OCCURRENCE AND RISK ASSESSMENT OF PERSISTENT ORGANIC POLLUTANTS IN FOODSTUFFS AND ORGANIC MICRO-POLLUTANTS IN WATERS, NORTH CHINA

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2016

THE UNIVERSITY OF KITAKYUSHU

GRADUATE SCHOOL OF ENVIRONMENTAL ENGINEERING

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by

LINGXIAO KONG

March 2016

This dissertation is submitted for the degree of Doctor of Engineering

Declaration

This dissertation is the result of my own work and contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution. It contains no material previously published or written by another person, except where due reference has been made in the text. This dissertation has not been previously submitted, in part or whole, to any university or other tertiary institution for any degree, diploma, or the other qualification.

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Acknowledgements

Foremost, I would like to express my sincere gratitude to my Supervisor Dr. Kiwao Kadokami for the continuous support of my Ph.D study and related research, for his patience, enthusiasm and expertise to hold me to a high research standard and enforcing strict validations for each research result, thereby teaching me how to do quality research. Thank you for always being there to listen and give advice. Also, I appreciate your effort regarding my publications and the possibility to attend conferences and to get to know other researchers. His guidance helped me in all the time of research and writing this thesis. I could not have imagined having a better advisor and mentor for my Ph.D. study.

Besides my professor, I would like to thank the rest of my thesis committee: Prof. Hidenari Yasui and Prof. Seiichi Ishikawa. Not only for their encouragement, insightful comments, but also for the hard questions which incented me to widen my research from various perspectives.

My sincere thanks also go to Prof. Graeme Allinson (RMIT University, Melbourne, Australia) and Dr. Mayumi Allinson (University of Melbourne, Melbourne, Australia) for proofreading my articles and giving their valuable comments and constructive suggestions.

I am particularly grateful to Prof. Shaopo Wang, Tianjin Chengjian University, for the great help on the water sampling in China and the kind assistance from their lab mates. My appreciation also extended to Prof. Katsuhisa Honda, Dr. Hiroyuki Fujita and Dr. Isao Watanabe for their concentrated guidance to get my graduate career and overcome many obstacles.

I thank my fellow lab mates: Hanh Thi Duong, Hong Thi Cam Chau, Shirasaka, Hanako, Matsuura Naoki, Hidaka Rento, Yoshida Yusuke and Katayama Shinsuke for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we have had in the last three years.

Last but not the least; I would like to thank my parents for supporting me spiritually throughout writing this thesis and my life in general.

Abstract

This thesis can be divided into two major parts: occurrence and risk assessment of persistent organic pollutants (POPs) in foodstuffs and organic micro-pollutants (OMPs) in waters, China. This work investigated the levels and patterns of organochlorine pesticides (OCPs) in 19 food items and 209 polychlorinated biphenyls (PCBs) congeners in 5 food items collected from the Shandong Peninsula to quantify the daily intake of OCPs through dietary exposure of persons living in the Shandong Peninsula and to assess the potential hazard of this exposure to human health. The monitoring of 1300 OMPs in surface waters from Tianjin and Jinan, and groundwater from Tianjin and Beijing was undertaken for the first wide survey to provide baseline information of pollution status in aquatic environment of China.

Even though the use and production of PCBs and OCPs have been regulated worldwide, in agreement with the Stockholm convention in 2001, they are still posing serious environmental threat both to wildlife and humans. Recently, OCPs and PCBs were still being detected in various environmental media in China, including water, sediments, soil, and aquatic organisms which in some regions contained elevated concentrations. It is generally accepted that human exposure to POPs is mainly through diet. Because of higher toxicities from and exposure to POPs, the World Health Organization (WHO), United States Environmental Protection Agency (US EPA), and Health Canada provide several guidelines for these contaminants to protect human health associated with adverse effects. Data on the residue levels of POPs in foodstuffs of China are still scarce. In this study HCHs (including α, β, γ and δ-HCH) were ubiquitous components in sampling area with the highest total concentration found in peanut oil (2.4 ng/g) and the composition of HCHs indicated the mainly historical usage of technical HCHs and recent input of lindane. Although high sum concentrations of DDTs (including o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT) were found in croaker (72 ng/g ww), the value was still far below the Chinese safety guidelines (500 ng/g). The composition of DDTs revealed the recent input which may be attributed to the antifouling paints leakage from transportation sources. However, the detection of ∑209 PCBs were only conducted in 5 marine food items with rather lower concentration ranged from 0.33 ng/g to 3.1 ng/g ww. It was interesting that PCB #11 and hexa-CBs were frequently detected with high proportion to total PCBs compared to other homologues. According to the Integrated

Risk Information System (IRIS), the average daily exposure for each contaminant in foodstuffs was lower than the corresponding benchmark concentration based on cancer and non-carcinogenic effects. To date, the work provided the first data about the existence of non-Aroclor PCB #11 in foodstuffs from China and should arouse much attention from a toxicity point.

In spite of the quantities and species of chemicals dramatically increased with rapid economic growth in China, water quality in China has deteriorated in the last decades. The increasingly evident water pollution problems have also led to serious ecological and environmental consequences. However, the focus of environmental research was mainly on limited number of priority pollutants. Therefore, to elucidate environmental pollution by organic micro-pollutants, this work was conducted as the first systematic survey on the occurrence of 1300 substances in surface water samples in Tianjin, and Jinan, North China. The results showed total 227 and 107 chemicals were detected in Tianjin and Jinan, respectively. As a major industrial city in North China, Tianjin received large amount of pollutants, and the most relevant compounds in terms of frequency of detection and median concentration were bis(2-ethylhexyl) phthalate (100%; 0.26 μg/L), siduron (100%; 0.20 μg/L), lidocaine (100%; 0.10 ng/L), antipyrine (100%; 0.08 ng/L), caffeine (95%; 0.28 μg/L), cotinine (95%; 0.20 μg/L), phenanthrene (95%; 0.17 μg/L), metformin (90%; 0.61 μg/L), diethyl phthalate (90%; 0.19 μg/L) and 2-(methylthio)-benzothiazol (85%; 0.11 μg/L). Principle component analysis identified four factors, corresponding to industrial wastewater, domestic discharge, tire production and atmospheric deposition, accounting for 78% of the total variance in the data set of Tianjin. Compared to Tianjin, levels of sterols observed in Jinan, a medium-sized city, were generally high, especially coprostanol, while other compounds found in >70% waters with median concentration were cholesterol (1.7 μg/L), beta-sitosterol (1.1 μg/L), sulfamethoxazole (1.1 μg/L), cotinine (0.73 μg/L), caffeine (0.38 μg/L) and 2,6-di-tert-butyl-4-benzoquinone (0.12 μg/L). However, metformin, an anti-diabetic drug, was predominant in both Tianjin and Jinan with concentration up to 20 μg/L and 34 μg/L, respectively. This work provides a wide reconnaissance on broad spectrum of organic micro-contaminants in surface waters in China, which indicates that the aquatic environment in China has been polluted by a large number of chemicals.

Groundwater contamination in China has become a growing public

concern in view of the rapid economic development and dramatically increasing fresh water demand. So far little information is available on groundwater quality which may be impacted by a large variety of organic micro-pollutants. As part of the continuing effort to provide a comprehensive understanding on the groundwater pollution status, this work was carried out for the first holistic survey on the occurrence of 1300 chemicals in 27 groundwater sites from Beijing and Tianjin, North China. The results showed 78 compounds (6% of the targeted compounds) were found in at least one sampling point, which included polycyclic aromatic hydrocarbons (PAHs), pesticides, plasticizers, antioxidants, pharmaceuticals and other emerging compounds,. The most frequently detected compounds in terms of median concentration were 2-ethyl-1-hexanol (152 ng/L), benzyl alcohol (582 ng/L), 2-phenoxy-ethanol (129 ng/L), acetophenone (74 ng/L), pentamethylbenzene (51 ng/L), nitrobenzene (40 ng/L) and dimethyl phthalate (64 ng/L). The pesticides with concentration exceeding the maximum residual limits (MRL) of 0.1 μg/L were 1,4-dichlorobenzene, oxadixyl, diflubenzuron, carbendazim, diuron, dimethomorph(E) and dimethomorph(Z). It should be noted the naphthalene and its 7 alkylated derivatives were predominant compounds with maximum concentration up to 30 μg/L which was still far below the Health Advisory Level of 100 μg/L. Compared to the survey in EU and US, the groundwater in this study was more polluted which demonstrated the groundwater in Beijing and Tianjin was impacted by the intensive industrial and agricultural activities.

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Abbreviations

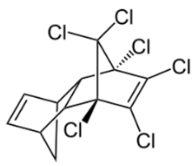
2-EH	2-ethyl-1-hexanol
4-NP	4-Nonylphenol
AIQS-DB	Automated identification and quantification system with a database
BBP	Butyl-benzyl phthalate
BHT	Butylated hydroxytoluene
BPA	Bisphenol A
BW	Body weight
CA	Cluster analysis
COD	Chemical oxygen demand
DBP	Di-n-butyl phthalate
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Ddichlorodiphenyltrichloroethane
DEET	N,N-diethyl-m-toluamide
DEHP	Bis(2-ethylhexyl) phthalate
DEP	Di-ethyl phthalate
DMP	Di-methyl phthalate
DOP	Di-n-octyl phthalate
DQ	Danger quotient
ET	Exposure time
FA	Factor analysis
FWHM	Full peak width at one-half maximum
HCB	Hexachlorabenzene
GC/MS	Gas chromatography–mass spectrometry
HCH	Hexachlorocyclohexane
HP	Highly polluted
HRGC/HRMS	High-resolution Gas Chromatography/High-Resolution Mass Spectrometry
LC/TOF/MS	Liquid chromatography/time-of-flight/mass spectrometry

LP	Less polluted
MDI	Maximum daily intake
MEC	Measured environmental concentration
MP	Medium polluted
MRL	Maximum residual limits
ND	Not detected
NOEC	No observed effect concentration
OCPs	Orgnochlorine pesticides
OMPs	Organic micro-pollutants
PAEs	Phthalic acid esters
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PNEC	Predicted no-effect concentration
POPs	Persistent Organic Pollutants
RfD	Reference dose
RQ	Risk quotients
RSD	Relative standard deviation
SIM	Selected-ion monitoring
SRM	Selected reaction monitoring
STP	Sewage treatment plant
TIM	Total-ion monitoring
UNEP	United Nations Environment Programme
WT	Time of weighing
WWTPs	Waste water treatment plants

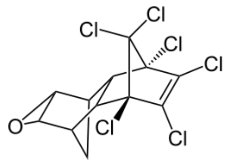
Chapter 1 Introduction, Motivation and Objectives

1.1 Persistent Organic Pollutants (POPs)

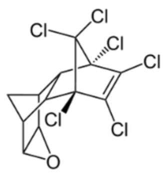
Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes, and can persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. Fig. 1.1 listed the molecule structure of POPs partially.



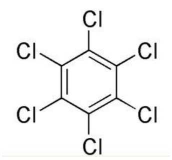
Aldrin



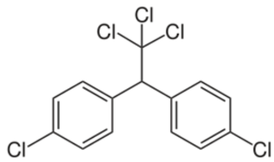
Dieldrin



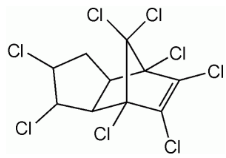
Endrin



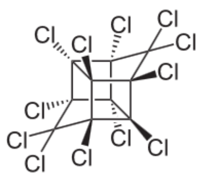
HCB



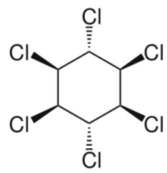
DDT



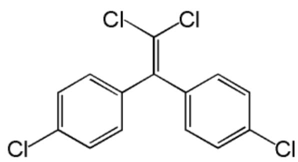
Chlordane



Mirex



HCH



DDE

Fig. 1.1 The molecule structure of partial POPs

In nature these substances affect plant and animal development and growth. They can cause reduced reproductive success, birth defects, behavioral changes and death. They are suspected human carcinogens and disrupt the immune and endocrine systems. There are four characteristic parameters (persistence, bioaccumulation, toxicity, and long-range environmental transport), which can distinguish POPs from a multitude of other organic chemicals. POPs are globally distributed through the air and ocean currents since they can travel long distances and enter into atmospheric processes, air–water exchange and cycles involving rain, snow and dry particles.

These processes lead to the exposure of even remote populations of humans and animals. POPs typically are halogenated organic compounds, such as OCPs and PCBs, and exhibit high lipid solubility. There are 12 substances prioritized for global action in the recently signed Stockholm Convention on Persistent Organic Pollutants, developed under the auspices of the United Nations Environment Programme (UNEP), including dieldrin, aldrin, endrin, chlordane, heptachlor, DDT, toxaphene, mirex, two kinds of industrial chemicals [polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB)], and two kinds of byproducts (polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins) (Stockholm Convention on Persistent Organic Pollutants, 2001).

1.1.1 Manufacturing and Emission Sources of POPs in China

Being a large agricultural country, China has a history of large scale production and application of OCPs which were predominantly used during the 1950s–1970s until its ban on production and agricultural use were enforced in 1983. China had been a significant producer and user of DDT since the 1950s. During its 30 years of production, 0.4 million tons of DDT were produced, accounting for 20% of the total world production (Fu et al., 2003). The total quantity of DDT used was estimated to be 43520 tons from 1960 to 1983, with large scale usage in agricultural practices (Nakata et al., 2002, Fu et al., 2003; Jaga and Dharmani, 2003). Even after the ban of technical DDT in 1983, its production continued to be used as an intermediate for producing dicofol, anti-fouling paint, as an ingredient in some mosquito-repellent incense, and for malaria prevention (including export) (Wong et al., 2005).

Technical HCH, as a broad-spectrum insecticide, has been produced and used in the world for both agricultural and nonagricultural purposes due to its effectiveness and low cost. China started to produce and use technical HCH in 1952, and the total amount of technical HCH produced in China was 4.5 million tons before its use was banned in 1983 (Li et al., 1998), which accounted for about 30% of total world production (Wei et al., 2007). In China, technical HCH was mainly used in agriculture, although a small portion was used in forestry and public health (Cai et al., 1992). Crops on which HCH was widely used in China were rice, wheat, maize, cotton, soybean, sorghum, orchards and some vegetables to attack a wide variety of pests for different crops. Among them, more than half of HCH was used in rice paddies, 25% on wheat, and 10% on each of soybean/sorghum and maize.

HCB has never been used as a pesticide in China, but it is used as an intermediate to produce sodium pentachlorophenol (Na-PCP), which was used extensively to kill snails in those places where schistosomiasis prevails. Owing to their specific characteristics, chlordane and mirex are still used to prevent and kill termites, and small amounts are used in agriculture, sericulture, and to kill cockroaches (Hu et al., 2007). Toxaphene and heptachlor, both were produced in industrial scale before the middle of 1980s in China. There were 16 toxaphene manufacturers, and the total production quantity was 3 kt in 1970s. Aldrin, dieldrin and endrin have never been produced at large scale in China, and the research or trial production has been stopped. There are no import records for aldrin, dieldrin and endrin.

In China, approximately 10000 t of PCBs were produced from 1965 to 1974 (the production of PCBs was banned in 1974), with 9000 t as trichlorobiphenyl (PCB3, chlorine content is 42%) used primarily as impregnants in power capacitors and 1000 t as pentachlorobiphenyl (PCB5, chlorine content is 54%). PCB3 and PCB5 are similar in compositions to Aroclor 1242 and Aroclor 1254, respectively, used mainly as additives of paint, printing ink, and as lubricants (Jiang et al., 1997; Qin et al., 2003). Moreover, during the 1950s to 1980s, China imported numerous capacitors containing PCBs from Belgium and France (Meng et al., 2000). After mass production and extensive usage, these PCBs entered the soil and adjacent water via waste emissions, oil leakage, volatilization, dry and wet deposition or other means, thus resulting in widespread environmental pollution. Recently, numerous reports have identified various levels of PCB residues in the water, soil, sediment, rice, fish, and birds in the Yangtz Delta industrialized area (Zhang et al., 2007).

1.1.2 Human Exposure to POPs and Health Effects

Humans can be exposed to POPs through diet, occupation, accidents and the environment, including the indoor environment. Exposure to POPs, either acute or chronic, can be associated with a wide range of adverse health effects, including illness and death. The greatest part of human exposure to the 12 specified POPs is attributed to the food chain. It is estimated that more than 90% of the human exposure to POPs is caused by consumption of contaminated food (Li et al., 2008). Fish consumption is considered a major source of dietary POPs exposure. POPs residues such as DDT, HCB, hexachlorocyclohexane (HCH), chlordane and PCBs have been found in marine fish, mollusks, crabs and shrimp in the coastal areas of China (Yang et al., 2006; Jiang et al., 2007; Liu et al., 2007). Residents of coastal areas who have a habit of consuming sea fish are vulnerable to POPs exposure. The contamination of food, including breast milk, by POPs is a worldwide phenomenon (Poon et al., 2005; Suna et al., 2005; Korrick and Altshul, 1988).

A number of incidents of acute toxic effects in humans, including death, have occurred as a result of contaminated food. Edible oils and foods of animal origin are most often involved. Effects observed in high-trophic level wildlife include the eggshell-thinning effects of DDT on fish-eating birds and their subsequent extirpation in large parts of the industrialized world (Hickey and Anderson, 1968; Wiemeyer and Porter, 1970). Evaluating the patterns, levels, trends, and effects of POPs in high trophic level consumers may therefore contribute to our understanding of both the contamination of aquatic ecosystems (freshwater and marine), and the risks posed to human health. Lessons learned from some of these more highly exposed groups of wildlife and humans are likely to be relevant to the health of the general public, where evidence is mounting that even relatively low exposures to POPs can affect human health.

1.2 Organic Micro-Pollutants (OMPs)

Over the last few decades, the occurrence of OMPs in the aquatic environment has become a worldwide issue of increasing environmental concern. OMPs consist of a vast and expanding array of anthropogenic as well as natural substances. These include pharmaceuticals, personal care products, steroid hormones, industrial chemicals, pesticides and many other emerging compounds. OMPs are commonly present in waters at trace concentrations, ranging from a few ng/L to several μg/L. The low concentration and diversity of OMPs not only complicate the associated detection and analysis procedures but also create challenges for water and wastewater treatment processes (Luo et al., 2014).

Current wastewater treatment plants (WWTPs) are not specifically designed to eliminate OMPs. Thus, many of these OMPs are able to pass through wastewater treatment processes by virtue of their persistency or/and the continuous introduction. In addition, precautions and monitoring actions for OMPs have not been well established in most WWTPs (Bolong et al., 2009). Consequently, many of these compounds may end up in the aquatic environment, becoming threats to wildlife and spelling trouble for drinking water industry. The occurrence of OMPs in the aquatic environment have been frequently associated with a number of negative effects, including short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganisms (Pruden et al., 2006). To date, discharge guidelines and standards do not exist for most OMPs. Some countries or regions have adopted regulations for a small number of OMPs. For example, environmental quality standards for a minority of OMPs (e.g. nonylphenol, bisphenol A, DEHP and diuron) have been stipulated in Directive 2008/105/EC (European Parliament and The Council, 2008). Nonylphenol and nonylphenol ethoxylates have also been recognized as toxic substances by the Canadian government (Canadian Environmental Protection Act, 1999). Other OMPs, such as pharmaceutical and personal care products (PPCPs) and steroid hormones, are not included in the list of regulated substances yet. To set regulatory limits for OMPs, further research on biological responses to these compounds (both acute and chronic effects) is of particular importance. Furthermore, scientific community and regulatory agencies should gain insight into not only the impact of individual OMPs, but also their synergistic, additive, and antagonistic effects.

1.2.1 Source of OMPs

Sources of OMPs in the environment are diverse and many of these originate from mass-produced materials and commodities, such as industrial wastewater (from product manufacturing discharges), landfill leachate (from improper disposal of used, defective or expired items), domestic wastewater (from excretion, laundry, dishwashing, bathing, shaving, spraying, swimming, run-off from gardens, lawns and roadways and etc.), hospital effluents and agricultural runoff.

