFOSA	0.06 \pm 0.07*	

* indicates mean value or composite sample.

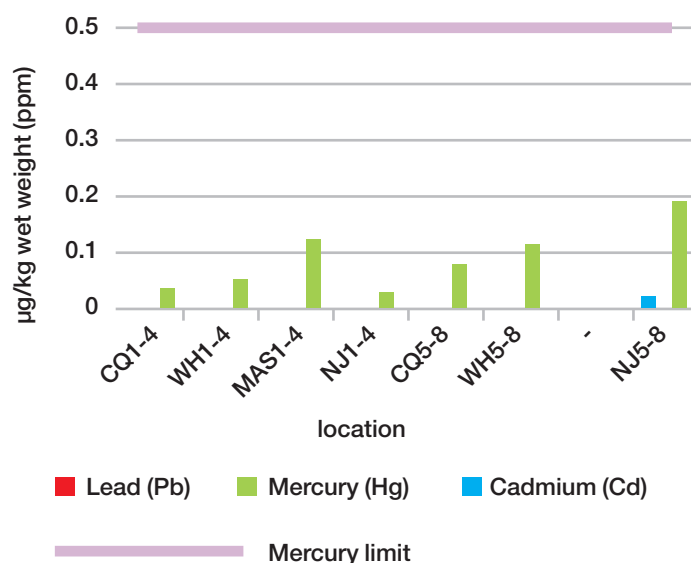
Not included are certain reports of far higher levels of PFCs which have been reported in carp livers (633-1822 $\mu\text{g}/\text{kg}$ ww), as these relate to fish collected in the vicinity of a fluorochemical manufacturing facility and so are not directly comparable with levels detected in the current study (Hoff *et al.* 2005).

Figure 5. Concentrations of cadmium, lead and mercury in carp (1-4) and catfish (5-8) liver samples (left) and muscle samples (right) by location from where the fish were collected (CQ-Chongqing; WH-Wuhan; MAS-Ma’anshan & NJ-Nanjing), showing the maximum mercury level allowed in fish muscle for consumption in China (MHPRC 2005).

Concentrations of metals in liver samples



Concentrations of metals in composite muscle samples



Metals: cadmium, lead and mercury

Muscle tissue

All muscle (fillet) samples contained detectable levels of mercury, in the range 0.034-0.13 mg/kg for carp and 0.083-0.19 mg/kg for catfish. At all locations, the concentrations in catfish muscle were higher than those for carp muscle by between 2 times (Chongqing and Wuhan) to 6 times (Nanjing).

The mercury concentrations in the catfish muscle progressively increased in samples collected along the Yangtze from upstream (Chongqing, 0.083 mg/kg) to downstream locations (Nanjing, 0.19 mg/kg). A similar pattern was found for the carp muscle samples, with one major difference. As for the catfish, the mercury concentrations progressively increased in samples collected from Chongqing (0.037

mg/kg) to Ma’anshan (0.13 mg/kg), however the composite carp muscle sample from Nanjing had the lowest concentration from all four sites (0.034 mg/kg).

The concentrations of lead and cadmium in all composite muscle samples, for both carp and catfish, were below limits of quantification (LOQ) (<0.05 mg/kg lead; <0.01 mg/kg cadmium) with one exception; catfish collected at Nanjing (NJ5-8) which contained 0.02 mg/kg cadmium.

Maximum allowed concentrations of cadmium, lead and mercury in fish muscle are regulated in China for fish intended to be used for human consumption (MHPRC 2005). This regulation sets maximum allowable wet weight concentrations of 0.5 mg/kg for mercury¹ and lead, and 0.1 mg/kg for cadmium in fish muscle (fillet). These limits are similar to, though in some cases less stringent than, equivalent limits in other countries. For example, the EU sets maximum allowable wet weight concentrations for mercury² (0.5 mg/kg), lead (0.3 mg/kg), and cadmium² (0.05 mg/kg) for fish muscle meat (EC 2006). None of the composite fish fillet samples contained concentrations of the three metals above their maximum allowed concentrations in China. The highest mercury concentration for all fillet samples (0.19 mg/kg, Nanjing Catfish) was less than half the maximum allowed

¹ Under this regulation, the mercury limit is defined for methyl mercury. Methyl mercury is the chemical form of greatest concern, and mercury in fish is generally present almost exclusively in this chemical form. It is usual for regulations concerning the level of mercury in fish to assume that levels of mercury and methyl mercury can be taken to be equivalent in this context (EFSA 2004).

² Limit of 1.0 mg/kg mercury and 0.1 mg/kg cadmium for certain species, which do not include those analysed in this study.

concentration of mercury for fish intended to be used for human consumption in China (MHPRC 2005). For comparison, all carp and catfish muscle concentrations were also below the somewhat lower equivalent EU limits (EC 2006).

Liver tissue

Mercury was detected in all liver samples, other than one carp liver from Chongqing, at concentrations in the ranges 0.008 to 0.052 mg/kg (carp livers) and 0.043 to 0.11 mg/kg (catfish livers). The average carp liver concentrations followed a similar pattern to that found for the composite carp muscle samples, *i.e.* the concentrations progressively increased in samples collected along the Yangtze from Chongqing (0.006 mg/kg) to Ma'anshan (0.033 mg/kg), with a lower average concentration in the sample from Nanjing (0.014 mg/kg). The catfish liver concentrations also followed a similar pattern to that found for the catfish muscle samples. The two upstream liver samples (Chongqing and Wuhan) had the lowest mercury concentrations, and the downstream sample from Nanjing contained the highest mercury concentration (0.11 mg/kg).

For each location and for both species, the muscle samples contained higher mercury concentrations than the average or composite livers concentrations, by between 2 to 6 times for the carp and 2 to 3 times for the catfish. Conversely, the liver samples contained higher cadmium concentrations than muscle, by up to 15 times. These patterns for these two metals have been previously reported in other studies (Čelechovská *et al.* 2007).

None of the mercury liver concentrations exceeded the maximum allowed mercury concentration (0.5 mg/kg) for fish muscle intended to be used for human consumption in China, although this limit is not directly applicable to fish livers (MHPRC 2005).

For cadmium, the concentrations in the carp livers ranged from <0.01 mg/kg (3 samples) to 0.05 mg/kg. The highest concentration was found in one of the samples from the most downstream location, Nanjing (NJ3), though for the second sample from Nanjing (NJ2) the concentration was below the LOQ (<0.01 mg/kg). Overall, no clear pattern was seen between carp liver concentrations and the fish collection locations along the Yangtze River.

Far higher cadmium concentrations were found in the catfish liver samples compared to the carp liver samples, and these were by far the highest cadmium concentrations among all the samples (liver and muscle) analysed in this study. Liver concentrations ranged from 0.15 mg/kg for catfish from Chongqing and Wuhan, to 0.34 mg/kg for catfish from the most downstream site, Nanjing, following a similar pattern to that found for the cadmium concentration in catfish muscle. It is known that cadmium accumulates to a greater extent in fish liver compared to muscle (Čelechovská *et al.* 2007).

For comparative purposes, the maximum concentration of cadmium allowed in fish muscle intended to be used for human consumption in China is 0.1 mg/kg, although this limit is not directly applicable to fish livers. The concentrations of lead in all carp liver samples were below the limit of quantification (<0.05 mg/kg). For the catfish liver samples, the levels were either below or just above the limit of quantification, with the Nanjing sample having the highest level (0.07 mg/kg).

For cadmium and mercury, some large differences were seen between the concentrations in individual carp livers from the same location, in a similar way to that seen for the AP and PFC concentrations in the carp liver samples. For samples from Nanjing, the individual cadmium values differed by over 5 times and for Nanjing and Ma'anshan the individual mercury values differed by 4 times. As for APs and PFCs, these data highlight the potentially high degree of variability of cadmium and mercury concentrations in similar fish from a single location and, therefore, caution is required in making any firm conclusions on the ranking of locations by the cadmium and mercury concentrations where the differences are relatively small. As mentioned above, the composite catfish samples prepared from four individuals are likely to provide a better measure for comparison between different locations.