The local production and usage/consumption of products containing OMPs determine the amount of OMPs reaching WWTPs. Studies suggested that PPCP concentrations in wastewater correlated well with their production amounts and usage/consumption patterns. K. Choi et al. (2008) reported that the occurrence concentrations of acetaminophen, carbamazepine, cimetidine, diltiazem, sulfamethoxazole and trimethoprim followed the same order (from highest to lowest) of their annual production amount in Korea. High concentrations (> 10 μg/L) of acetaminophen, tramadol, codeine, gabapentin and atenolol were detected at highest levels in raw wastewater in Wales, UK and this could be explained by the high quantities of these pharmaceuticals dispensed (Kasprzyk-Hordern et al., 2009). As orally ingested products containing potential contaminants (e.g. pharmaceuticals) are metabolized in human body and are subsequently excreted via urine and feces, excretion rate plays a role in determining the introduction of pharmaceuticals into raw wastewater. Pharmaceutical compounds with low excretion rates (e.g., ibuprofen, carbamazepine, sulfamethoxazole, diclofenac and primidione) are not necessarily present at low levels in the raw wastewater. This is possibly because the low excretion rates are offset by the massive use of these compounds. In addition, local common diseases can induce a higher consumption of specific pharmaceuticals in certain periods. Research showed climatic conditions could cause fluctuating OMPs input (Kolpin et al., 2004). The use of pesticides can be seasonal due to the prevalence of pests in different climatic conditions. Another important factor is rainfall, as it affects the flow pattern of wastewater influent when a combined sewer system is employed. Kasprzyk-Hordern et al. (2009) found that the concentrations of most PPCPs in the raw wastewater were doubled when the flow was halved during dry weather conditions, suggesting that rainwater could dilute the concentrations of the compounds within the sewage. Other weather conditions, such as temperature and level of sunlight also can affect the discharge of OMPs from WWTPs.

Most OMPs occurred in WWTP influent in the concentration range between 0.1 and 10 μg/L, while some pharmaceutical compounds (acetaminophen, caffeine, ibuprofen, naproxen and salicylic acid), one biocide (triclosan), one surfactant (nonylphenol) and one industrial chemical (DEHP) exhibit relatively high occurrence concentrations (Luo et al., 2014). Generally, the compounds with highest concentrations in WWTP influent were ibuprofen, atenolol, caffeine and nonylphenol. For instance, ibuprofen was the most abundant compound detected in the influent of four WWTPs in Spain, with the concentration levels ranging from 3.73 to 603 μg/L (Santos et al., 2009). The particularly high levels could be explained by the high consumption and easy accessibility (over the counter drugs) of the compound. Caffeine was detected at the highest levels approaching 50 μg/L on average in the raw sewage of three WWTPs in China (Zhou et al., 2010). The abundant presence of caffeine is likely associated with the high consumption of coffee, tea and soft drinks as well as the disposal of these items.

1.2.2 Occurrence of OMPs in Surface Water

The release of WWTP effluent into surface water has been considered as a main cause of the presence of OMPs in surface water in comparison to other sources (Kasprzyk-Hordern et al., 2009). Following treatment processes in WWTPs, OMPs are subjected to varying degrees of natural attenuation (e.g., dilution in surface water, sorption onto suspended solids and sediments, direct and indirect photolysis and aerobic biodegradation) (Pal et al., 2010). Due to river water dilution, pharmaceutical compounds may occur at levels at least one order of magnitude lower than effluent levels (Gros et al., 2007). Gómez et al. (2012) found that the natural attenuation of PPCPs is more likely to result from river water dilution, or sorption to solids, than from degradation. Furthermore, river water dilution can be affected by rainfall. Consistent increase in OMPs occurrence levels during dry weather conditions and marked reduction during wet weather conditions have been reported. Wang et al. (2011) indicated that pharmaceuticals in summer water samples showed lower occurrence levels than those in winter. This could be due to promoted biodegradation of pharmaceuticals in warmer temperature, and elevated dilution during wetter summer. However, rainfall did not always reduce the concentration levels of OMPs released. In some cases, rainfall was identified as a contributor to the emission of OMPs to surface water. Some studies revealed that the chemicals (e.g., bisphenol A and biocides) used in building material (e.g. pavement materials, facades and roof paintings) were able to leach during precipitation and accumulate to remarkable levels in roof runoff and subsequently ended up in surface water (Jungnickel et al., 2008, Sakamoto et al., 2007, Schoknecht et al., 2009 and Singer et al., 2010). In addition, rainfall events could intensify combined sewer overflows, resulting in a higher level of contaminant discharge. Regarding pesticides, the contamination of surface water by these compounds depends on crop type, soil properties, characteristics of the water bodies (depth and flow rate), features of the land close to the water bodies (soil use, slope, and distance from water bodies) and climatic conditions (temperature, rainfall, moisture and wind) (Bermúdez-Couso et al., 2013).

In general, the pollution of emerging contaminants in the natural water bodies of the densely populated regions is more severe because of the massive usage of these chemicals by the large population. For example, the concentrations of nonylphenol, bisphenol A and triclosan in surface water in Guangzhou (one of the largest cities in China) were at rather high levels (Peng et al., 2008). Nonylphenol was also found at relatively high concentrations in a Greek river, with a maximum of 2704 ng/L. The maximum nonylphenol concentrations in China and Greece were well above the reported PNEC (Predicted no-effect concentration) for nonylphenol. In addition to above mentioned factors, population aging has also been linked to the high occurrence levels of pharmaceuticals (Al-Rifai et al., 2007).

1.2.3 Occurrence of OMPs in Groundwater

In comparison to surface water, ground water was found to be less contaminated with OMPs (Loos et al., 2010 and Vulliet and Cren-Olivé, 2011). Hence, the presence of OMPs in groundwater has been put far less emphasis on. Better characterization of OMPs in groundwater has been only done regionally (mainly in some parts of Europe and North America). OMPs contamination of groundwater mainly results from landfill leachate, groundwater–surface water interaction, infiltration of contaminated water from agricultural land or seepage of septic tanks and sewer systems. Concentrations of OMPs in landfill leachate and septic tank leakage generally range from 10 to 104 ng/L and 10 to 103 ng/L, respectively (Lapworth et al., 2012).

Soil is the major pathway for groundwater pollution by some OMPs (e.g. pesticides) (González-Rodríguez et al., 2011). OMPs can also be introduced in groundwater via bank filtration or artificial recharge using reclaimed water (Stepien et al., 2013). Generally, the processes governing subsurface flow and transport (such as dilution, adsorption to aquifer material, degradation and travel time) can decrease OMPs' concentrations from the sources (e.g., landfill leachate and septic tank leakage) to groundwater (Teijon et al., 2010).

The physicochemical properties of OMPs are therefore important for the transfer of the compounds to groundwater. For example, octanol–water partition coefficient (K_{ow}) indicates contaminant mobility in the subsurface, where the compounds (e.g., trimethoprim and TCEP) with K_{ow} < 1.5 tend to stay in the dissolved phase (more mobility) and are more likely to occur in groundwater (Dougherty et al., 2010 and Karnjanapiboonwong et al., 2011). In a study conducted in the US, Fram and Belitz (2011) found good correlation of pharmaceutical levels in groundwater and presence of modern water (water recharged since 1953), occurrence of other synthetic contaminants (urban-use herbicides and insecticides and volatile organic compounds) and land application.

1.2.4 The Removal and Fate of OMPs in WWTPs

Municipal WWTPs are designed to control a wide range of substances, such as particulates, carbonaceous substances, nutrients and pathogens. While these substances can be efficiently and consistently eliminated, the removal of OMPs is often insufficient. Wastewater treatment plants generally employ a primary, a secondary and an optional tertiary treatment process. Tertiary treatment processes are commonly used to produce higher quality of discharged water for certain purposes (e.g. water reuse), and are always associated with high treatment cost. Thus, the requirement for tertiary treatment processes is generally based on public and environmental health objectives.

Primary treatment processes aim to remove suspended solids that enter WWTPs and are ineffective in removal of most OMPs (Carballa et al., 2005). OMPs are removed mainly by sorption on primary sludge, as distribution of a compound into organic (lipophilic) layer is a predominant way of sorption (Ternes et al., 2004). Fragrances (galaxolide and tonalide) were found to be well removed (40%) during primary treatment (aerated grit chamber followed by circular sedimentation tank) due to their high partition coefficients between the solid and liquid phase (Carballa et al., 2004). Primary treatment (sedimentation tank) was also able to remove some EDCs moderately with removal efficiency ranging from 13% (nonylphenol monoethoxylate) to 43% (bisphenol A) (Stasinakis et al., 2013). However, primary treatment using aerated grit chamber could cause significant increase of phenolic compounds, such as bisphenol A and nonylphenol, because the compounds originally attached to the grits could be peeled off due to air agitation in grit chamber (Nie et al., 2012). For pharmaceuticals and hormones, removal efficiency in primary treatment ranged up to only 28% (diclofenac and estriol), which suggested that adsorption of investigated compounds to sludge particles was rather limited (Behera et al., 2011). No considerable reduction was also reported for ibuprofen, naproxen, sulfamethoxazol and estrone (Carballa et al., 2004).

In secondary treatment, OMPs are subjected to a range of processes, including dispersion, dilution, partition, biodegradation and abiotic transformation. The total removal during secondary treatment generally refers to the losses of a parent compound contributed by different mechanisms of chemical and physical transformation, biodegradation and sorption to solids (Jelic et al., 2011). Biodegradation/biotransformation and sorption are the two major removal mechanisms during biological treatment, while volatilization occurs to a minor degree (Verlicchi et al., 2012). During secondary treatment, OMPs are biologically degraded to various degrees, resulting in mineralization or incomplete degradation (production of by-products). For pharmaceuticals, even if the compounds fall into the same therapeutical group, their biodegradability can show great variability. For example, Salgado et al. (2012) reported that, among NSAIDs, diclofenac exhibited low (< 25%) biodegradation, whereas ibuprofen and ketoprofen were biodegraded to a much higher extent (> 75%). Antibiotics are generally not readily biodegradable (Verlicchi et al., 2012). Bisphenol A and triclosan were also found to be susceptible to biodegradation (up to 85% and 81% respectively), while nonylphenol was biologically transformed to a lesser degree (up to 56%) in two WWTPs using activated sludge (Samaras et al., 2013). In the case of pesticide, Stasinakis et al. (2009) found that almost 60% of diuron was biodegraded during an activated sludge process.

In WWTPs, there are circumstances where the effluent concentrations of some OMPs exceed their influent concentrations. This can be explained by the presence of some substances, e.g. human metabolites and/or transformation products in the influent, which can subsequently be transformed back to parent compounds during biological treatment (e.g. diclofenac, carbamazepine, erythromycin, and sulfamethoxazole) (Göbel et al., 2007; Kasprzyk-Hordern et al., 2009). In addition, some pharmaceuticals excreted with feces are probably partly enclosed in feces particles and released during biological treatment. The negative removal has also been ascribed to the daily concentration fluctuations during the sampling period, the analytical uncertainty, or desorption of molecules from sludge and suspended particulate matter (Clara et al., 2004 and Köck-Schulmeyer et al., 2013).

1.2.5 Development of Monitoring Methods for OMPs

Thousands of organic chemicals have been produced and released into the aquatic environment, and new chemicals are being continuously introduced. Some of these contaminants pose risks to human health and/or the environment even at extremely low concentrations. Due to the increasing sensitivity of analytical methods, the number of OMPs detected in the aquatic environment is on the rise over the past decade. However, our knowledge of OMPs contamination levels in the aquatic environment is still limited because only a small fraction of OMPs can be probed by the vast majority of traditional target analysis. The target analysis used to assess

OMPs contamination levels usually covers few compounds and is time-consuming and costly. Alternatively, methods that fulfill the goal of high throughput monitoring of OMPs in environmental samples are gaining attractive prospects for environmental scientists and managers, because the screening method could analyze several hundreds or even more OMPs simultaneously.

Recent progress in technology has improved the ability to detect and quantify a large variety of chemicals in environmental samples, although there are as yet few papers reported (Du et al., 2013; Hanh et al., 2013; Kadokami et al., 2009; Loos et al., 2009; Vryzasa et al., 2009). In that context, Kadokami et al. (2005) has developed a new, fully automated identification and quantification database system (AIQS-DB) to permit quantification of nearly 1000 chemical substances using a gas chromatograph-mass spectrometer (GC-MS). The AIQS-DB, containing mass spectra, retention times, and calibration curves, allows identification and quantification of more than 1000 substances, without the use of chemical standards (Fig. 1.2).

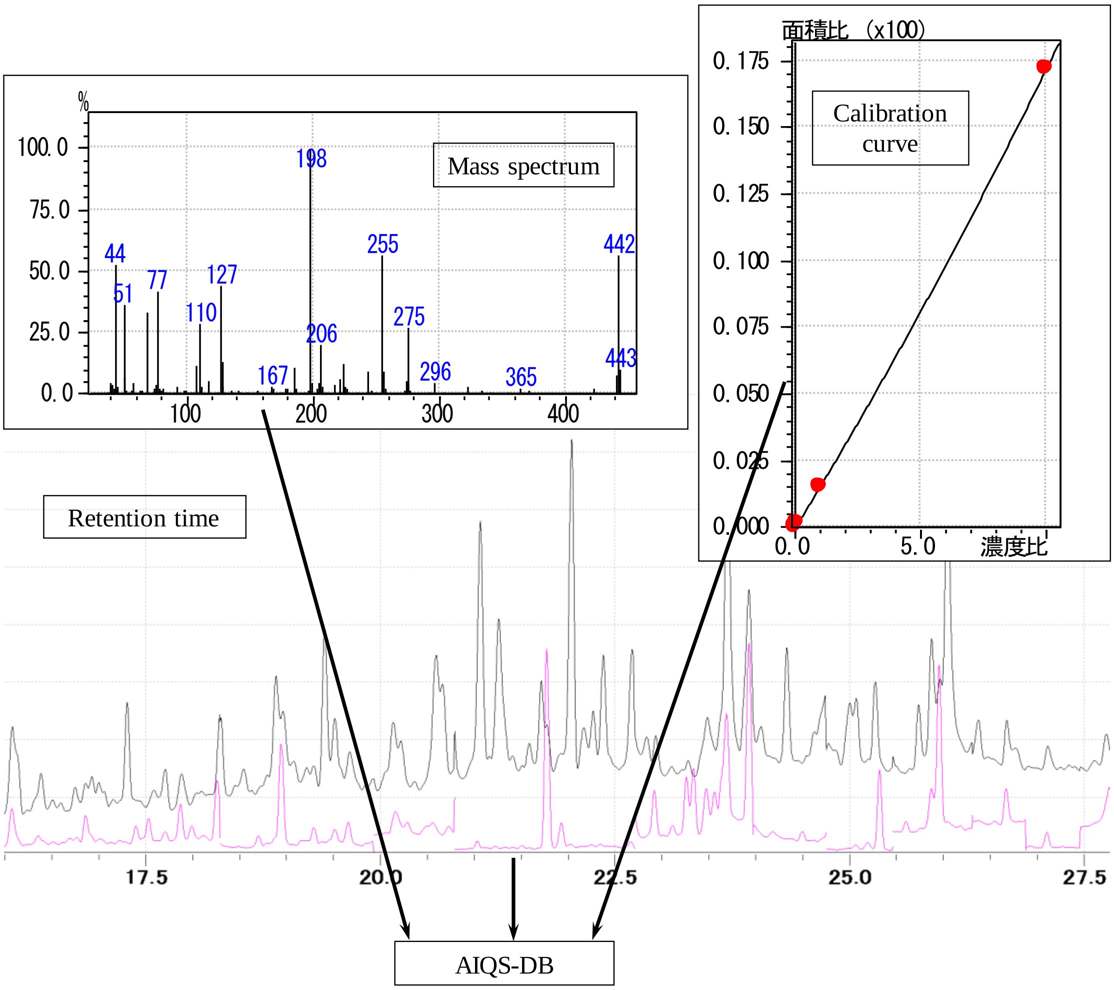


Fig. 1.2 The interface of AIQS-DB

With a projected retention time error of ±3 seconds during sample measurement, reliable identification was possible in conjunction with the mass spectrum. Reproducibility of quantitative values was less than 20%, which is comparable to conventional sample measurement using the calibration curve method. Furthermore, more than 90 percent of the registered substances were below the detection limit of 10 pg. Because the AIQS-DB permits measurement of a large number of chemical substances without using chemical standards, it can be applied to a wide range of applications (Kadokami et al., 2005). In addition, liquid chromatography time-of-flight mass spectrometry (LC–TOF/MS) analysis provides an expansive technique for identifying many known and unknown analytes. The time-of-flight (TOF)-MS analyzer provides the selectivity and the sensitivity required for efficient, wide-range screening, as it combines high, full-spectral sensitivity with high mass resolution so as to measure accurately the mass of any ionizable component in the sample. TOF-MS instruments are capable of 10000 or more resolving power expressed in terms of FWHM (full peak width at one-half maximum). TOF-MS has a high acquisition speed and provides accurate mass measurement (possibility to yield mass accuracy <2 ppm with an adequate calibration range) as well as full scan spectral sensitivity. Accurate mass measurement gives the elemental composition of parent and fragment ions, used to identify unknown species and a greater differentiation of isobaric species (two different compounds with the same nominal mass but different elemental composition, and thus, different exact masses). The environmental issue of OMPs is tied to the analysis of wastewater samples using the new analytical methods of the last decade, especially TOF/MS techniques. Because of the high complexity of some environmental samples (i.e. wastewater and sludge samples), high-resolving power techniques are needed to provide additional structural information.

1.3 Water Pollution in China

China's extraordinary economic growth, industrialization, and urbanization, coupled with inadequate investment in basic water supply and treatment infrastructure, have resulted in widespread water pollution. In China today approximately 700 million people over half the population consume drinking water contaminated with levels of animal and human excreta that exceed maximum permissible levels by as much as 86% in rural areas and 28% in urban areas (Wu et al., 1999). While the total amount of released industrial wastewater fluctuated around 22 billion tons from 1995 to 2004, the domestic sewage discharge increased from 13.1 billion tons in 1995 to 22.1 billion tons in 2000, and up to 26.1 billion tons in 2004 (State Environmental Protection Administration [SEPA] 1995–2004).

As a consequence, surface water quality has become an issue of great concern in China. A national survey of seven major rivers in China, carried out in 2004, revealed that water quality measurements in 28% of 412 monitored sections were below grade V, the worst grade in the national standard for water quality in China. These results indicate that, for these sections of river at least, the water supply is virtually of no practical or functional use, even for agricultural irrigation. For the Haihe River, which provides the cities of Beijing and Tianjin with the bulk of their drinking water, this figure was as high as 57%, and for the Liaohe River, which supplies water to Northeast China, it was 38%. Overall, more than 90% of the river sections that flowed through urban areas showed a water quality of grade V or worse (SEPA 1995–2004). The higher the grade, the worse the water quality; only water with a grade lower than III is drinkable. The same survey suggested that even the water quality of the Yangtze and Pearl Rivers, both of which have relatively abundant water flow, was a cause for concern; approximately 10% of the monitored sections of these two rivers also revealed water quality worse than grade V, and all monitored sections in the urban area of Guangzhou (on the Pearl River) had water quality around grade V or worse (Shao et al., 2006). The water quality of the rivers shown was characterized only by conventional indicators, such as chemical oxygen demand (COD), ammonia, and volatile phenols, among others. The situation is even more worrisome when endocrine disrupting organic substances are taken into consideration as well (An and Hu 2006).

Groundwater pollution in China is severe due to lax enforcement of pollution and illegal tapping of groundwater for industrial and agricultural use. However, little information is known for groundwater commination status in China. In May 2012, the Ministry of Land and Resources of China issued a Communique on Land and Resources of China 2011 which tested groundwater quality in 4727 spots in 200 cities and found that 55% of the groundwater samples were not recommended for human touch. The government has previously admitted that there is no other alternative water source for many cities in China other than groundwater. It has also recognized the difficulty in solving groundwater pollution. The best way to protect groundwater is the restrict water use and pollutants entering the system. In late 2011, the government issued the first-ever National Plan on groundwater Pollution Control in November 2011, setting aside RMB35 billion to tackle groundwater pollution. The plan also limits access to groundwater. The government reiterated their intention to exercise strict control on underground water exploitation in some decrees early 2013. A new Ministry of Land and Resources survey shows that the North China Plain suffers from severe groundwater pollution with over than 70% of overall groundwater quality classified as Grade IV+, in other words, unfit for human touch. The survey which started in 2006, is the most comprehensive regional groundwater quality and pollution investigation and was conducted by the institute of Hydro-geology and Environmental Geology Academy of Geological Sciences. The results show that groundwater pollution is more serious for shallow groundwater in the North China Plain compared to deep groundwater. There was almost no shallow groundwater of Grade I quality and only sporadic existence of groundwater at Π and Ш quality, putting the amount of groundwater at unfit for human touch at 77.8%. Deep groundwater fared only slightly better at 73.55%. These levels are much higher than the national overall groundwater quality levels of 55%. This level of pollution of groundwater is particularly worrying as the North China Plain is one of the China's most important agricultural regions, producing corn, sorgum, winter wheat, vegetables and cotton. It covers much of Henan, Hebei and Shandong and northern Jiangsu and Anhui provinces. Incidentally, Shandong, Henan, Jiangsu and Hebei are the top four farming provinces of China accounting for around 30% of national agricultural output value (China Water Risk).