Many previous studies have reported a wide range of concentrations of cadmium, lead and mercury in fish muscle and liver, including for common carp and catfish. For example, similar levels of mercury to those found in this study have previously been reported for fish from the Yangtze River; in common carp muscle (0.104 mg/kg) and liver (0.058 mg/kg) as well as catfish (*Silurus meridionalis*) muscle (0.075-0.080 mg/kg) and liver (0.072 mg/kg) (Wang 2008, Chen *et al.* 2007). Likewise, similar cadmium levels have also been reported in Yangtze River catfish muscle (0.002-0.035 mg/kg), with slightly higher levels reported for liver (0.572 mg/kg) (Wang 2008, Chen *et al.* 2007). In contrast, considerably higher cadmium levels than those found in this study have been reported for common carp from the Yangtze River (muscle 0.24 mg/kg; liver 0.31 mg/kg). Considerably higher levels of lead have also been reported for both common carp (muscle 0.46 mg/kg; liver 1.14 mg/kg) and catfish (muscle 0.21-1.06 mg/kg; liver 2.32 mg/kg) from the Yangtze River (Wang 2008, Chen *et al.* 2007).

Conclusions

This study has demonstrated the widespread presence of certain hazardous chemicals within wild fish from the upper, middle and lower sections of the Yangtze River. For all four locations investigated (Chongqing, Wuhan, Ma'anshan and Nanjing), common carp and/or southern catfish livers contained detectable levels of APs and PFCs. Chemicals from both groups were detected in both species for all but one location (Chongqing, at which PFCs were only detected in catfish). For both chemical groups, concentration ranges were comparable with the ranges previously reported for tissues from freshwater fish from other countries. The levels of NP dominated the mixtures of APs detected, and PFOS dominated the total concentrations of PFCs.

Furthermore, cadmium and mercury were detected in livers and/or muscle of both species, with cadmium being particularly evident in catfish livers. However, none of the muscle (fillet) samples contained levels of any of the three metals above their maximum allowed concentrations for human consumption in China.

These data not only provide information on the levels of the hazardous chemicals investigated within the bodies of the fish, but also provide an indication of the levels of exposure to the fish for these hazardous chemicals, and therefore of the extent to which the Yangtze River itself is contaminated at the locations investigated. Furthermore, although chemicals entering to the Yangtze River, either from point sources or due to diffuse inputs, will to some extent move along the river with the flow of water and sediments within it, this study does provide some indications of differences in the quantities and composition of the local sources of the substances investigated at the four locations.

Clearly, for the hazardous chemicals identified in the fish tissues, there are well recognised environmental or human health concerns, including as a result of their ability to accumulate and persist in the environment following their release, including within biota. Ongoing releases of these chemicals are likely to lead to ever increasing levels in the receiving environment, which are unlikely to significantly decrease for long periods of time, even after any controls on their release have been introduced.

Although maximum allowed concentrations of cadmium, lead and mercury apply for fish muscle intended to be used for human consumption in China, there are no such limits for APs or PFCs. Some regulations do apply to the release of the three metals investigated within China under certain circumstances, though these do not prohibit all releases which derive from human activities. However, the manufacture, use and release of APs and PFCs are currently not regulated within China, and this situation also applies to the majority of other hazardous chemicals currently used and released within China.

In many countries and regions, the manufacture and use of some of the most hazardous chemicals has greatly reduced in recent years, largely as a result of legislation. However, in the case of certain hazardous chemicals, the opposite trend is being seen in China, where their manufacture and/or use has either continued largely unchanged or, in some instances, actually increased considerably in the last decade.

There is an urgent need for the development of a more sustainable approach to the management of chemicals within China. This approach will require an understanding of the current uses of hazardous substances for as wide a range of substances as possible, as well as of their release to the aquatic and wider environment.

Regulations seeking to address impacts arising from the release of hazardous chemicals into the environment, by setting either acceptable levels of release or acceptable levels in the receiving environment, are, however, unable to address the serious and potentially irreversible consequences arising from ongoing releases of persistent pollutants to the environment, particularly those able to bioaccumulate. The most effective measures to address hazardous substances are those which seek alternatives to their use in manufacturing processes, progressively replacing them with less hazardous, and preferably non-hazardous, alternatives in order to bring about rapid reductions and ultimate cessation in their discharges, emissions and losses. This approach can lead to a more sustainable industry, eliminating both the waste of resources and the pervasive threats to the environment and human health which the ongoing use and release of hazardous chemicals entails.



Taicang City, Jiangsu Province. Because of pollution in the Yangtze River fishing nets have to be cleaned every time they are used; a net only lasts one year.

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Swimming in Chemicals

Perfluorinated chemicals, alkylphenols and metals in fish from the upper, middle and lower sections of the Yangtze River, China

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Appendix: Analytical methods

Sample preparation

All fish were thawed, weighed and their lengths recorded. The fish were then gutted and the intact livers isolated. For catfish, the livers from all samples from each location were combined to obtain one composite sample. For carp, individual livers from specific fish were analysed separately. In addition, a composite muscle sample was prepared for each species from each location.

AP and PFC extraction

All samples were freeze-dried and target substances were subsequently extracted from the freeze-dried, homogenised sample material (0.5-1g) using ultrasonic extraction with acetonitrile (3-fold extraction).

For PFC extraction, a mixture of seven ¹³C-labelled PFC congeners (PFOS and six PFCAs) was added to the homogenised fraction of the dried sample material prior to ultrasonic-extraction. The extracts from each sample were combined, and the clean-up of all extracts was performed by hexane partitioning to remove much of the lipid content, followed by ENVI-Carb clean-up. The final extract was evaporated to dryness by a gentle stream of nitrogen and re-dissolved in 150 µl MeOH/H₂O (1:1) containing ¹³C₄ PFOA as a recovery standard for LC-MS analysis.

For AP quantification, two internal labelled standards (d₁₇ 4-n-octylphenol & ¹³C p-n-nonylphenol) were added to the homogenised fraction of the dried sample material prior to ultrasonic-extraction. The extracts from each sample were combined, and clean-up was performed by hexane partitioning to remove much of the lipid content, followed by derivatisation with N,O-bis-trimethylsilyl-trifluoroacetamide (BSTFA) to form trimethylsilyl (TMS) derivatives. The final extract was evaporated nearly to dryness by a gentle stream of nitrogen. The residue was purified by column chromatography (SiO₂) and subsequently evaporated to 100 µl, to which ¹³C PCB (#28) was added as a recovery standard.

PFC and AP analysis

All analyses were performed following the isotope dilution method. For PFC quantification, the sample extracts were analysed by high performance liquid chromatography-electrospray mass spectrometry (LC/ESI-MS-MS) using a security guard cartridge (C18 × 2.0 mm i.d., Phenomenex) and a Synergy 4u Fusion RP C-18 column (100 mm × 2.0 mm i.d., 80A, Phenomenex) for liquid chromatographic separation (5mM aqueous ammonium acetate/methanol gradient over 20 minutes). For AP quantification, the sample extracts were analysed by gas chromatography-mass spectrometry using electron impact ionisation (GC/LRMS-EI).

Quality assurance/quality control (QA/QC)

For both PFC and AP quantification, every sample batch (maximum of 10 samples) included a procedural blank (prepared in the same way as the samples) and at least one sample was extracted in duplicate. The recoveries of the labelled internal standards were between 50% and 120%.

Metals quantification: cadmium, lead and mercury

Each freeze-dried, homogenised sample material (approximately 1g) was digested using nitric acid, at 90°C for 3 hours, followed by a further 4 hours at 160°C. The filtered sample was made up to an exact volume (25ml). The concentrations of cadmium and lead were determined in the sample extracts using inductively coupled plasma-mass spectrometry (ICP-MS), and the concentrations of mercury were determined using cold vapour-atomic absorption spectroscopy (AAS). Quality assurance/quality control (QA/QC) checks were performed using inter-laboratory reference material, and at least one sample was extracted in duplicate.

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