1.4 Motivation and Objectives

Although the production and usage of POPs has been banned since 1970-1990s, small-scale production still exists in China (Leng et al., 2009). Recently, OCPs and PCBs were still being detected in various environmental media in China, including water, sediments, soil, and aquatic organisms which in some regions contained elevated concentrations (Yang et al., 2005). PCBs are a set of 209 congeners that were extensively manufactured between the late 1920s and 1970s. Most of the recent surveys have paid more attention to major and dioxin-like PCBs (i.e., IUPAC #28, #52, #101, #118, #138, #153 and #180) and have ignored the investigation of non-Aroclor PCBs because of the limited availability of commercial standards and difficulties in detecting all PCBs, quantification of which requires a high-resolution mass spectrometer (King et al., 2002). In the past decade, the rapid industrialization and urbanization of China especially around coastal areas including Shandong

Peninsula has led to serious pollution of the environment. In addition, the widespread use (since the 1950s) of OCPs to control soil-dwelling insects on the farmland surrounding Shandong Peninsula has exerted a heavy toll on the local environment. Several reviews have presented evidence that residues of OCPs and PCBs in different environmental media from coastal areas are relatively high, whereas information about the concentrations of these contaminants in foodstuffs is scarce. The likelihood that dietary intake which is an important route of human exposure to OCPs and PCBs has become a great concern and should receive more attention. High concentrations of OCPs have been detected in the breast milk of nursing women whose daily intake of OCPs via fish consumption was high (Sudaryanto et al., 2006; Shoiful et al., 2013). Given this information, one of the main objectives of the current study was to quantify the daily intake of OCPs through dietary exposure of persons living in the Shandong Peninsula and to assess the potential hazard of this exposure to human health.

Surface water quality in China has deteriorated as mentioned above in the last decade as a result of the rapid expansion of industrialization and urbanization, with many examples of acute impacts on aquatic organisms. For example, 100 tons of benzene, aniline, nitrobenzene and other toxicants were spilled into the Songhua River following a plant explosion in 2005 (He et al., 2013). In January 2013, more than 39 tons of aniline leaked into rivers in Shanxi province, posing a great threat to the safety of drinking water for downstream provinces (Areddy, 2013).

Tianjin is the fourth largest city in China, with a population of over 10 million. The city is located on the North West coast of Bohai Bay, and covers about 11200 km^2 of land. As a coastal city, Tianjin suffers from a lack of water resources, and the wastewater that is discharged into surface waters from major industries without effective treatment has caused serious pollution to the aquatic environment. Surface waters passing through Tianjin also provide important drainage and wastewater discharge functions for Beijing City and Hebei Province, ultimately entering into Bohai Bay and pose a significant threat to local ecosystems. Jinan, a medium-sized and less industrialized city in China, was also chosen for a comparison. Jinan，known as springe city, is the capital of Shandong province which located on China's east coast, between Shanghai and Beijing and ranked around 28th among the main cities in China according to the GDP figure in 2014.

Groundwater was the most vulnerable and a main reliable source of public drinking water supply in many regions of the world because of its good organoleptic properties. Increasing water demands associated with rapid urban development and expansion in China have led to overexploitation of groundwater resources, and the growing water scarcity has become a big challenge. In north China, groundwater is a critical source, and 400 out of 657 cities use groundwater for drinking water while 65% of all drinking water originates from groundwater (Ma et al., 2015). Beijing and Tianjin, among four municipalities directly controlled by the central government, are the most economically regions in north China along with highly industrialized areas and intensive agricultural activity. The major water source for Beijing and Tianjin is groundwater, which accounts for 75% and 30% of total water supply, respectively (IGES 2006). Facing increasing pressure on fresh water supplies, great efforts have been taken in conserving and augmenting the limited water resources in Beijing and Tianjin, such as waste water irrigation and groundwater recharge using reclaimed water. In addition, soil manure applications together with leaching from land fill and contaminated surface water also could pose a risk to the groundwater quality.

The aims of this study were to use a comprehensive method developed by Kadokami (Kadokami et al., 2005) using GC-MS and an analogous method utilizing liquid chromatography-time of flight mass spectrometry (LC-TOF-MS) to monitor 1300 OMPs in surface water from Tianjin and Jinan, and groundwater from Tianjin and Beijing. The results obtained in this study provide valuable information to refine pollutants inventories and develop appropriate strategies for water sources management, also help to precede with future development policies of water sources management and regulation.

Chapter 2 Materials and Analytical Methods

2.1 Study Areas and Sampling

2.1.1 Foodstuffs Collection for POPs Analysis

Samples of a total of 27 different food items, including foodstuffs of terrestrial and marine origin (each sample being about 500 g), were purchased during July and August of 2011 from local markets and supermarkets in urban areas of Yantai, Weihai, and Qingdao. We chose these cities in the Shandong Peninsula on the basis of their large populations and prosperous economies. Qingdao is located on the south facing coast of the Shandong Peninsula and estimated to be the home of about 8 million inhabitants. Lying across the Shandong Peninsula while looking out to the Yellow Sea, Qingdao is a major seaport, naval base, and industrial center. Yantai is the largest fishing seaport in Shandong and a robust economic center today. It is currently the second largest industrial city in Shandong, next only to Qingdao. However, the region's largest industry is agriculture. Weihai is a city in eastern Shandong Province. It is the easternmost prefecture-level city of the province and a major seaport. Figure 2.1 and Table 3.1 provide information about the samples.

Fig. 2.1 Map showing locations of Yantai, Weihai and Qingdao

The criterion for selection of foodstuffs was based on daily food consumption data from the Chinese Health and Family Planning Commission in 2002 (Zhai et al., 2005) and the FAO food balance sheet (FAO 2009), the goal being to account for 70% of the daily food consumption of local residents after taking into consideration their dietary habits. After collection, the samples were put into clean polyethylene bags and kept cool with frozen gel ice during transportation to a laboratory. They were then stored in a freezer at –20°C prior to analysis.

2.1.2 Surface Water Sampling

A total of 20 sampling sites were selected from Tianjin, including locations in three watersheds (Jiyun River, Hai River and Duliu River) and two sewage canals (Fig. 2.2); these sites were chosen to represent the dominant surface water quality in Tianjin. Sites J1—J6 were located in the Jiyun River watershed; Site J6 (Luann River) is the primary drinking water supply for Tianjin inhabitants. Eleven sites (H1—H11) were along Hai River watershed, the largest catchment in the northern China. Site D1 was in the Duliu River. Stations S1 and S2 were on the north and south sewage canals, respectively.

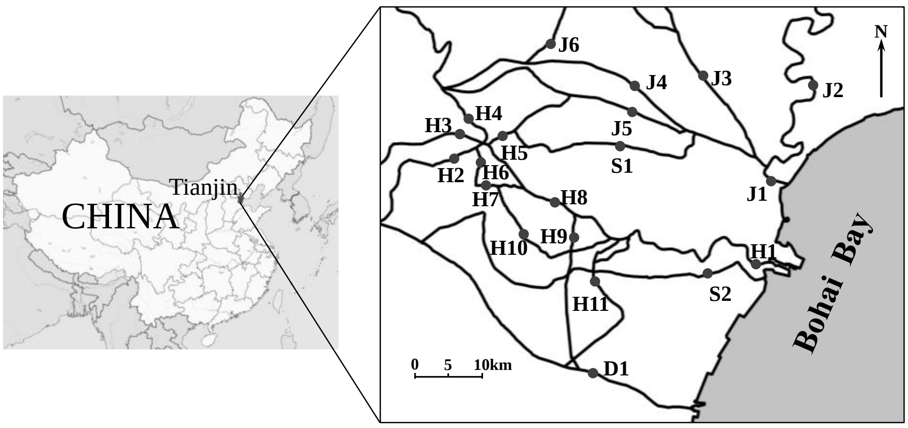


Fig. 2.2 Map of surface waters monitoring locations in Tianjin

A total of 14 sampling sites were selected from Jinan, including Yellow River, Xiaoqing River, two reservoirs and spring water (Fig. 2.3). Qiaoqing River is an important flood channel. Its functions contain flood protection, waterlogging elimination, irrigation and so on. In recent years, water environment of Xiaoqing River is deteriorated more and more because of the discharge of industry and living sewage. Yellow river (JN1, JN2 and JN3) and two reservoirs (JN13 and JN 14) were mainly used as drinking water source; JN12 was situated in spring water.

Samples were taken from surface waters no deeper than 1.0 m depth using amber glass bottles in December 2013. All sampling vessels were pre-cleaned with acetone, purified water, and water from the point of collection. After collection, samples were kept in the dark and cooled with icepacks during transport to a laboratory where the water samples were stored at 4°C for a maximum of 48 h until treatment.

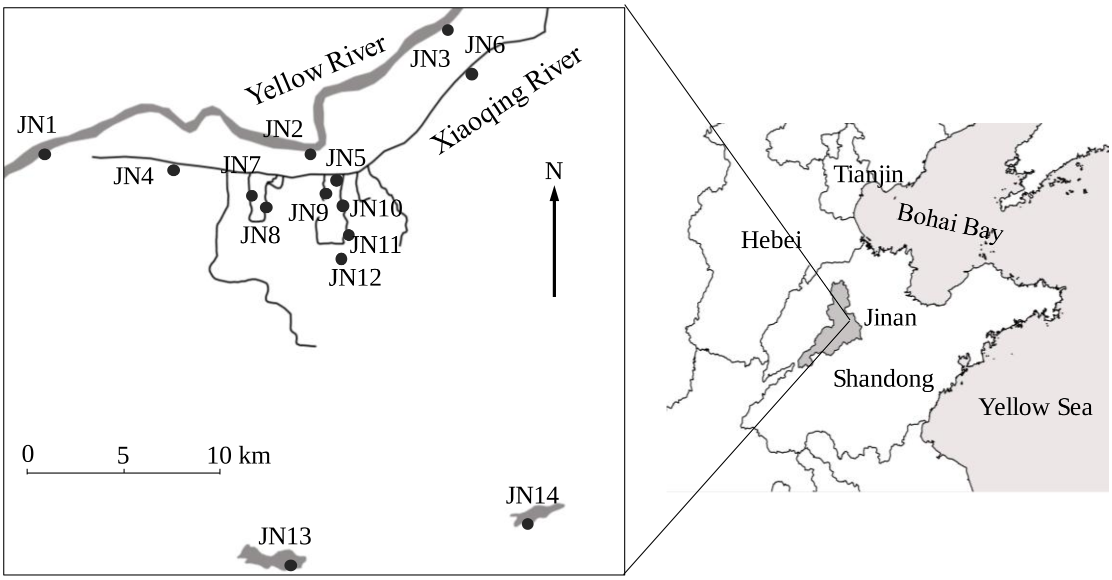


Fig. 2.3 Map of surface waters monitoring locations in Jinan

2.1.3 Groundwater Sampling

A total of ten and seventeen domestic wells were sampled during April 2015 throughout Beijing and Tianjin, respectively (Fig. 2.4), which have a total population of approximately 19 million inhabitants.

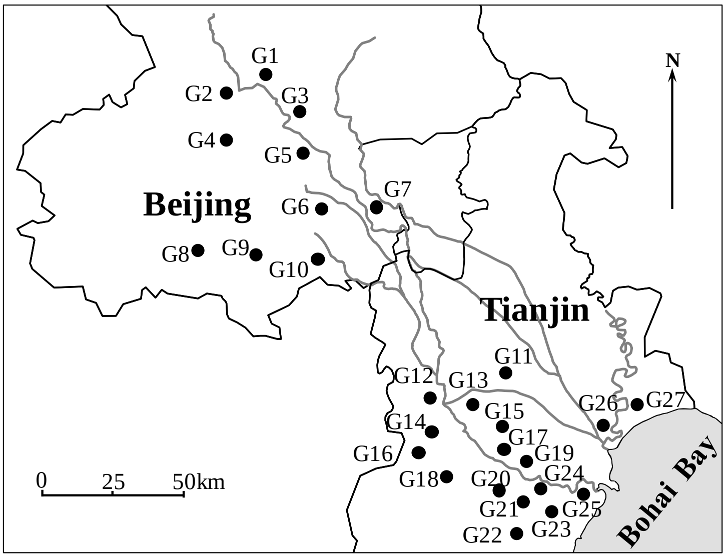


Fig. 2.4 Map of ground waters monitoring locations in Beijing and Tianjin

However, there is no attempt to determine the temporal patterns in organic micro-pollutants concentrations. Since little information is available on the suspected contaminated groundwater, samples were selected to across the urban, rural and remote areas. In addition, the sampling sites near the contaminated surface water were also collected. However, there were no strict selection criteria for the representative sampling stations. For all sites, a total of 1 L raw groundwater sample was taken using pre-cleaned Teflon-capped amber glass bottles, and all sampling vessels were pre-cleaned with acetone, purified water and water from the point of collection. The field blank samples consisting of milli-Q water were deployed to undergo the same procedure. Then samples were kept on ice during transport to a laboratory and analyzed within 48 h.

2.2 Analytical Procedures

2.2.1 Reagents for Extraction of POPs in Foodstuffs

Silica gel: Place the silica gel for the column chromatograph in a beaker, and put it into muffle furnace for 4h at 450°C. Transfer the silica gel into an evaporating dish so that it forms a layer of 10 mm or less. After heating the gel for approximately 18 h at 130°C, allow it to stand to cool for approximately 30 min in a desiccator. After preparation, then transfer the gel into a reagent bottle which can be sealed and store it in a desiccator.

Silica gel impregnated with silver nitrate [10% (mass fraction)]: After adding 28 ml of silver nitrate solution (400 g/L) prepared with silver nitrate to 100 g of silica gel, remove the moisture thoroughly in a rotary evaporator at 70°C in water bath under less than 10 hPa. Silica gel impregnated with silver nitrate shall, after preparation, transfer the mixture into a colored brown bottle which can be sealed and store it in a desiccator. In addition, light shall be shaded at the time of preparation and preservation as much as possible.

Silica gel impregnated with sulfuric acid [44% (mass fraction)]: After adding 78.6 g of sulfuric acid to 100 g silica gel, shake the mixture sufficiently so that it forms a powder. After preparation, transfer the powdered mixture into a reagent brown bottle which can be sealed and store it in a desiccator.

Silica gel impregnated with potassium hydroxide [2% (mass fraction)]: After adding 40 ml of potassium hydroxide solution (50 g/L) preparing with potassium hydroxide to 100 g of silica gel, dehydrate it under the reduced pressure at approximately 70°C in a rotary evaporator. After removing almost all the moisture raise the temperature from 50°C to 80°C, continue the dehydration under the reduced pressure (less than 10 hPa) at this temperature for approximately 1 h to pulverize the silica gel. After preparation, place it in an air tight reagent brown bottle and store in a desiccator.

2.2.2 Extraction Methods for POPs in Foodstuffs

Analysis of OCPs in foodstuffs was conducted based on QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe). About 10 g homogenized sample were placed into the 50 ml glass centrifuge tube and spiked with the internal standard, then added 5 ml buffer solution (pH=6). Then the sample was extracted with 30 ml acetonitrile shaking 2 times by hand. Then supernatants was obtained after centrifugation 5 min at 3500 rpm, and filtered with anhydrous sodium sulfate. Concentrated the solution with rotary evaporator to 1ml approximately, and transfer to the 20 ml tube until the mark of 20 ml with acetonitrile. Then take 4 ml solution exactly and pass through the DSC-18 column after washing with 5 ml acetonitrile, then eluted by 10 ml acetonitrile. The eluate was concentrated with rotary vacuum evaporator and exchanged solvent to hexane. Then the effluents were subjected to further cleanup with a glass column packed with 0.5 g PSA and 0.5 g Envi-Carbon after washing with 10ml hexane: toluene (3:1). About 20ml hexane: toluene (3:1) was used to elute the column, and then concentrated the eluate to 1 ml approximately. Finally, the solution was evaporated to 100 µL under the slight nitrogen flow after adding ^{13}C-labeled PCB IUPAC #15 and #28 (Wellington Laboratories, Canada), then transferred into the vial ready for HRGC/HRMS analysis.

Marine species samples were subjected to PCB analysis. Briefly, 5 g homogenized sample were placed into 500 ml separatory funnel, then added 50 ml 2N KOH/Ethanol to saponify the tissue and spiked with 50 µl internal standard (Cambridge Isotope Laboratories Inc., MA USA). The method of extraction was based on Liquid-Liquid extraction. Then extracted with 50 ml hexane shaking 3 times and combine the extracts, then washed with distilled water and 5 ml 0.1N hydrochloric acid to neutralize standing for 30 min. The organic solvent phase was dehydrated with anhydrous sodium sulfate and concentrated to 1 ml with rotary vacuum evaporator. Then cleaned up by a multilayer silica gel column in ascending order of anhydrous sodium, 10% $AgNO_3$ impregnated silica, activated silica, 44% H_2SO_4 impregnated silica, anhydrous sodium and after washing with 30 ml hexane, then eluted by 100 ml 2% dichloromethane in hexane. Then effluent was evaporated to 50 µL under slight nitrogen flow after adding ^{13}C-labeled PCB #138 (Wellington Laboratories, Canada), then transferred into the vial and ready for HRGC/HRMS analysis.

2.2.3 Surface Water and Groundwater Pretreatment

The surface water and groundwater share the same SPE extraction. Samples were prepared for measurement of both 944 semi-volatile organic compounds (SVOCs, Table S1) by GC/MS and 88 persistent organic pollutants (POPs, Table S2) by GC/MS/MS sharing the same method from Jinya et al. (2013). In short, surface water samples (1 L), spiked with surrogate standards (Table 2.5) were passed through a stack of multiple SPE disks (in ascending order, a glass membrane fiber disk (GMF 150, 47 mm, Whatman, Maidstone, UK), a styrene-divinylbenzene disk (Empore™ SDB-XD, 47 mm, 3M Co., St. Paul, MN, USA), and an activated carbon disk (Empore™ AC, 47 mm, 3M Co., St. Paul, MN, USA)), after which the disks were subjected to vacuum for 30 min to remove water. The GMF and XD disks were eluted sequentially with acetone and dichloromethane, whereas the AC disk was eluted with only acetone. Both eluates were mixed and concentrated to 1 mL, then reconstituted to 5 mL with hexane. The final volume was reduced to 0.4 mL under a gentle stream of nitrogen, and mixed internal standards (Table S1) were added prior to instrumental analysis.

Samples were prepared for measurement of 303 water-soluble chemicals (WSCs, Table S3) by filtration of surface water (1 L) through a 47 mm glass microfiber filter GF/C (Whatman, Maidstone, UK) after adding surrogate standards (Table 2.5). The suspended solid (SS) was subjected to sonication extraction with methanol twice. The filtrate was passed through a PS 2 Sep-Pak cartridge and an AC 2 Sep-Pak cartridge (Waters Associates, Milford, MA, USA) at a flow rate of 10 mL/min. The cartridges were eluted with methanol and dichloromethane. After combining the eluates and the extract from SS extraction, the mixture was concentrated to 50 µL under a gentle stream of nitrogen. Mixed internal standards (Table S3) were added and reconstituted to 1 mL with purified water prior to LC/TOF/MS analysis.

2.3 Instrumental Analysis

2.3.1 High-resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) analysis for OCPs and PCBs

The concentrations of OCPs and PCBs were determined on an Agilent-6890 GC gas chromatography (GC) system equipped with a high-resolution mass spectrometer (JEOL JMS-800, Japan). The separation was performed with a fused silica capillary column (HT8PCB, 60 m × 0.25 mm ID and 0.25 μm film thickness). Helium was employed as a carrier gas at a constant flow rate of 1.5 mL/min. The temperature of the injector was 220°C. The GC oven temperature was programmed as follows: initial temperature 120°C held for 1 min, then increased to 180°C at a rate of 20°C/min, increased to 210°C at a rate of 2°C/min, followed by 5°C/min until to 310°C which was maintained for 5 min. The high-resolution mass spectrometer HRMS was set programmed as follows: a temperature of the interface and ion source was both 280°C. The ionization mode, current, and energy were EI positive, 500 μA, and 10 kV, respectively. The resolution was set higher than 10000, and the analysis was conducted in selected-ion monitoring. The mass and retention time information for OCPs was showed in Table 2.1.

Table 2.1 Retention time and accurate mass for each OCPs of HGGC/HRMS analysis

Group	Compound	Retention time (min)	The accurate mass (m/z)	
Target compounds				
1	*α*-HCH	13.255	216.9145	218.9116
1	HCB	13.592	246.8443	248.8413
1	*γ*-HCH (Lindane)	15.149	216.9145	218.9116
1	*β*-HCH	15.426	216.9145	218.9116
1	*δ*-HCH	17.213	216.9145	218.9116
1	Heptachlor	17.901	271.8102	273.8072
1	Aldrin	20.306	262.857	264.854
2	Oxychlordane	22.938	386.8052	388.8023
2	*cis*-Heptachlor Epoxide	22.744	352.8442	354.8413
2	*trans*-Heptachlor Epoxide	23.038	352.8442	354.8413
3	*o,p'*-DDE	24.256	246.0003	247.9974
3	*trans*-Chlordane	24.45	372.826	374.823
3	*Trans*-Nonachlor	24.688	406.787	408.784

3	*Cis*-Chlordane	25.027	372.826	374.823
4	*p,p'*-DDE	26.116	235.0081	237.0052
4	Dieldrin	26.373	262.857	264.854
4	*o,p'*-DDD	26.845	235.0081	237.0052
4	Endrin	27.763	262.857	264.854
4	*o,p'*-DDT	28.25	235.0081	237.0052
4	*Cis*-Nonachlor	28.387	406.787	408.784
4	*p,p'*-DDD	28.988	235.0081	237.0052
4	*p,p'*-DDT	30.376	235.0081	237.0052
5	Mirex	33.539	278.8102	273.8072
Interal standards				
1	^{13}C-α-HCH	13.239	222.9347	224.9317
1	^{13}C-HCB	13.583	252.8644	254.8614
1	^{13}C-γ-HCH (Lindane)	15.133	222.9347	224.9317
1	^{13}C-β-HCH	15.41	222.9347	224.9317
1	^{13}C-2 CB(PCB #15)	15.431	234.0406	236.0376
1	^{13}C-δ-HCH	17.196	222.9347	224.9317
1	^{13}C-Heptachlor	17.874	276.8269	278.824
1	^{13}C-Aldrin	20.274	269.8805	271.8775
2	^{13}C-Oxychlordane	22.369	396.8388	398.8358
2	^{13}C-*cis*-Heptachlor Epoxide	22.718	362.8788	364.8748
3	^{13}C-*o,p'*-DDE	24.241	327.9783	329.9573
3	^{13}C-*trans*-Chlordane	24.424	382.8595	384.8566
3	^{13}C-*Trans*-Nonachlor	24.664	416.8205	418.8176
4	^{13}C-*p,p'*-DDE	26.099	258.0406	260.0376
4	^{13}C-Dieldrin	26.345	267.8834	269.8805
4	^{13}C-*o,p'*-DDD	26.826	247.0484	249.0454
4	^{13}C-Endrin	27.736	267.8834	269.8805
4	^{13}C-*o,p'*-DDT	28.234	247.0484	249.0454
4	^{13}C-Cis-Nonachlor	28.368	267.8834	269.8805
4	^{13}C-*p,p'*-DDD	28.97	247.0484	249.0454
4	^{13}C-*p,p'*-DDT	30.36	247.0484	249.0454
5	^{13}C-Mirex	33.159	276.8269	278.824

2.3.2 Analytical Methods for Monitoring 1300 OMPs by GC/MS, GC/MS/MS and LC/TOF/MS

Monitoring of 944 SVOCs (Table S1) was performed with a GC/MS (Shimadzu, QP-2100 Plus, Kyoto, Japan) in both selected ion monitoring (SIM) and total ion monitoring (TIM). Target SVOCs information and GC/MS conditions were described in Table S1 and 2.2, respectively. Total ion current chromatograms obtained by a

GC/MS-TIM were treated with an Automated Identification and Quantification System with a GC/MS database (AIQS-DB) in order to identify and quantify of 944 SVOCs (Kadokami et al., 2005).

Table 2.2 GC-MS conditions for comprehensive analysis

GC-MS: Shimadzu GCMS-QP 2010 Plus		
Column: J&W DB-5 ms (5% phenyl-95% methylsilicone) fused silica capillary column, 30 m X 0.25 mm i.d., 0.25 μm film		
Column: temperature programmed: 2 min at 40°C, 8°C/min to 310°C, 5 min at 310°C		
Transfer line: 300°C	Ion source: 200°C	Injector: 250°C
Injection method: splitless, 1 min for purge-off time		
Carrier gas: He	Linear velocity: 40 cm/s, constant flow mode	
Ionization method: EI		
Tuning method: target tuning for US EPA method 625		
Measurement method: SIM/Scan		
Scan range: 45 amu to 600 amu	Scan rate: 0.3 s/scan	

The prepared samples were analyzed for 81 compounds including organochlorine pesticides and PCBs with a GC/MS/MS (TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama, Japan) in selected reaction monitoring (SRM) mode. The details of compounds and instrument conditions were listed in Table S2 and 2.3, respectively. The 303 WSCs (Table S3) were measured with a LC/TOF/MS (Agilent 1200 HPLC Systems equipped with an Agilent 6220 TOF mass spectrometer, Tokyo, Japan). The LC/TOF/MS conditions were shown in Table 2.4.

Table 2.3 GC/MS/MS conditions

GC-MS-MS: Thermo Scientific TSQ Quantum XLS		
Column: J&W DB-5 ms (5% phenyl-95% methylsilicone) fused silica capillary column 30 m X 0.25 mm i.d., 0.25 μm film		
Column: temperature programmed: 2 min at 40°C, 8°C/min to 310°C, 4 min at 310°C		
Ion source: 250 °C	Transfer line: 300°C	Injector: 250°C
Injection method: splitless, 1 min for purge-off time		
Carrier gas: He	Flow rate: 1.2 ml/min, constant flow mode	
Ionization method: EI	Emission current: 50 μA	
Measurement method: SRM		

Table 2.4 LC/TOF/MS conditions

LC-TOF/MS: Agilent 1200 series equipped with 6220 Accurate-Mass LC/TOF/MS
Column: Inertsil ODS-4 column, 15 cm X 2.1 mm i.d., particle size 3 μm
Column Temperature: 40°C
Mobile phase: A Methanol (0.1% ammonium acetate); B Water (0.1% ammonium acetate)

Mobile phase programmed: 0 min at 5% A, increase to 95% A at 30 min and manitained 20 min		
	Post run time: 12.5 min	
Injection volume: 2 μL	Flow rate: 0.3 ml/min	
Ion Polarity: Positive	Gas temperature: 325 °C	
Drying Gas: 10 L/min	Fragmentor: 100 v	Vcap: 3500 v
Skimmer: 65 v	OCT 1 RF Vpp: 250 v	Nebulizer: 50 psi
Scan mode: full scan 50-1700 range	Reference masses: 121.0509 and 922.0098	

2.4 Risk Assessment

Average daily exposure for OCPs was calculated on the basis of food consumption and the corresponding concentration.

Average daily exposure (ng/kg body weight) =

Food consumption (g/kg body weight) × Contaminant concentration (ng/g ww)

Statistical data on food consumption were obtained from an investigation by the Chinese Health and Family Planning Commission (Zhai et al., 2005) and FAO food balance sheet (FAO, 2009). Chronic health hazard assessments for non-carcinogenic effects and assessment of carcinogenicity for lifetime exposure were considered separately. The reference dose for chronic oral exposure (RfD), obtained from the United States Environmental Protection Agency Integrated Risk Information System, was adopted to assess non-carcinogenic effects. The benchmark concentration for carcinogenic effects was calculated on the basis of risk level and oral slope factors[7)]. Risk level and body weight were set at one in a million due to lifetime exposure and 60 kg for an adult, respectively.

The environmental risk for OMPs in surface water and groundwater was assessed as described by several authors (EMEA, 2005; Tauxe-Wuersch et al., 2005). Risk quotients for aquatic organisms were calculated from the measured environmental concentration (MEC) and the predicted no effect concentration (PNEC) of the OMPs. MEC corresponds to the highest concentration measured in water samples during the sampling period. PNECs are the concentrations for which no adverse effect is suspected to occur. PNEC values for individual detected compounds were based on aquatic toxicity data from U.S. EPA.

There are no drinking water quality standards for human health for most of the chemicals screened in this work. Calculated human health impact values (CHIVs) were modeled for chemicals for which no drinking water guideline is available based on the approach currently used in Australia (NRMMC–EPHC–NHMRC, 2008). Effect values for chemicals for which there are no established guidelines and for which relevant health or toxicological information does not exist at this time are derived from TTCs (thresholds of toxicological concern) (EPHC–NHMRC–NRMMC, 2008). The TTCs were assigned to three levels based on their chemical structure, presence of structural alerts for toxicity and known metabolic pathways, according to the classification scheme of Cramer et al (1976). Toxicological information, such as acceptable daily intake (ADI), tolerable daily intake (TDI), reference dose (RfD), minimal risk level (MRL) and no observed effect level (NOEL), was used to calculate CHIVs by the equation 1 or equation 2. This information was mainly obtained from IRIS (Integrated Risk Information System), WHO (World Health Organization), ATSDR (Agency for Toxic Substances and Disease Registry), NJDEP (New Jersey Department of Environmental Protection) and CEPA (California Environment Protection Agency). It should be noted that TDI, RfD and MRL are considered as the equivalent safe ingestions of chemicals with an ADI.

$$\text{CHIV (mg/L)} = \frac{\text{NOEL (mg/kg bw/day)} \times \text{bw (kg)} \times \text{P}}{\text{SF} \times \text{V (L/day)}} \quad \text{(Equation 1)}$$

where NOEL is No Observed Effect Level; bw, average body weight of an adult (assumed to be 70 kg; Wu et al., 2010); P, proportion of chemical intake from water; SF, toxicological safety factor. The default value of 10% was adopted for P, and the SF set at 1000 to address the uncertainty inherent in extrapolating from animal studies to human populations, was (EPHC–NHMRC–NRMMC, 2008).

$$\text{CHIV (mg/L)} = \frac{\text{ADI (mg/kg bw/day)} \times \text{bw (kg)} \times \text{P}}{\text{V (L/day)}} \quad \text{(Equation 2)}$$

where ADI, average daily intake; V, volume consumed

Calculation of CHIVs for pharmaceuticals was undertaken using the lowest daily oral therapeutic dose for an adult (LDTD) obtained from the Monthly Index of Medical Specialties (MIMS) based on equation 3.

$$\text{CHIV (mg/L)} = \frac{\text{LDTD (mg/day)} \times \text{P}}{\text{SF} \times \text{V (L/day)}} \quad \text{(Equation 3)}$$

The risk quotient was calculated as the maximum concentration of detected chemicals by the corresponding drinking water guideline. Thus an RQ below 1 suggested there is no adverse health effect on human health.

2.5 Quality Assurance and Quality Control (QA/QC)

All data were subjected to strict quality control procedures. The limit of detection for POPs was calculated by three times of standard deviation obtained from five times duplicates of the blank sample, which spiked with lowest concentration of target compounds on the calibration curve, while ten times of standard deviation was defined as limit of quantitation. The limit of detection and limit of quantitation for the 209 PCB congeners were 0.11–4.0 pg/g and 0.36–13 pg/g ww, while for each OCPs compound were 0.006–0.3 ng/g and 0.02–1 ng/g ww, respectively. Each sample was analyzed in duplicate and relative standard deviations of detected compounds were less than 8%. A solvent blank and procedure blank were run in every batch of samples to check for the cross-contamination and interference. However, no target compounds for OCPs and PCBs were detected (less than the limit of detection). The recoveries of internal standards of individual compounds for each OCPs and PCBs were showed in Fig. 2.5 and Fig. 2.6, respectively.

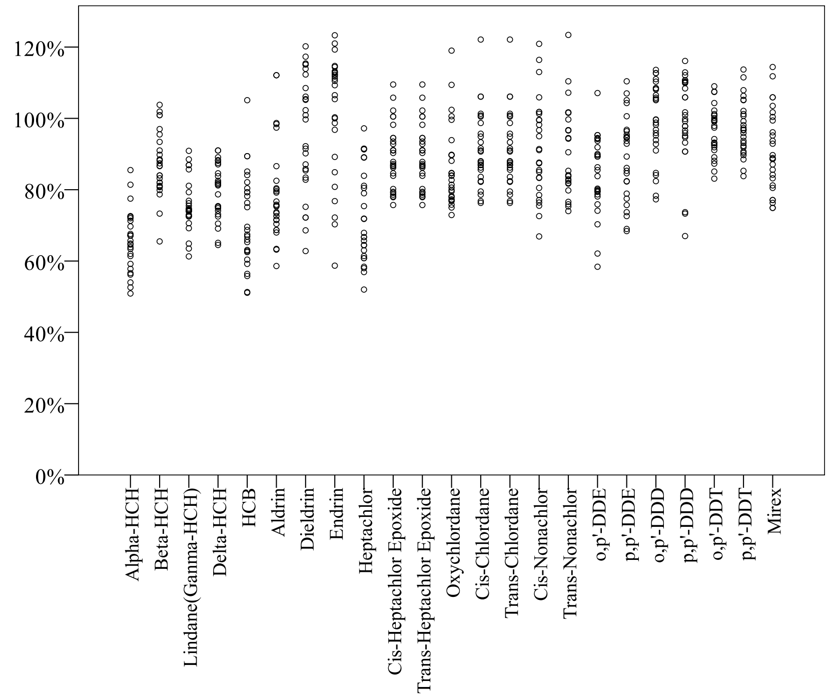


Fig. 2.5 The recovery of individual OCPs

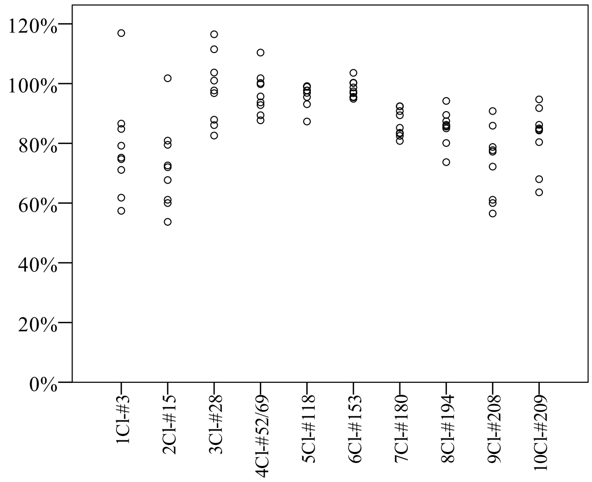


Fig. 2.6 The recovery ratio of individual PCBs isomer

The lowest quantification limits of each chemical for GC–MS, GC–MS/MS, and LC–TOF/MS were calculated by dividing the lowest amounts on individual calibration curve by sample volume, which were 5－1000 ng/L, 0.1－1.0 ng/L and 4－200 ng/L, respectively. Surrogate standards were spiked into all samples prior extraction to check recovery and matrix effects. For GC–MS/MS and GC–MS, average of recovery rates for 10 surrogates, which represented the same spectrum of physico-chemical characteristics as the chemicals in the analytical screen, including non-polar to polar chemicals, ranged from 67%－135% (Table 2.5), while for LC–TOF/MS the average of recovery rates for 3 surrogate standards ranged from 64% to 85% (Table 2.5). The recoveries were not used to correct the concentrations of the detected compounds. Reagent blanks and procedure blanks were run in every 5 samples to check for cross-contamination and interference. The results of reagent and procedure blank samples were shown in Table 2.6. It should be noted that less than 6% of screened chemicals were detected at concentrations higher than instrumental quantification limits in blank samples during GC–MS analysis; in such cases, sample data were blank-subtracted.

Table 2.5 Recovery of surrogate compounds

No	Detector	Compounds	Average, %	RSD, %
1	GC/MS	1,2-Dichlorobenzene-d_4	89	11.0
2	GC/MS	2,4-Dichlorophenol-d_3	76	14.4
3	GC/MS	4-Chloroaniline-d_4	70	7.0
4	GC/MS	Benzophenone-d_{10}	135	15.4
5	GC/MS	Pentachlorophenol-$^{13}C_6$	67	12.6
6	GC/MS	$C_{20}D_{42}$	97	15.0

7	GC/MS	Bisphenol A-d_{14}	69	9.2
8	GC/MS	p-Terphenyl-d_{14}	80	7.0
9	GC/MS	4,4'-DDT-$^{13}C_{12}$	117	8.6
10	GC/MS	Tris(2-ethylhexyl)phosphate-d_{51}	91	13.9
11	LC–TOF/MS	Imidacloprid-d_4	85	16.1
12	LC–TOF/MS	Simazine-d_{10}	64	9.3
13	LC–TOF/MS	Carbary-d_7	83	14.4

Table 2.6 Concentration of detected chemicals in procedure samples (ng/L)

No.	Compounds	Detector	Procedure blank （n=4)			Reagent blank （n=4)		
			Mean ng/L	Minimum ng/L	Maximum ng/L	Mean ng/L	Minimum ng/L	Maximum ng/L
1	Bis(2-ethylhexyl)phthalate	GC–MS	139	123	155	82	75	89
2	Phenol	GC–MS	50	27	82	n.d.	n.d.	n.d.
3	Benzyl alcohol	GC–MS	214	158	274	n.d.	n.d.	n.d.
4	Cholesterol	GC–MS	257	114	562	n.d.	n.d.	n.d.
5	Naphthalene	GC–MS	97	68	114	n.d.	n.d.	n.d.
6	Benzothiazole	GC–MS	124	88	155	n.d.	n.d.	n.d.
7	2–Ethyl-1-hexanol	GC–MS	152	64	195	n.d.	n.d.	n.d.
8	2-Methylnaphthalene	GC–MS	99	57	146	n.d.	n.d.	n.d.
9	2,6-Dimethylnaphthalene	GC–MS	136	55	166	n.d.	n.d.	n.d.
10	1,3-Dimethylnaphthalene	GC–MS	133	54	163	n.d.	n.d.	n.d.
11	Di(2-ethylhexyl)adipate	GC–MS	124	121	135	121	106	132
12	Diethyl phthalate	GC–MS	125	103	141	83	80	85
13	Diisobutyl phthalate	GC–MS	106	47	160	n.d.	n.d.	n.d.
14	Di-n-butyl phthalate	GC–MS	67	38	103	18	17	19
15	Methyl octanoate	GC–MS	88	61	131	n.d.	n.d.	n.d.
16	Biphenyl	GC–MS	39	12	85	n.d.	n.d.	n.d.
17	Acetophenone	GC–MS	66	44	89	n.d.	n.d.	n.d.
18	Oxabetrinil	GC–MS	54	n.d.	73	n.d.	n.d.	n.d.
19	1,4-&2,3-Dimethylnaphthalene	GC–MS	52	22	62	n.d.	n.d.	n.d.
20	Longifolene	GC–MS	43	25	66	n.d.	n.d.	n.d.
21	Pentamethylbenzene	GC–MS	51	23	77	n.d.	n.d.	n.d.
22	Dimethyl phthalate	GC–MS	39	11	54	7.8	6.7	8.9
23	Biphenyl	GC–MS	16	12	24	n.d.	n.d.	n.d.
24	1-Nonanol	GC–MS	32	n.d.	130	n.d.	n.d.	n.d.

25	Acenaphthene	GC–MS	29	17	42	n.d.	n.d.	n.d.
26	Phenanthrene	GC–MS	27	8.8	41	n.d.	n.d.	n.d.
27	Dibenzofuran	GC–MS	19	12	26	n.d.	n.d.	n.d.
28	Quinoline	GC–MS	29	19	34	n.d.	n.d.	n.d.
29	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	GC–MS	23	n.d.	42	n.d.	n.d.	n.d.
30	Ethanol, 2-phenoxy-	GC–MS	27	n.d.	50	n.d.	n.d.	n.d.
31	1,4-Dichlorobenzene	GC–MS	29	n.d.	41	n.d.	n.d.	n.d.
32	Octanol	GC–MS	18	n.d.	47	n.d.	n.d.	n.d.
33	4-Cymene	GC–MS	27	17	38	n.d.	n.d.	n.d.
34	Fluorene	GC–MS	14	7.2	17	n.d.	n.d.	n.d.
35	4-tert-Octylphenol	GC–MS	16	8.5	21	n.d.	n.d.	n.d.
36	Tributyl phosphate	GC–MS	25	n.d.	43	n.d.	n.d.	n.d.
37	Isophorone	GC–MS	11	n.d.	22	n.d.	n.d.	n.d.
38	Acenaphthylene	GC–MS	10	5.8	13	n.d.	n.d.	n.d.
39	Nonylphenol	GC–MS	8.5	n.d.	18	n.d.	n.d.	n.d.
40	2,6-Diisopropylnaphthalene	GC–MS	9.1	n.d.	36	n.d.	n.d.	n.d.
41	Methyl palmitate	GC–MS	6.8	n.d.	20	n.d.	n.d.	n.d.
42	N-Nitrosopiperidine	GC–MS	4.8	n.d.	19	n.d.	n.d.	n.d.
43	Methyl dodecanoate	GC–MS	4.7	n.d.	19	n.d.	n.d.	n.d.
44	Bis(2-ethylhexyl) sebacate	GC–MS	2.8	n.d.	11	n.d.	n.d.	n.d.
45	Diphenylmethane	GC–MS	2.2	n.d.	8.7	n.d.	n.d.	n.d.
46	Nitrobenzene	GC–MS	1.5	n.d.	5.9	n.d.	n.d.	n.d.
47	PCB#1	GC–MS/MS	0.20	0.11	0.41	n.d.	n.d.	n.d.
48	Hexachlorobenzene	GC–MS/MS	0.12	0.12	0.12	n.d.	n.d.	n.d.

2.6 Statistical Analysis

The statistical analysis was performed using Microsoft Excel 2010 (Microsoft Japan, Tokyo, Japan) and IBM SPSS Statistics Ver. 20 (IBM Japan, Tokyo, Japan).

The multivariate statistical techniques such as cluster analysis (CA), factor analysis (FA) and principal component analysis (PCA) have widely been used as unbiased methods in analysis of water-quality data for drawing meaningful information (Bengraine and Marhaba, 2003; Voncina et al., 2002; Singh et al., 2004; Reghunath et al., 2002; Wunderlin et al., 2001; Simeonov et al., 2003). Cluster analysis helps in grouping objects (cases) into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes. The class characteristics are not known in advance but may be determined from the analysis. The results of CA help in interpreting the data and indicate patterns (Vega et al., 1998). Factor analysis, which includes PCA is a very powerful technique applied to reduce the dimensionality of a data set consisting of a large number of inter-related variables, while retaining as much as possible the variability present in data set. This reduction is achieved by transforming the data set into a new set of variables, the principal components (PCs), which are orthogonal (non-correlated) and are arranged in decreasing order of importance. Mathematically, the PCs are computed from covariance or other cross-product matrix, which describes the dispersion of the multiple measured parameters to obtain eigenvalues and eigenvectors. Principal components are the linear combinations of the original variables and the eigenvectors (Wunderlin et al., 2001).

Monitoring programs for thousands of organic micro-pollutants in surface water and groundwater inevitably generate complicated data matrix associated with a large number of parameters. Multivariate statistical techniques such as cluster analysis (CA) and principal component analysis (PCA) were employed in this work to offer an attractive approach to interpret the datasets and refine the inventory information.

Chapter 3 Occurrence and Risk Assessment of POPs in Foodstuffs

3.1 Levels of OCPs in Foodstuffs

Organochlorine Pesticides (OCPs) was detected in 27 food items from Shandong Peninsula. The results of detection frequency were shown in Fig. 3.1. Among the OCPs the most frequently detected in foodstuffs was HCHs which has been detected in above 69% of the samples, followed by DDTs and mirex (in above 25%). The endrin, heptachlor, cis-nonachlor, cis-heptachlor epoxide and dieldrin were not detected in the foodstuffs. The OCPs were produced massively and used extensively in China from 1950s to 1980s (Jin et al., 2008). The production and usage of HCH were extensive during 1950s–1980s. Since it was banned in 1983, the total amount of technical HCH produced in China was 4.5 million tons. So far HCH was ubiquitous and widely detected in the environment include sea, sediments, soils, human breast milk etc. with respect to the low volatility and high melting point.

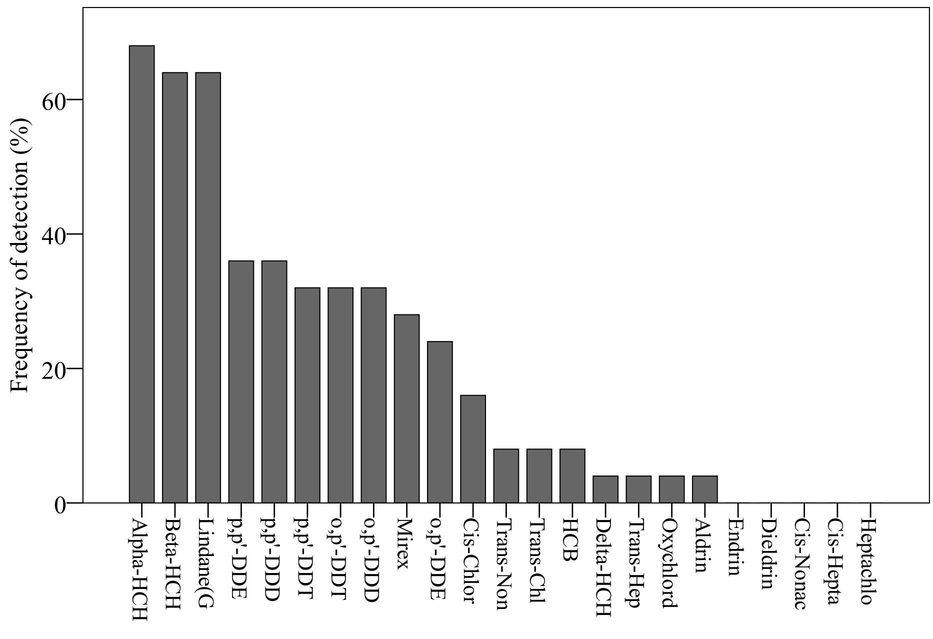


Fig. 3.1 Frequency of detection of OCPs in foodstuffs from Shandong Peninsula

The concentrations of OCPs in foodstuffs collected from Shandong Peninsula are summarized in Table 3.1. The total concentration of OCPs in all the foodstuffs ranged from not detected (ND) to 73 ng/g ww.

Table 3. 1 Concentrations of OCPs (ng/g ww) in foodstuffs from Shandong Peninsula

Food items	Sampling site		∑HCHs	HCB	∑Drins	∑Heptachlor	∑CHLs	∑DDTs	Mirex	∑OCPs
Mackerel (n=3)	Each from Yantai,Qingdao and Weihai	Mean	0.05	0.23.	n.d.	n.d.	0.08	24	0.05	24
		Minimum	n.d.	n.d.	n.d.	n.d.	0.03	3.1	0.01	3.1
		Maximum	0.16	0.68	n.d.	n.d.	0.17	36	0.08	36
Squid (n=2)	Each from Qingdao and Weihai	Mean	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05
		Minimum	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Maximum	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09
Clam (n=2)	Each from Qingdao and Weihai	Mean	0.15	n.d.	n.d.	n.d.	n.d.	5.9	0.01	6.1
		Minimum	0.14	n.d.	n.d.	n.d.	n.d.	5.1	n.d.	5.2
		Maximum	0.15	n.d.	n.d.	n.d.	n.d.	6.7	0.01	6.9
Corn (n=2)	Each from Qingdao and Weihai	Mean	0.04	0.43	n.d.	n.d.	n.d.	n.d.	0.01	0.48
		Minimum	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Maximum	0.08	0.86	n.d.	n.d.	n.d.	n.d.	0.01	0.95
Mung bean (n=2)	Each from Qingdao and Weihai	Mean	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04
		Minimum	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Maximum	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07
Red bean (n=2)	Each from Qingdao and Weihai	Mean	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04
		Minimum	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Maximum	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07
Soybean (n=2)	Each from Qingdao and Yantai	Mean	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.26
		Minimum	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08
		Maximum	0.45	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.45
Sea weed	Weihai		0.06	n.d.	n.d.	n.d.	n.d.	0.44	n.d.	0.50
Shrimp	Yantai		0.26	n.d.	n.d.	n.d.	n.d.	1.8	0.02	2.1
Croaker	Weihai		0.30	n.d.	n.d.	n.d.	0.32	72	0.22	73
Wine	Yantai		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Date	Yantai		0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1

Rice	Yantai	0.27	n.d.	n.d.	n.d.	n.d.	0.10	n.d.	0.37
Peanut oil	Yantai	2.4	n.d.	n.d.	0.17	n.d.	7.8	n.d.	10
Colza oil	Weihai	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tea	Weihai	0.50	n.d.	n.d.	n.d.	n.d.	0.13	0.02	0.66
Raisin	Qingdao	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06
Millet	Qingdao	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.26
Honey	Qingdao	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

∑HCH=sum of *α*-, *β*- ,*γ*- and *δ*-HCH n.d.= lower than quantitation

∑Drins=sum of aldrin, dieldrin and endrin

∑Heptachlor=sum of heptachlor, cis-heptachlor epoxide and *trans*-heptachlor epoxide

∑CHLs= sum of oxychlordane, cis-chlordane, *trans*-chlordane, *cis*-nonachlor and *trans*-nonachlor

∑DDTs=sum of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT

The highest concentration was found in croaker, followed by mackerel (mean level 24 ng/g ww), peanut oil (10 ng/g ww), clams (mean level 6.1 ng/g ww), and shrimp (2.1 ng/g ww). The concentrations in other samples were lower than 1 ng/g ww. High concentrations of OCPs in marine fish and peanut oil in the present study have also been found in food items collected from Hong Kong (Qin et al., 2011).

Among the OCPs, HCHs were the prevalent compounds detected in most of the samples, except for wine, colza oil and honey. The concentrations of HCHs ranged from n.d. to 2.4 ng/g ww. The highest concentration was found in peanut oil, followed by tea (0.50 ng/g ww) and soybean (0.45 ng/g ww). These concentrations were higher than the residue levels in marine species (n.d. to 0.3 ng/g ww) in the study which can be explained by the fact that HCHs were used mainly in agriculture for controlling pests in the study area and prone to accumulate in fatty tissues of terrestrial organisms, while only a small portion of the HCHs used on agriculture fields was transported to the aquatic environment through surface runoff. Low concentrations of HCHs in marine samples have also been found in other coastal areas of China, for example 0.39 ng/g ww in croaker from Shanghai (Yang et al., 2006), 0.07–0.70 ng/g ww in fish from Daya Bay (Guo et al., 2008), and 0.19–0.93 ng/g in marine species from Xinghua Bay (Yatawara et al., 2010). The concentration of HCHs in peanut oil in the present study was comparable or lower than that from other regions. For example, the concentration of HCHs was 4.6 ng/g in peanut oil from Hong Kong (Qin et al., 2011) and 30–1400 ng/g in groundnut oil from India (Bajpai et al., 2007). The composition of HCH isomers in foodstuffs from the Shandong Peninsula are shown in Fig. 3.2.

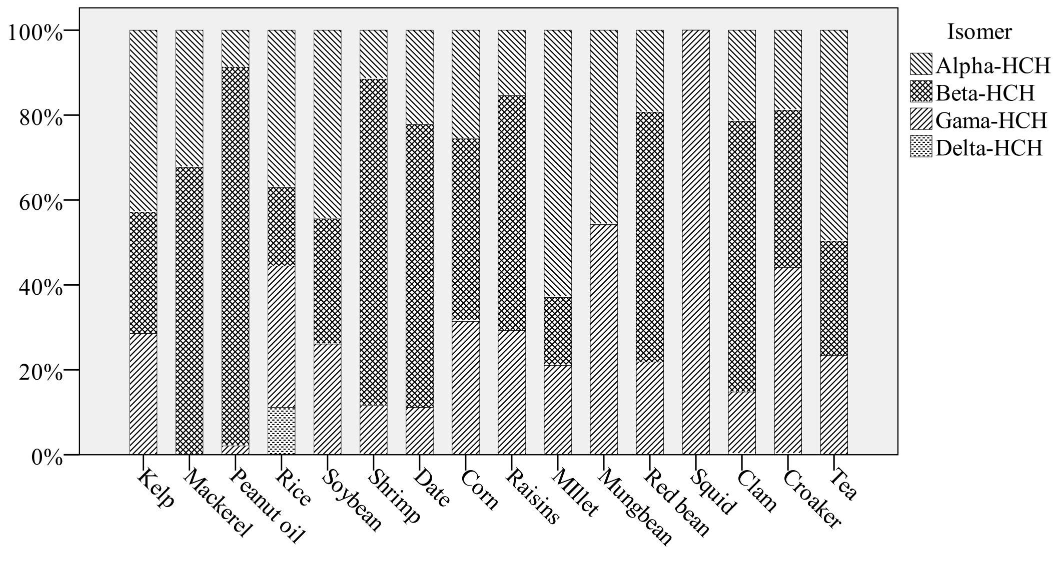


Fig. 3.2 HCH isomer profiles in foodstuffs from the Shandong Peninsula

The composition of the HCHs varied among samples in the present study. The results showed α-HCH and β-HCH were the main isomers in foodstuffs and on average accounted for 32% and 41% of the total HCHs, respectively. The mean composition of γ-HCH was 22%, and the δ-HCH was only detected in peanut oil. It was obvious that β-HCH was dominant in our samples, which can be attributed to its low vapor pressure, higher lipophilicity, and greater stability in the environment compared to α-HCH and γ-HCH. Commercial HCH has two forms, technical HCH [α-HCH (55–80%), β-HCH (5–14%), γ-HCH (8–15%), and δ-HCH (2–16%)] and lindane (pure γ-HCH) (Gong et al., 2007). Compared to technical HCH, low proportion of α-HCH in our study reflects major environmental degradation effects and high proportion of γ-HCH presumably reflects recent inputs of lindane.

DDTs were the predominant compounds in foodstuffs from Shandong Peninsula. The concentrations of DDTs in the study ranged from n.d. to 72 ng/g ww, and the elevated concentrations were found in marine fish species. The difference between the concentrations of DDTs between mackerels (mean concentration 24 ng/g) and clam (mean concentration 5.9 ng/g) in this study reflects differences in habitats and feeding habits (Shailaja et al., 1997). The concentrations of DDTs in marine fish in our study were higher than those from Sweden (8.2–14 ng/g in fish) (Darnerud et al., 2006) and the central Adriatic Sea (0.78–8.9 ng/g ww in marine species) (Perugini et al., 2004). Concentrations of DDTs reported from other coastal areas in China include 120 ng/g ww (adjusted level) in croaker from the Hangzhou Bay (Nakata et al., 2005) and a median level of 80 ng/g ww in fish from the Daya Bay (Guo et al., 2008). The concentrations of DDTs in our study were comparable to these high levels and should arouse much attention, although the concentrations were still far below the Chinese maximum residue limit (500 ng/g).

The composition of the DDTs in foodstuffs from the Shandong Peninsula is shown in Fig. 3.3. The ratio of DDE (*o,p'*-DDE and *p,p'*-DDE) to DDTs is a good indicator of recent inputs of DDT, which lower than 60% indicating a recent input. In the present study the ratio of DDE to DDTs was 100% in peanut oil, rice, and tea, the implication being that the DDT had been almost completely metabolized, and the source of the DDTs in these samples may mainly from the atmosphere, since adsorption of DDTs from soil would have been impossible for these plants. However, the ratios of DDE to DDTs in marine species were 0 in seaweed, 33% in mackerel, 58% in shrimp, 41% in clam, and 23% in croaker, the implication being that the input of DDT into the marine environment was recent, especially in the case of the seaweed.

The source of DDT may originate from the antifouling paints which applied to the fishing fleet considering the well-developed fishing industry in the Shandong Peninsula. It has been reported that DDT is still produced in China for the synthesis of dicofol as an intermediate for controlling mites and in antifouling paints for ship maintenance. To eliminate and replace the application of DDT in antifouling paints, the Chinese government is developing new alternative compounds together with the United Nations Development Programme.

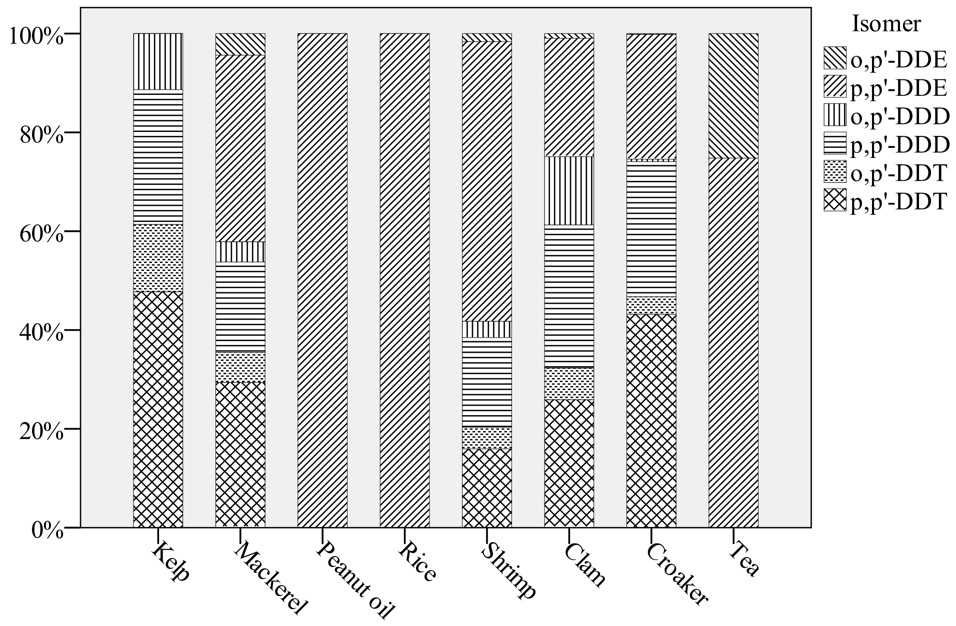


Fig. 3.3 Compositions of DDTs in foodstuffs from the Shandong Peninsula

Drins (aldrin, dieldrin and endrin) in foodstuffs collected from the Shandong Peninsula were not detected in the present study because they have never been produced and applied on a large scale in China. HCB was detected only in mackerel (0.23 ng/g ww) and corn (0.86 ng/g). Similar results have also been reported by Yang (Yang et al., 2006), who found that the concentrations of HCB in fish and shellfish were 0.27–0.35 ng/g ww from Tianjin and 0.04–1.19 ng/g ww from Shanghai. Heptachlor was only detected in peanut oil (0.17 ng/g ww) in this study which may come from the historical use because it has been banned since 1982 in China. Chlordanes (sum of oxychlordane, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor and *trans*-nonachlor) were detected in mackerel (0.08 ng/g ww) and croaker (0.32 ng/g ww). The concentration of mirex was on the order of 0.22 ng/g ww in croaker, >0.05 ng/g ww in mackerel, >0.02 ng/g ww in shrimp and tea, and >0.01 ng/g in clams from Qingdao. In foodstuffs collected from Cambodia (Wang et al., 2011), the levels of chlordanes were 0.03–1.21 ng/g ww, the level of mirex was 0.03–0.78 ng/g ww, and the level of HCB was 0.01–0.66 ng/g ww; the levels of these compounds in the present study were comparable or lower.

3.2 PCBs Levels in Marine Species

The concentrations of detected PCB congeners in marine organisms (including mackerel, clam, croaker, squid and shrimp) collected from the Shandong Peninsula are shown in Table 3.2. The concentrations of ∑209PCBs from Shandong Peninsula were in the range of 0.33–3.1 ng/g ww. The highest concentration was found in mackerel (mean, 3.1 ng/g ww), followed by squid (mean, 2.6 ng/g ww) and shrimp (0.93 ng/g ww). For comparison, fish from Russia contained 0.31–30 ng/g ww (Polder et al., 2010), and fish from Sweden contained 8.2–14 ng/g ww (Darnerud et al., 2006). The concentrations of ∑209PCBs in the present study were rather low compared to these values, presumably because of the historically low production in China (8000 tons) (Jiang et al., 1997). According to published data (Pan et al., 2010), the concentrations of PCBs in marine sediments from the Shandong Peninsula are comparatively low and range from 0.27 to 0.64 ng/g. The concentrations of PCBs measured in the environment matrix in China have been generally lower than those reported in developed industrial countries such as the United States and Japan due to less historical usage (Jiang et al., 2005). The composition of the different PCB homologues in foodstuffs from the Shandong Peninsula is presented in Fig. 3.4.

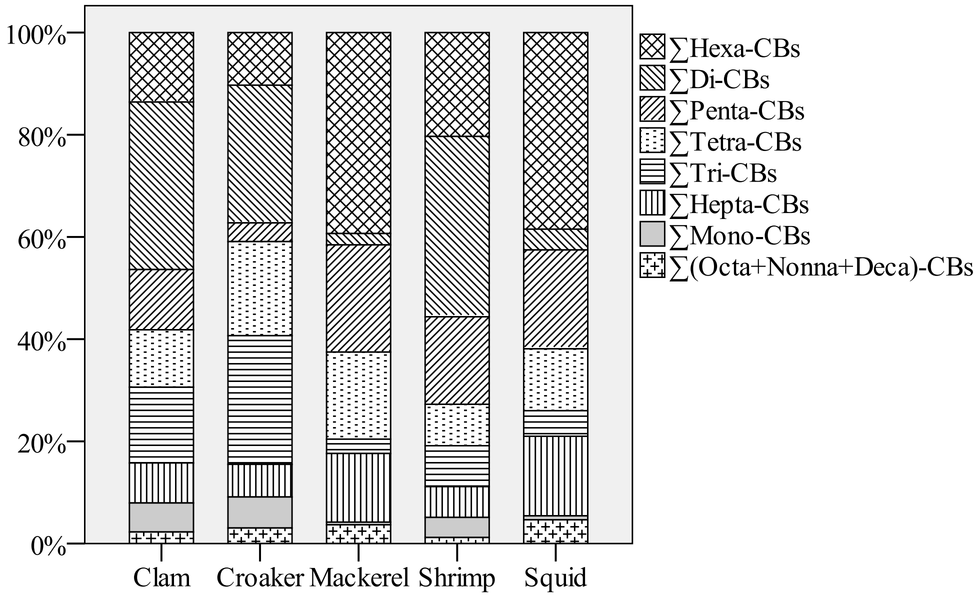


Fig. 3.4 PCB homologue profiles in marine foodstuffs

Table 3.2 Concentrations of detected PCBs in marine species from Shandong Peninsula (pg/g ww)

*IUPAC numbers of PCB	Shrimp	Croaker	Mackerel (n=3)			Squid (n=2)			Clam (n=2)		
			Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
1	21	10	11	2.0	19	8.2	4.2	12	9.3	8.8	10
2	7.0	3.4	2.5	n.d.	4.3	4.8	1.8	7.9	4.3	2.5	6.1
3	9.2	6.3	2.5	1.8	3.9	6.9	2.0	12	6.1	4.0	8.3
10	n.d.	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4	n.d.	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8/5	n.d.	n.d.	1.5	n.d.	4.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
11	330	84	66	18	110	110	n.d.	210	110	35	190
19	n.d.	1.8	n.d.	n.d.	n.d.	2.2	1.5	3.0	0.80	n.d.	1.6
18	12	13	12	7.2	15	17	12	23	8.5	6.3	11
17	3.6	4.5	4.6	2.1	5.9	2.9	n.d.	5.7	3.0	2.1	3.9
24	n.d.	n.d.	n.d.	n.d.	n.d.	0.38	n.d.	0.76	n.d.	n.d.	n.d.
27	0.92	1.1	0.40	n.d.	1.2	0.90	n.d.	1.8	0.53	n.d.	1.1
32	4.2	5.5	4.4	3.0	5.4	6.3	4.6	7.9	3.7	2.6	4.7
16	3.2	3.3	2.5	n.d.	3.8	3.4	3.2	3.5	2.5	2.0	3.0
26	2.5	3.0	4.1	2.1	5.3	5.9	2.7	9.1	1.3	n.d.	2.5
25	n.d.	1.3	4.0	n.d.	6.4	1.5	n.d.	3.0	n.d.	n.d.	n.d.
31	14	16	16	10	19	32	14	51	9.1	6.0	12
28	14	17	22	9.0	29	34	13	55	9.0	6.0	12
21	n.d.	n.d.	4.1	n.d.	12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
20/33	7.3	7.8	5.4	n.d.	12	8.2	7.7	8.6	5.7	4.4	7.0
22	4.3	4.8	5.7	3.7	7.0	8.4	5.9	11	3.1	2.1	4.2
36	n.d.	n.d.	0.28	n.d.	0.84	3.5	n.d.	7.0	3.1	n.d.	6.1
39	2.6	n.d.	n.d.	n.d.	n.d.	0.54	n.d.	1.1	0.48	n.d.	1.0
35	2.8	0.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	n.d.	2.0
37	3.0	2.2	n.d.	n.d.	n.d.	1.2	n.d.	2.4	n.d.	n.d.	n.d.
50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.69	n.d.	1.4
53	1.4	1.5	2.5	n.d.	3.7	1.8	n.d.	3.7	0.72	n.d.	1.4
51	n.d.	n.d.	13	n.d.	22	1.3	n.d.	2.6	n.d.	n.d.	n.d.
45	n.d.	n.d.	0.88	n.d.	2.6	0.81	n.d.	1.6	n.d.	n.d.	n.d.
46	n.d.	n.d.	0.48	n.d.	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
52/69	25	13	41	18	58	57	13	102	6.0	n.d.	12
73	n.d.	n.d.	38	n.d.	58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
49	n.d.	9.8	19	11	24	43	7.7	79	3.9	n.d.	7.8
65/75	n.d.	n.d.	17	n.d.	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
48/47	9.0	9.5	65	10	130	52	10	94	4.2	n.d.	8.3
44	14	n.d.	16	n.d.	25	27	n.d.	54	n.d.	n.d.	n.d.
59	n.d.	7.3	2.3	n.d.	6.8	3.8	n.d.	7.7	3.6	n.d.	7.2
42	n.d.	n.d.	10	n.d.	17	5.6	n.d.	11	n.d.	n.d.	n.d.
64	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2	n.d.	4.4
72	n.d.	n.d.	6.7	n.d.	12	26	n.d.	52	n.d.	n.d.	n.d.
71	n.d.	n.d.	3.8	n.d.	11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
68	n.d.	n.d.	180	n.d.	290	10	n.d.	19	1.9	n.d.	3.7
40	n.d.	n.d.	n.d.	n.d.	n.d.	2.4	n.d.	4.8	n.d.	n.d.	n.d.
74	n.d.	5.3	2.6	n.d.	7.8	22	n.d.	44	2.6	n.d.	5.3
70	4.9	7.8	15	n.d.	28	28	10	46	4.2	n.d.	8.5
66	n.d.	6.1	50	13	77	26	7.5	45	3.5	n.d.	6.9
60	n.d.	n.d.	38	7.1	56	n.d.	n.d.	n.d.	3.9	n.d.	7.8
56	n.d.	n.d.	n.d.	n.d.	n.d.	4.2	n.d.	8.4	n.d.	n.d.	n.d.
77	22	n.d.	0.82	n.d.	2.5	n.d.	n.d.	n.d.	1.6	n.d.	3.3
104	n.d.	n.d.	7.9	n.d.	13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
103	n.d.	n.d.	8.0	n.d.	14	5.5	n.d.	11	1.3	n.d.	2.6
100	n.d.	n.d.	70	0.87	120	6.7	n.d.	13	n.d.	n.d.	n.d.
94	n.d.	n.d.	1.3	n.d.	2.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
102/93	8.0	n.d.	7.8	n.d.	23	3.7	n.d.	7.4	n.d.	n.d.	n.d.

98/95	9.9	n.d.	33	7.8	66	37	9.1	64	4.5	n.d.	8.9
88	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
91	3.8	n.d.	40	n.d.	74	0.59	n.d.	1.2	1.2	n.d.	2.5
121	n.d.	n.d.	35	n.d.	54	16	1.4	31	n.d.	n.d.	n.d.
92	4.9	n.d.	7.1	n.d.	12	13	2.4	24	0.95	n.d.	1.9
84	n.d.	n.d.	5.8	4.3	6.6	4.2	1.9	6.4	n.d.	n.d.	n.d.
89	n.d.	n.d.	12	n.d.	29	n.d.	n.d.	n.d.	0.94	n.d.	1.9
90	n.d.	n.d.	25	n.d.	39	5.4	n.d.	11	n.d.	n.d.	n.d.
101	15	2.2	58	25	110	89	12	170	6.0	n.d.	12
113	13	n.d.	11	n.d.	32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
99	16	n.d.	31	14	49	72	6.2	140	2.6	n.d.	5.2
112/119	n.d.	n.d.	20	1.0	41	6.7	1.4	12	n.d.	n.d.	n.d.
83	n.d.	n.d.	6.8	n.d.	14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
109	n.d.	n.d.	1.5	n.d.	4.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
86	n.d.	n.d.	6.2	n.d.	17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
117/97	n.d.	n.d.	33	n.d.	95	16	n.d.	33	n.d.	n.d.	n.d.
125/116	3.4	n.d.	17	n.d.	52	2.1	n.d.	4.3	n.d.	n.d.	n.d.
87/115	4.1	n.d.	26	10	36	28	4.8	52	2.4	n.d.	4.9
111	3.1	n.d.	0.53	n.d.	1.6	n.d.	n.d.	n.d.	1.7	n.d.	3.4
85	n.d.	n.d.	15	n.d.	26	12	n.d.	24	0.81	n.d.	1.6
120	1.5	1.1	10	n.d.	30	50	n.d.	100	3.7	n.d.	7.4
110	6.3	1.8	47	19	85	6.9	n.d.	14	3.1	n.d.	6.1
82	n.d.	n.d.	5.7	n.d.	9.4	4.2	n.d.	8.5	n.d.	n.d.	n.d.
124	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
107/108	n.d.	0.90	13	3.8	19	11	2.2	20	1.1	n.d.	2.1
123	6.0	n.d.	n.d.	n.d.	n.d.	0.16	n.d.	0.32	n.d.	n.d.	n.d.
106	5.8	n.d.	n.d.	n.d.	n.d.	6.4	n.d.	13	n.d.	n.d.	n.d.
118	37	4.3	54	23	78	57	12	100	7.2	3.6	11
114	1.3	n.d.	n.d.	n.d.	n.d.	5.2	n.d.	10	n.d.	n.d.	n.d.
122	1.3	n.d.	n.d.	n.d.	n.d.	5.8	n.d.	12	n.d.	n.d.	n.d.
105	10	1.5	24	10	35	28	5.4	50	1.7	n.d.	3.3
127	10	n.d.	0.86	n.d.	2.6	2.6	n.d.	5.2	0.94	n.d.	1.9
126	2.9	n.d.	6.9	3.7	9.1	3.2	2.2	4.2	1.1	n.d.	2.1
155	n.d.	n.d.	570	7.1	910	61	4.9	120	2.3	n.d.	4.5
150	n.d.	n.d.	3.0	n.d.	9.0	4.0	n.d.	8	n.d.	n.d.	n.d.
152	n.d.	n.d.	0.77	n.d.	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
145	n.d.	n.d.	4.0	n.d.	6.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
136	n.d.	n.d.	11	n.d.	22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
148	n.d.	n.d.	2.6	n.d.	6.0	15	n.d.	30	1.2	n.d.	2.4
154	n.d.	n.d.	14	2.8	22	16	n.d.	32	n.d.	n.d.	n.d.
151	8.8	n.d.	19	7.5	30	25	4.5	45	n.d.	n.d.	n.d.
135	1.7	n.d.	3.5	n.d.	10	12	2.8	22	1.3	n.d.	2.6
144	n.d.	n.d.	6.8	n.d.	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
147	n.d.	n.d.	5.4	n.d.	13	7.5	n.d.	15	n.d.	n.d.	n.d.
149	6.6	5.2	64	21	120	95	15	180	2.2	n.d.	4.5
139	5.8	n.d.	9.4	n.d.	28	84	13	160	n.d.	n.d.	n.d.
140	n.d.	n.d.	2.6	n.d.	7.9	2.3	n.d.	4.6	6.0	n.d.	12
143	n.d.	n.d.	2.3	n.d.	6.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
134	n.d.	n.d.	1.9	n.d.	5.8	1.2	n.d.	2.5	n.d.	n.d.	n.d.
142	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
131	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
133	1.6	n.d.	n.d.	n.d.	n.d.	5.6	n.d.	11	n.d.	n.d.	n.d.
165	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
146	12	2.5	27	10	43	2.4	n.d.	4.8	n.d.	n.d.	n.d.
132	1.9	n.d.	7.1	n.d.	21	54	3.8	105	2.3	n.d.	4.5
161	n.d.	n.d.	71	4.5	175	16	n.d.	32	1.8	n.d.	3.7
153	35	8.8	78	32	118	165	15	315	10	8.6	11
168	32	5.5	73	27	113	120	14	226	6.3	5.1	7.4
141	3.8	n.d.	13	5.8	20	13	1.9	25	n.d.	n.d.	n.d.
137	2.1	n.d.	5.7	n.d.	10	n.d.	n.d.	n.d.	1.0	n.d.	1.9
130	2.2	n.d.	7.7	n.d.	14	0.71	n.d.	1.4	n.d.	n.d.	n.d.

163	8.9	3.5	42	18	66	62	8.0	116	1.6	n.d.	3.1
138	9.4	n.d.	94	37	147	137	6.7	267	n.d.	n.d.	n.d.
160	23	6.6	11	n.d.	27	3.2	n.d.	6.3	6.1	6.0	6.2
158	20	n.d.	8.5	1.8	15	n.d.	n.d.	n.d.	3.6	n.d.	7.2
129	n.d.	n.d.	2.0	n.d.	6.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
166	n.d.	n.d.	3.8	n.d.	6.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
159	n.d.	n.d.	0.79	n.d.	2.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
128	n.d.	n.d.	33	11	51	35	2.6	67	n.d.	n.d.	n.d.
162	3.7	n.d.	n.d.	n.d.	n.d.	28	2.1	53	n.d.	n.d.	n.d.
167	4.0	0.63	10	4.8	15	4.3	1.7	6.9	1.1	n.d.	2.2
156	n.d.	n.d.	14	7.3	21	13	n.d.	27	n.d.	n.d.	n.d.
157	6.0	0.81	8.6	n.d.	15	6.2	1.4	11	1.0	n.d.	2.1
184	n.d.	n.d.	240	13	420	77	n.d.	153	0.6	n.d.	1.1
179	1.5	n.d.	4.1	n.d.	9.1	14	2.4	26	1.1	n.d.	2.1
176	n.d.	n.d.	2.0	n.d.	5.0	4.0	n.d.	8.1	n.d.	n.d.	n.d.
178	3.0	0.43	6.7	n.d.	12	12	1.6	23	0.78	n.d.	1.6
175	0.60	n.d.	1.5	n.d.	3.6	1.5	n.d.	3.0	n.d.	n.d.	n.d.
182/187	15	4.0	36	19	53	99	8.0	189	6.6	5.5	7.7
183	2.3	1.2	15	7.2	23	25	1.3	50	1.4	1.2	1.6
185	n.d.	n.d.	1.4	n.d.	3.0	2.3	0.48	4.2	n.d.	n.d.	n.d.
174	1.3	n.d.	6.2	n.d.	13	n.d.	n.d.	n.d.	1.0	n.d.	2.0
181	n.d.	n.d.	6.6	n.d.	18	14	2.3	25	0.32	n.d.	0.64
177	n.d.	n.d.	7.1	3.1	14	20	n.d.	40	1.3	n.d.	2.6
171	1.0	n.d.	4.7	n.d.	11	12	n.d.	25	n.d.	n.d.	n.d.
173	n.d.	n.d.	0.71	n.d.	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
172	1.4	n.d.	2.7	n.d.	8.1	n.d.	n.d.	n.d.	0.31	n.d.	0.62
192	n.d.	n.d.	0.31	n.d.	0.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	12	5.8	26	n.d.	48	1.9	n.d.	3.8	4.1	n.d.	8.3
193	12	5.7	24	n.d.	71	88	3.8	172	6.5	4.8	8.2
191	0.78	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
170	4.5	2.1	13	n.d.	24	0.80	n.d.	1.6	2.0	1.8	2.2
190	n.d.	1.6	13	4.1	27	29	n.d.	58	0.86	n.d.	1.7
189	1.2	n.d.	2.9	n.d.	5.0	n.d.	n.d.	n.d.	0.44	n.d.	0.87
202	n.d.	n.d.	3.8	n.d.	6.3	5.6	n.d.	11	n.d.	n.d.	n.d.
200	n.d.	n.d.	3.5	1.7	5.0	4.5	n.d.	8.9	n.d.	n.d.	n.d.
204	n.d.	n.d.	2.5	n.d.	4.0	1.1	n.d.	2.3	n.d.	n.d.	n.d.
197	n.d.	n.d.	5.7	n.d.	10	4.0	n.d.	7.9	n.d.	n.d.	n.d.
199	n.d.	n.d.	0.63	n.d.	1.9	1.4	n.d.	2.8	n.d.	n.d.	n.d.
198/201	2.4	2.6	10	7.2	14	20	n.d.	41	n.d.	n.d.	n.d.
196	1.6	1.9	6.9	5.3	9.3	8.7	n.d.	17	n.d.	n.d.	n.d.
203	n.d.	n.d.	4.5	2.1	7.6	10	n.d.	19	n.d.	n.d.	n.d.
195	n.d.	n.d.	3.2	2.0	4.6	3.9	n.d.	7.7	n.d.	n.d.	n.d.
194	1.8	2.9	11	10	14	17	1.2	32	n.d.	n.d.	n.d.
205	n.d.	n.d.	2.6	1.9	3.3	2.0	n.d.	3.9	n.d.	n.d.	n.d.
208	n.d.	n.d.	7.7	2.6	12	5.9	n.d.	12	1.1	n.d.	2.2
207	n.d.	n.d.	11	5.4	16	4.8	n.d.	10	n.d.	n.d.	n.d.
206	n.d.	2.4	11	10	12	11	n.d.	22	1.1	n.d.	2.1
209	5.3	n.d.	28	8.2	41	20	10	30	5.7	n.d.	11
∑Mono-CBs	37	20	16	7.2	27	20	8.0	32	20	16	23
∑Di-CBs	330	88	68	22	110	110	n.d.	210	110	35	190
∑Tri-CBs	75	82	86	42	108	130	76	180	52	31	72
∑Tetra-CBs	76	60	520	99	767	310	70	550	39	n.d.	78
∑Penta-CBs	160	12	640	130	1000	500	120	880	41	3.6	78
∑Hexa-CBs	190	34	1200	210	1900	1000	110	1900	47	30	65
∑Hepta-CBs	56	21	410	110	650	400	25	780	27	26	29
∑Octa-CBs	5.8	7.5	55	32	79	78	1.2	160	n.d.	n.d.	n.d.
∑Nona-CBs	n.d.	2.4	30	18	39	22	n.d.	43	2.1	n.d.	4.3
∑Deca-CBs	5.3	n.d.	28	8.2	41	20	10	30	5.7	n.d.	11
Total PCBs	930	330	3100	680	4600	2600	650	4500	350	140	550

It is apparent that the main homologues corresponded to di-CB to hexa-CB; these homologues accounted for 90% of the total PCBs in most cases. The tendency of the PCB homologues to accumulate in tissue reflected their lipophilicity which increased with the number of chlorine atoms. However, compounds that are almost fully chlorinated are so large that they have great difficulty passing through the cell membranes (Yang et al., 2006). In the present study the dominant congeners were PCB #11, #18, #28, #101, #118, #155, #153, #138, and #180. The contribution of main congeners to ∑209PCBs is shown in Fig. 3.5.

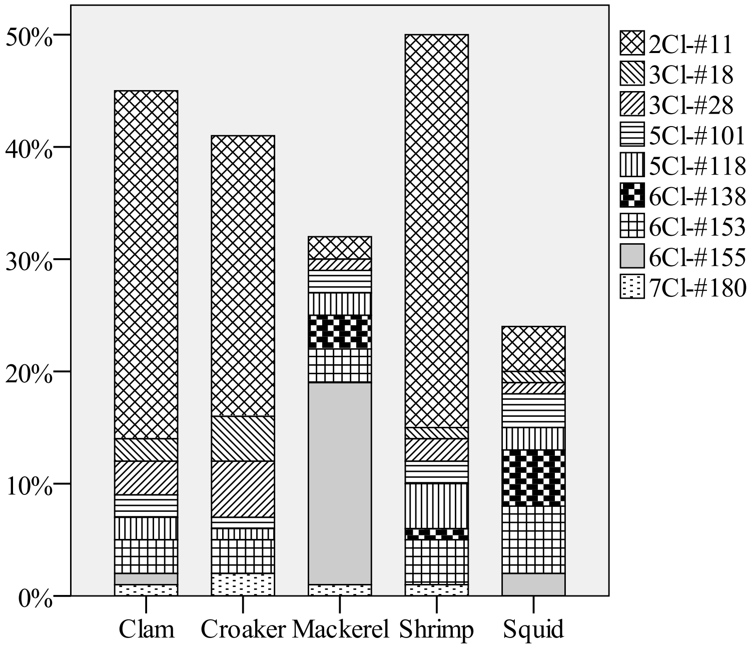


Fig. 3.5 Contribution of main congeners to ∑209PCBs

PCB #11, #153, and #155 were predominant and ubiquitous in the marine samples from the Shandong Peninsula. It is interesting to note that PCB #11 accounted for a large proportion in clams (41%), croaker (25%) and shrimp (35%). The source of PCB #11 is unclear at present. In recent years, PCB #11 has been detected in various media, including air, water, sediments, and biota (Rodenburg et al., 2010). The environmental source of PCB #11 is significantly different from other Aroclor PCBs, and in some special areas PCB #11 has become the dominant pollutant. Hu et al. (2008) reported that PCB #11 was not detected or was present in low levels in commercial Aroclor mixtures. Instead, it is produced as a by-product during the production of diarylide yellow pigments (Hu et al., 2008). Although the commercial PCB mixtures, such as the Aroclors, are (even today) the most significant sources of PCBs to the environment, individual PCB congeners can also be produced as byproducts during the production of other chemicals and can be released to the environment. These so-called “incidental PCBs” include 3,3’-dichlorobiphenyl (PCB-11), which may come from the production of dichlorobenzidine dyes. Perhaps as a result of this process, PCB-11 has been found in New York/New Jersey wastewater (Litten et al., 2002), in Delaware River water (Du et al., 2008), in Arctic and Antarctic air (Choi et al., 2008), in Chicago air (Hu et al., 2008), and in Philadelphia air (Du et al., 2009). PCB-11 is not a component of the commercial Aroclor mixtures produced in the United States or in the Clophen PCB mixtures produced in Europe (Schultz et al., 1989; Frame et al., 1996).

A separate study has demonstrated that PCB IUPAC #11 produces neurochemical effects in rat cerebellar granule cells (Mariussen et al., 2001). Based on these results, large-scale field and laboratory studies have focused on this specific compound and have found the existence of PCB IUPAC #11 in water, biota, and sediments (Rodenburg et al., 2010). The detection of PCB #11 could have important impacts on regulatory decisions in the future, although identifying the source of PCB #11 and assessing its toxicity and potential effects on human health will require further investigation.

3.3 Risk Characterization

The oral RfD value and cancer benchmark concentrations for organochlorine pesticides associated with food consumption are summarized in Table 3.3.

In the present study, the average daily exposure from foodstuffs was highest for DDTs (32 ng/kg/d), followed by HCH (2.2 ng/kg/d). However, these values were much lower than the corresponding non-carcinogenic RfD value and cancer benchmark concentration (Table 3.3). It should be noted the DDTs and HCHs are still a potential threat to human health because of their lipophilicity and low biodegradability. Marine fish containing high concentrations of OCPs play a significant role in daily human exposure, and people who consume more fish may have a higher potential exposure risk. Similar evaluation of these pollutants in marine fish has also been conducted in other coastal areas around China and has shown that DDTs may be of particular concern (Jiang et al., 2005).

Table 3.3 Average daily exposure and benchmark concentration for OCPs in foodstuff

Foodstuff	Consumption (g/person/d)	∑HCH	HCB	∑Drins	∑Heptachlor	∑CHLs	∑DDTs	Mirex
Sea weed	22	1.3	0	0	0	0	9.7	0
Sea food Mackerel Shrimp Croaker Squid Clam	85	20	0	0	0	6.8	1700	4.9
Bean Soybean Red bean Mung bean	4.2	0.91	0	0	0	0	0	0
Vegetable Oil Peanut oil Colza oil	33	40	0	0	2.8	0	130	0
Cereals Corn Millet	24	4	10	0	0	0	0	0.12
Honey	0.68	0	0	0	0	0	0	0
Tea	2.2	1	0	0	0	0	0.28	0.04
Wine	3.5	0	0	0	0	0	0	0
Rice	240	64	0	0	0	0	24	0
Date	0.29	0.03	0	0	0	0	0	0
Raisin	11	0.66	0	0	0	0	0	0
Total exposure (ng/person/d)		130	10	0	2.8	6.8	1900	5
Total exposure (ng/kg bw/d)		2.2	0.17	0	0.05	0.11	32	0.08
Oral RfD (μg/kg/d)		-	0.8	-	0.5	0.5	0.5	0
Cancer slope [per (mg/kg/d)]		1.3	1.6	-	4.5	0.35	0.34	-
Cancer (μg/kg/d)		0.11	0.09	-	0.03	0.4	0.42	

3.4 Conclusion

This work provides important data about the existence of PCB #11 in foodstuffs in China, which accounts for a large proportion of total PCB concentration. The potential source of PCB #11 is important from a toxicity standpoint and its ubiquity as an environmental pollutant. The origin of non-Aroclor PCB #11 was estimated to be its production as a by-product during the production of diarylide yellow pigments. However, the concentrations of ∑209PCBs were relatively low compared to concentrations reported from Russia and Sweden. This difference can be explained by the lower background levels in marine sediments surrounding the Shandong Peninsula.

Among the OCPs, HCH and DDTs were the dominant compounds. The highest concentration of HCHs was found in peanut oil, but the level was lower than concentrations reported from India and Vietnam. The composition of HCH reflected the historical use of technical HCH and recent inputs of lindane. The concentrations of DDTs in our study were similar to those from other coastal regions of China. The composition of the DDTs indicated a recent input of DDT into the marine environment. The potential source of DDT may be antifouling paints on the fishing fleet. Daily exposure was somewhat lower than the non-carcinogenic RfD value and cancer benchmark concentration. The results implied that intake of OCPs has no impact on human health in Shandong Peninsula.

Chapter 4 Occurrence of OMPs in Surface Water and Groundwater, China

4.1 Overall Levels and Detection Frequency of OMPs

4.1.1 Overview of Surface Water in Tianjin and Jinan

A total of 227 compounds were detected (Table S4) in surface water from Tianjin, including sterols, antioxidants, pharmaceuticals and PPCPs, PAHs, organophosphate ester flame retardants, plasticizers, and pesticides as well as other industrial chemicals in concentrations ranging from nanograms to micrograms per liter. The sum concentration and number of detected compounds were presented in Fig. 4.1. The total concentrations in south sewage canal (S1, 195 μg/L) and north sewage canal (S2, 141 μg/L) were several times higher than those observed in river samples from the Jiyun River, Hai River and Duliu River (which ranged from 7.7 μg/L to 82 μg/L). The lowest total residue concentration was found at H6 (7.7 μg/L), followed by J3 and H10 with a total concentration of 10 μg/L and 11μg/L, respectively.

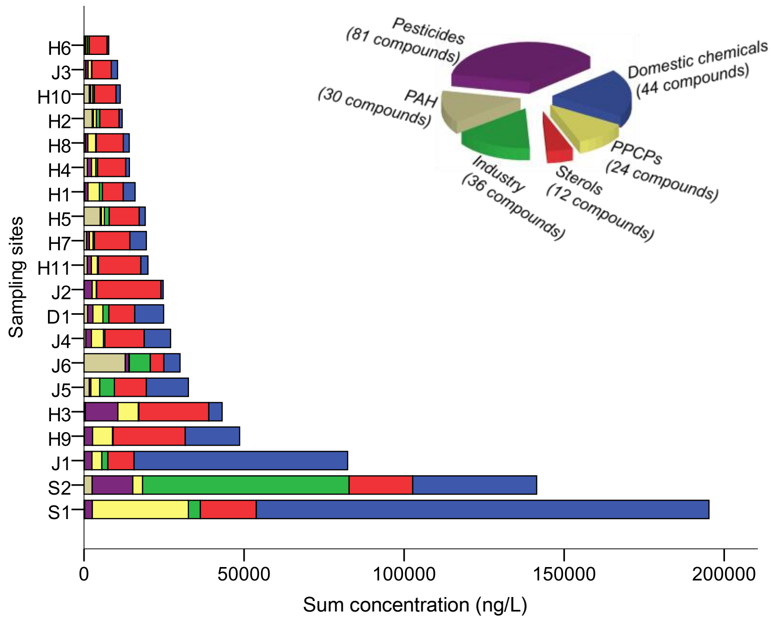


Fig. 4.1 Sum concentration and number of detected compounds in Tianjin

The number of substances detected in the twenty surface waters ranged from 50 to 105. The maximum compounds detected in surface water from Tianjin were for pesticides, while sterols were dominant compounds in all the rivers, except for J1, S1 and S2. The elevated concentration of industrial compounds was found in S2, and high levels of domestic compounds were observed in J1and S1. Ubiquitous residues in terms of the median concentration (Table 4.1) were cholesterol (2770 ng/L), *β*-sitosterol (1210 ng/L), bis(2-ethylhexyl) phthalate (DEHP) (259 ng/L), siduron (198 ng/L), coprostanone (126 ng/L), lidocaine (96 ng/L), antipyrine (76 ng/L), hexachlorobenzene (2.1 ng/L) and *p,p'*-DDD (0.70 ng/L); the number of chemicals detected only once was 70.

Table 4.1 Concentration of ubiquitous compounds in Tianjin

Chemicals	Median ng/L	Minimum ng/L	Maximum ng/L
Cholesterol	2770	1141	6378
β-sitosterol	1210	665	3270
DEHP	259	85	5454
Siduron	198	51	428
Coprostanone	126	15	1310
Lidocaine	96	7.5	218
Antipyrine	76	13	293
Hexachlorobenzene	2.1	0.14	39
p,p'-DDD	0.7	0.12	5.5

A total of 107 compounds were detected in Jinan including sterols, PPCPs, PAHs, pesticides, domestic and industrial compounds (Table S5). The number of substances detected in the twenty surface waters ranged from 8 to 64. The sum concentration and number of detected compounds were presented in Fig. 4.2. The high concentration was observed in JN5, JN7, JN6 and JN9, where are all located in Xiaoqing Watershed. It was not surprising because Xiaoqing River receives the effluent from the wastewater treatment plant (WWTP) as the only sewage canal in Jinan city. Also the sampling sites near the city center (JN5 and JN6) were more polluted than the downstream, which may be attributed to the dilution. However, the lowest concentration was found in JN12 and JN11 which were related to the spring water, followed by JN14, JN1, JN2 and JN3 which were important water source for drinking in Jinan. Different from Tianjin, Jinan was a less industrialized city and the results showed the PPCPs and sterols were predominant compounds in Jinan indicated municipal wastewater was a main contributor to its water pollution.

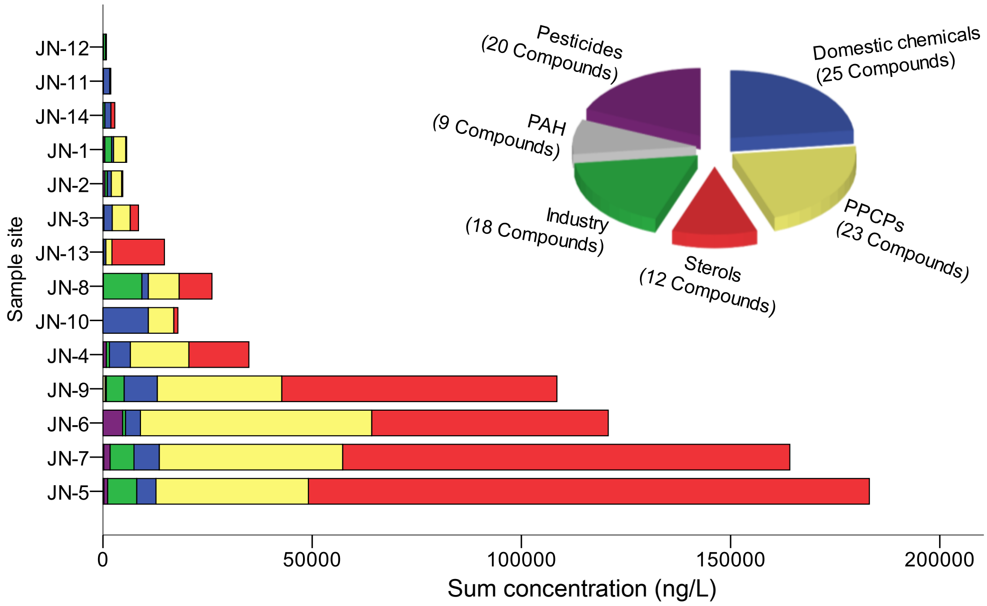


Fig. 4.2 Sum concentration and number of detected compounds in Jinan

The frequently detected compounds in more than 60% sampling sites in terms of median concentration were beta-Sitosterol (1120 ng/L), 2,6-di-tert-butyl-4-benzoquinone (123 ng/L), cholesterol (1730 ng/L), sulfamethoxazole (1070 ng/L), cotinine (734 ng/L), caffeine (383 ng/L), atrazine (13.2 ng/L) and carbendazim (12.7 ng/L) (Table 4.2).

Table 4.2 Concentration of ubiquitous compounds in Jinan

Chemicals	Frequency	Median ng/L	Minimum ng/L	Maximum ng/L
beta-Sitosterol	86	1120	n.d.	12600
2,6-Di-tert-butyl-4-benzo quinone	79	123	n.d.	255
Caffeine	71	383	n.d.	6090
Cholesterol	71	1730	n.d.	40900
Cotinine	71	734	n.d.	13700
Sulfamethoxazole	71	1070	n.d.	5000
Atrazine	64	13	n.d.	31
Carbendazim	64	13	n.d.	204

4.1.2 Overview Groundwater in Beijing and Tianjin

Over 90 percent of the chemicals surveyed were measured below the limit of determination. A total of 78 (6%) OMPs were observed in at least one sampling point including pesticide (21), PAHs (13), intermediate in organic synthesis (9), industrial compounds (5), fragrance (5), sterol (5), plasticizer (5), PPCPs (6), antioxidant (2), leaching from tire (2) and others with summary statistics shown in Table S6. The results presented that none of the water was free of OMPs. However, the number of compounds detected in Beijing and Tianjin were 38 and 75, respectively. The maximum number of compounds detected in groundwater was found in G21 (43) followed by G15 (30), and the median number of pollutants per site was 16. The sum concentration and number of compounds detected in groundwater from Beijing and Tianjin were showed in Fig. 4.3.

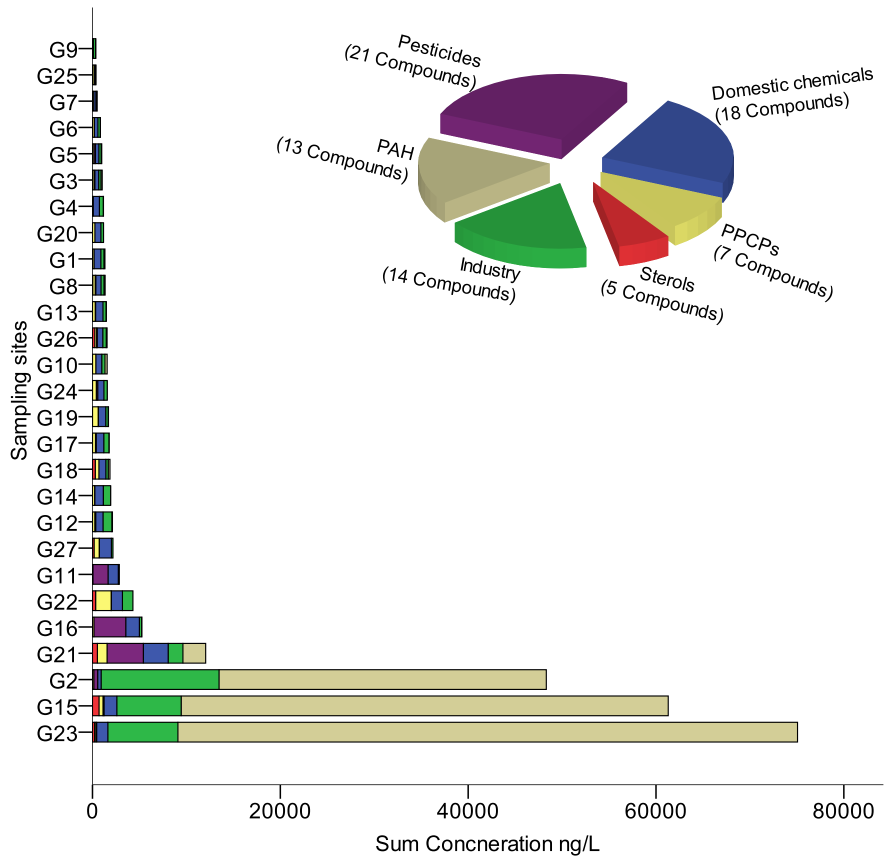


Fig. 4.3 Sum concentration and number of detected compounds in Jinan

The ubiquitous residues with frequency over 80% in terms of median concentration (Table 4.3) were 2-ethyl-1-hexanol (152 ng/L), benzyl alcohol (582 ng/L), 2-phenoxy-ethanol (129 ng/L) and acetophenone (74 ng/L). The high total concentrations were found at 25 (75 µg/L), 23 (61 µg/L) and 10 (48 µg/L). Overall the chemicals detected at elevated concentration were for the PAHs 1,4-&2,3-dimethylnaphthalene (30 µg/L), 1,3-dimethylnaphthalene (19 µg/L), 1,2-dimethylnaphthalene (14 µg/L) and 2,6-dimethylnaphthalene (10 µg/L). However, approximately 90% of the detected chemicals were measured at concentrations of less than 0.1 µg/L. The elevated total concentration over 10 µg/L was observed in s25 (75 µg/L), s23 (61 µg/L), s10 (48 µg/L) and s18 (12 µg/L), which were dominated by

PAHs. Compared to the previous monitoring in surface waters from Tianjin, the total concentration and number of compounds detected in this work indicated the groundwater were much less polluted and affected by anthropogenic activities.

Table 4.3 Concentration of ubiquitous compounds in Jinan

Chemicals	Frequency	Median ng/L	Minimum ng/L	Maximum ng/L
Benzyl alcohol	96	582	n.d.	1160
2-Ethyl-1-hexanol	96	152	n.d.	997
Ethanol, 2-phenoxy-	93	1290	n.d.	1330
Acetophenone	89	73.9	n.d.	204
Pentamethylbenzene	78	50.6	n.d.	5050
Nitrobenzene	78	39.8	n.d.	548
Dimethyl phthalate	74	63.5	n.d.	1230
2-Methylnaphthalene	70	15.2	n.d.	9570
Naphthalene	70	17.4	n.d.	5890
3,5-Dimethylphenol	67	41.3	n.d.	130
2,6-Di-tert-butyl-4-benzo	67	12.1	n.d.	51.1

4.2 Sterols

Cholesterol was observed in every sample from Tianjin. Cholesterol is an important membrane component of animal cells, and is present in the feces of herbivores, omnivores and carnivores. It is therefore not diagnostic for any particular animal group. Coprostanol, a 27-carbon stanol formed from the biohydrogenation of cholesterol, however, is formed from cholesterol when animal tissues pass through an omnivores/carnivore’s digestive system, and the presence of coprostanol has frequently been used as a biomarker for the presence of human fecal matter in the environment. Ccoprostanol has a low water solubility, and consequently a high octanol–water partition coefficient (log K_{ow} = 8.82). This means that in most environmental systems, 5β-coprostanol will be associated with the solid phase. In anaerobic sediments and soils, 5β-coprostanol is stable for many hundreds of years enabling it to be used as an indicator of past fecal discharges. In that context, the elevated levels of coprostanol were perhaps not unsurprisingly observed in samples from the south sewage canal (S1, 5.3 μg/L), north sewage canal (S2, 4.9 μg/L), although similar levels were observed at sites H3 (4.5 μg/L) and J2 (4.1 μg/L) both of which are surrounded by densely populated urban areas (Table S4). The lowest coprostanol concentration was found in J6 (not detected), a strictly protected drinking water source. Very low coprostanol concentrations were also observed at J3 (0.03 μg/L), a site located in a more remote northern area of Tianjin. The concentrations of corprostanol in surface water of Tianjin and Jinan were showed in Fig. 4.4. However, the maximum concentration of corprostanol found in surface water in Jinan was 29.6 µg/L (JN5), followed by 19.6 µg/L (JN7) and 13.2 µg/L (JN9). Compared to Tianjin, high level of corprostanol observed in Jinan indicated the surface water in Jinan was more polluted by sewage wastewater discharge.

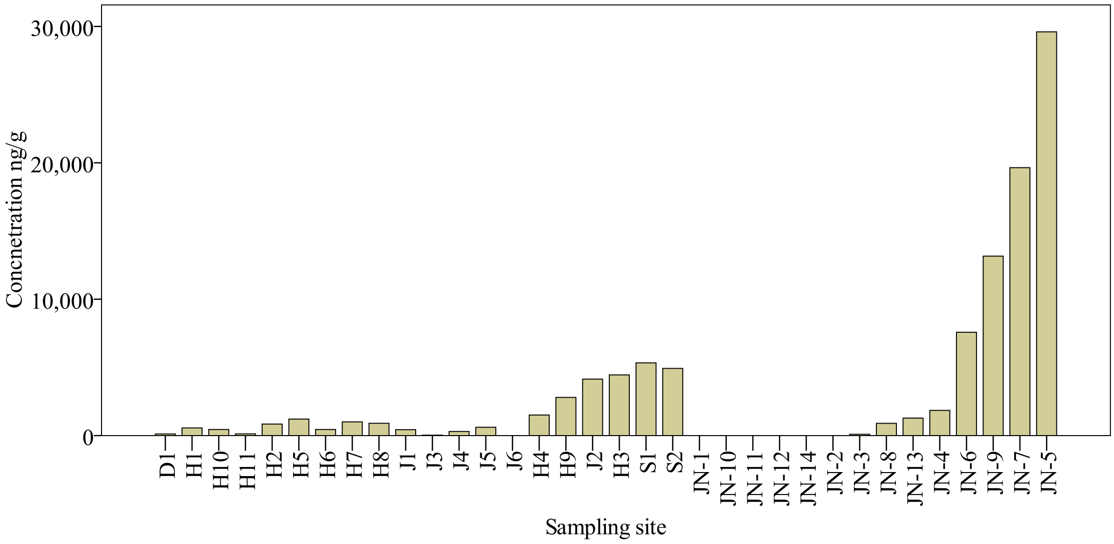


Fig. 4.4 Concentration of corprostanol in surface water from Tianjin and Jinan

The C_{27}, C_{28}, and C_{29} cholestane-based sterols found in fecal material are typically formed as reduction products of cholesterol and several higher molecular-weight isomers (campesterol, sitosterol, and stigmasterol) in the intestinal tracts of higher mammals. The sterol profiles of the feces reflect the diet of the source animal and conversions in the digestive tract and sterol/stanol ratios have been used to identify the origin of fecal material. Since 5*β*-coprostanol is formed from cholesterol in the vertebrate gut, the ratio of the product over reactant can be used to indicate the degree of fecal matter in samples. Raw untreated sewage typically has a 5*β*-coprostanol/cholesterol ratio of >10 which decreases through a sewage treatment plant (STP) such that in the discharged liquid wastewaters the ratio is >2. Undiluted STP wastewaters may be identified by this high ratio. As the fecal matter is dispersed in the environment, the ratio will decrease as more (non-fecal) cholesterol from animals is encountered. Grimalt et al. (1990) have suggested that a ratio of coprostanol/cholesterol greater than 0.2 indicates fecal pollution. In Tianjin the coprostanol/cholesterol ratio was generally highest in sewage canals and urban regions, and low in rural and remote areas (Table S4). In Jinan the slightly high ratio of coprostanol/cholesterol was found in Xiaoqing River. Further evidence for fecal contamination of the canals and urban waterways was provided by the coprostanol/(coprostanol+cholestanol) ratios (referred as 5β/(5β+5α)). 5α-Cholestanol is formed naturally in the environment by bacteria and generally does not have a fecal origin (Martins et al., 2007). A joint evaluation of 5β/(5β + 5α) against coprostanol/cholesterol (Fig. 4.5) clearly showed a similar linear tendency between the two parameters.

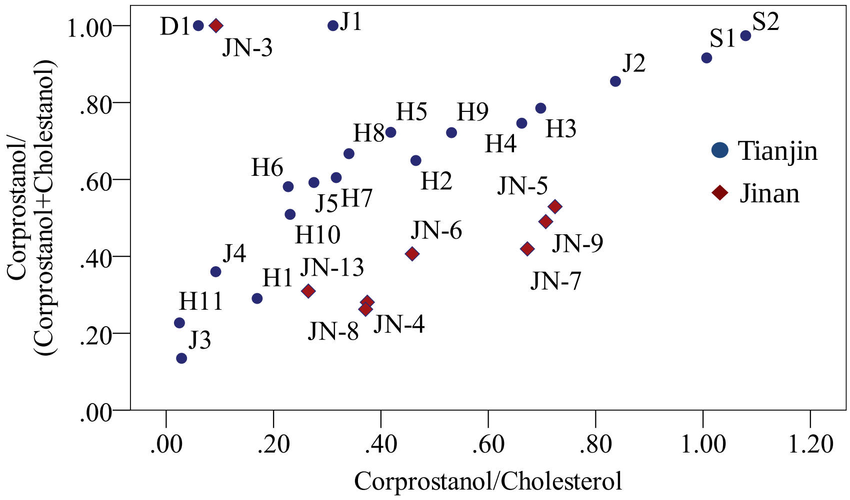


Fig. 4.5 A cross plot of coprostanol/cholesterol against 5β/(5β+5α) in surface waters of Tianjin and Jinan

Epicoprostanol, a coprostanol isomer, can be used as indicators of level of treatment since it is formed during the process of sewage degradation and found in human feces at very low concentrations (Martins et al., 2007). A cross-plot of the coprostanol/cholesterol ratio against the epicoprostanol/coprostanol ratio (Fig. 4.6) suggests that there are point sources of sewage discharge in both Tianjin and Jinan, although contamination at H11 may be attributed to old sewage pollution.

Compare to the surface water, groundwater collected in Beijing and Tianjin was less polluted, and corprostaol was not detected in any sites, which indicated that there are no sewage leachate effects on groundwater. Only cholesterol, beta-sitosterol, ergosterol, stigmasterol, campesterol were observed and the source may come from the emission of natural algae.

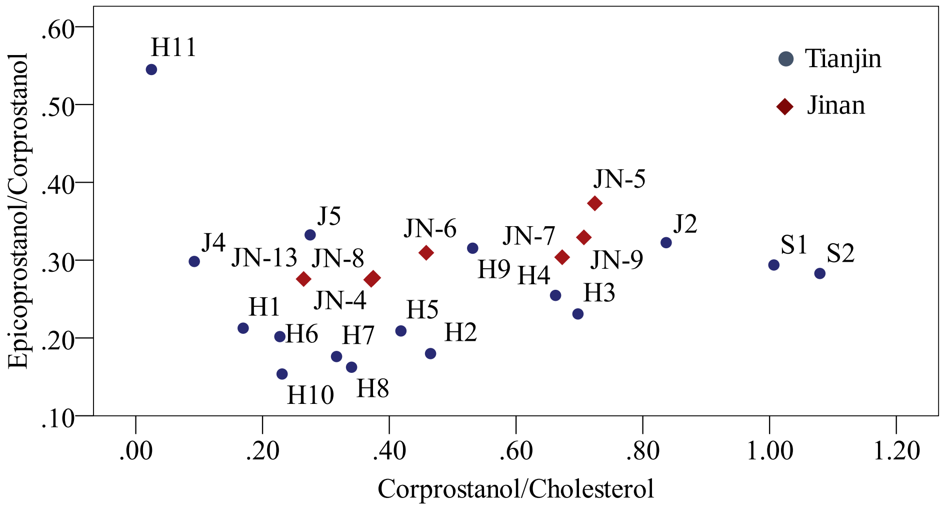


Fig. 4.6 A cross-plot of the coprostanol/cholesterol against the epicoprostanol/coprostanol in surface water of Tianjin and Jinan

4.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic compounds consisting of 2 to 7 fused aromatic rings in a linear, angular, or clustered arrangement. They are of considerable concern primarily because of their ubiquitous presence in the environment and well-recognized carcinogenicity, teratogenicity and mutagenicity (Gouin et al., 2004; Tobiszewski and Namiesnik, 2012). Human exposure to PAHs occurs mainly through ingestion of contaminated food, inhalation or skin contact (Cocco et al., 2007; Pongpiachan, 2015). Epidemiologic evidence revealed an excess risk of lung, skin, and bladder cancers in workers with high occupational exposure to PAHs (Hemminki, 1993 and Bosetti et al., 2007). Other studies have demonstrated the effects of exposure to airborne PAHs on children's neurological development (Perera et al., 2009), intrauterine growth retardation (Dejmek et al., 2000; Šrám et al., 2005), and arteriosclerosis risk (WHO, 2000). Atmospheric PAHs may cause respiratory problems, impair pulmonary function and cause bronchitis (Tsapakis and Stephanou, 2005; Tobiszewski and Namieśnik, 2012). The European Community and the U.S. Environmental Protection Agency have listed them as priority pollutants.

Combustion processes are important sources of PAHs. Also, there are natural sources, such as oil, which contains nearly 4000 hydrocarbons. Consequently, PAHs are widespread within the environment (Mari et al., 2010). Combustion engines, biomass burning, power plants, waste incineration, oil spills, food processing, manufacturing, and industrial processes are all sources of PAHs. Traffic is a very important emission source of these pollutants (Nadal et al., 2011). Although, the emissions of PAHs from fossil fuel burning are well known and controlled in developed countries, the situation in developing countries is unknown and environmental control related to such pollutants is weak.

The total concentration of PAHs in surface water of Tianjin and Jinan was showed in Fig. 4.7.

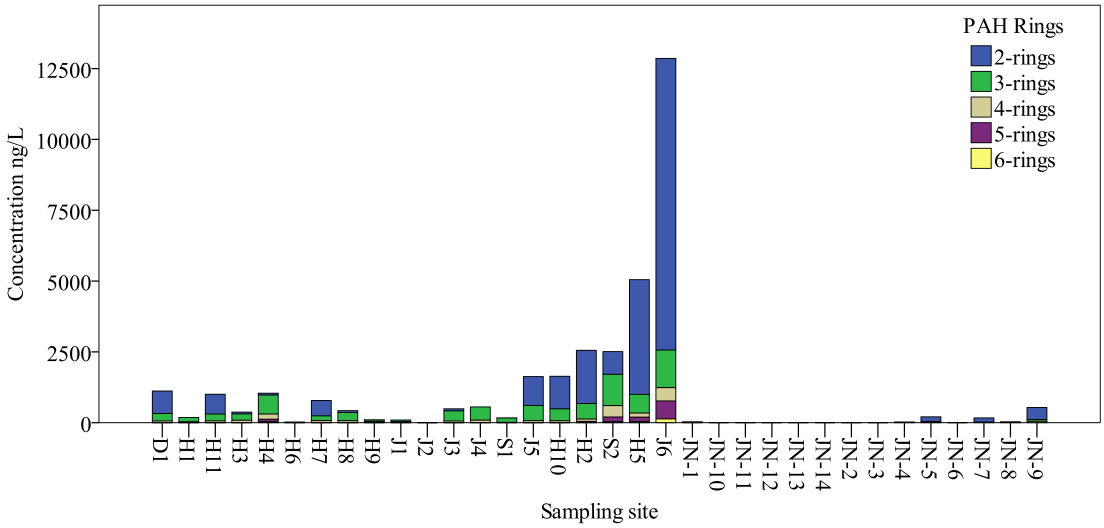


Fig. 4.7 Total concentration of PAHs in surface water of Tianjin and Jinan

The level of PAHs in Jinan was several times lower than that in Tianjin. Low molecular weight PAHs (2-3 rings) were predominant in surface water samples in Tianjin and, on average, accounted for 78% of the total PAHs. It should be noted that naphthalene was dominant individual PAH and occurred at the highest concentration at J6 (5.1 μg/L) and H5 (3.0 μg/L); these concentrations are higher than that found at the outlet of the sewage treatment plant discharging into the Tonghui River, Beijing, with a maximum concentration of 1.8 μg/L (Zhang et al., 2004). The Luan River (J6) was observed with maximum concentration of naphthalene which was surprising since J6 was the main drinking water supply for the inhabitants of Tianjin City and the source needs further investigation. Most naphthalene is derived from coal tar.

From the 1960s until the 1990s, significant amounts of naphthalene were also produced from heavy petroleum fractions during petroleum refining, but today petroleum-derived naphthalene represents only a minor component of naphthalene production. Naphthalene is the most abundant single component of coal tar. Although the composition of coal tar varies with the coal from which it is produced, typical coal tar is about 10% naphthalene by weight. In industrial practice, distillation of coal tar yields oil containing about 50% naphthalene, along with twelve other aromatic compounds. Naphthalene has been used as a household fumigant. It was once the primary ingredient in mothballs. Other fumigant uses of naphthalene include use in soil as a fumigant pesticide, in attic spaces to repel animals and insects, and in museum storage-drawers and cupboards to protect the contents from attack by insect pests.

PAHs can originate from natural processes such as biomass burning, volcanic eruptions and digenesis (Wang et al., 2007). However especially in heavily urbanized or industrialized regions, the majority of these compounds are anthropogenic: coal and wood burning, petrol and diesel oil combustion, and industrial processes (Mostert et al., 2010). Liquid fuels spills are further sources (da Silva and Bícego, 2010). PAHs are always emitted as a mixture, and the relative molecular concentration ratios are considered (often only as an assumption) to be characteristic of a given emission source. Understanding the impact of particular emission sources on the different compartments of the environment is crucial for proper risk assessment and risk management. PAH diagnostic ratios may provide an important tool for the identification of pollution emission sources. Nevertheless, the unquestioning application of PAH diagnostic ratios have recently been criticized (Galarneau, 2008; Katsoyiannis et al., 2007; Zhang et al., 2005): some authors have applied them unaware of the fact that they are not usually conservative in the environment.

For the source apportionment of PAHs in surface water of Tianjin, Pies et al. (2008) suggest that a ratio of anthracene/(anthracene + phenanthrene) below 0.1 is diagnostic for a pyrogenic source for observed PAHs; otherwise the PAHs are of petrogenic origin. In this study the median anthracene/(anthracene + phenanthrene) ratio was 0.12 (ranged from ND to 0.17), which suggests the input of combustion products through the atmospheric deposition into Tianjin aquatic environment. The ratio of fluoranthene/(fluoranthene + pyrene) is also used to identify the PAH sources (De La Torre-Roche et al., 2009), and when calculated in this study the ratio in most surface waters (> 0.5, except for sites J2, S1 and S2; Fig. 4.8) was indicative of PAHs from the burning of coal for heating during the winter in Tianjin City and industrial heavy fuel combustion.

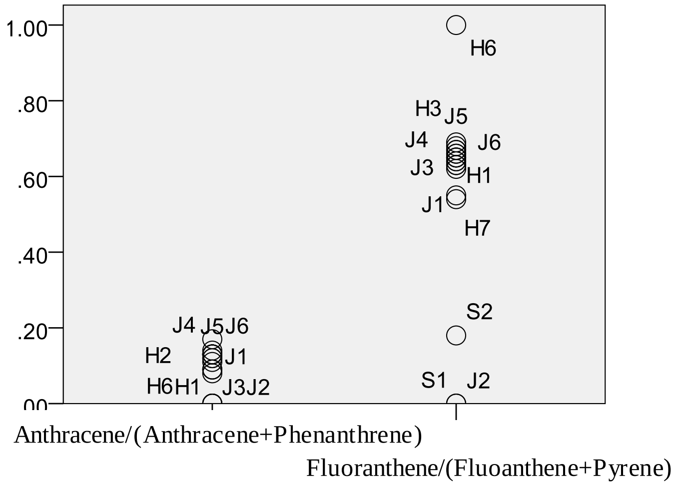


Fig. 4.8 Source apportionments of PAHs in surface water of Tianjin

PAHs were detected in groundwater from Beijing and Tianjin at elevated level and all referred to 2 or 3 rings. The ubiquitous compounds with frequency were naphthalene (70%), 2-methyl naphthalene (70%), 1-methyl naphthalene (44%) and 1,3-dimethyl naphthalene (33%). The PAHs concentrations in groundwater from Beijing and Tianjin varied from ND to 65.97 µg/L, with a median value of 46.04 ng/L. The total PAHs concentrations observed in G23 (72.16 µg/L), G15 (53.25 µg/L)， G2 (44.37 µg/L) and G21 (2.5 µg/L) were one or two order magnitude higher than that in other sites with an average concentration of 57.25 ng/L. However, the predominant compounds were naphthalene and its 7 alkylated derivatives including 1,4-&2,3-dimethyl naphthalene, 1,2-dimethyl naphthalene, 1,3-dimethyl naphthalene, 2,6-dimethyl naphthalene, 1-methyl naphthalene and 2-methyl naphthalene. The alkylated naphthalenes have been practiced as high-quality lubricants for several decades owing to their excellent thermo-oxidative and hydrolytic stability (Hourani et al., 2007). The elevated level of alkylated naphthalenes in this work indicates the well pumps are assumed likely to leak lubricating oils and get into the groundwater. Although there is less toxicity information available for most of the alkyl PAHs than for their parent compounds, most alkyl PAHs tend to be equally or more toxic than the parent compound. In that context, the total naphthalene concentration including alkyl naphthalene concentrations plus the parent compound was used for risk assessment and comparing the sum to known toxicological effect benchmarks for the parent compound. Although the maximum value of sum naphthalene in this study was well below the Health Advisory Level of 100 µg/L (U.S. EPA, 2012e), the non-point source was still a public concern and need further investigation.

4.4 Pharmaceuticals and Personal Care Products (PPCPs)

PPCPs contain diverse groups of organic compounds, such as antibiotics, hormones, anti-inflammatory drugs, antiepileptic drugs, blood lipid regulators, β-blockers, contrast media, and cytostatic drugs for pharmaceuticals; and antimicrobial agents, synthetic musks, insect repellants, preservatives, and sunscreen UV filters for personal care products (Daughton and Ternes, 1999). Among the pharmaceutical group, antibiotics have received special attention for their wide application in human therapy and livestock agriculture. Persistent exposure of antibiotics can result in the emergence of resistant bacteria strains with public health concerns (Zhang et al., 2009). Antibiotics contain several subgroups, such as macrolides (e.g. erythromycin, roxithromycin), sulfonamides (e.g. sulfamethoxazole, sulfadimethoxine), and fluoroquinolones (e.g. norfloxacin, ciprofloxacin) (Heberer, 2002). Hormones are another most studied group of pharmaceuticals which are believed to be connected with the endocrine disrupting effects of polluted water bodies (Lai et al., 2002). Other pharmaceutical groups include analgesics and anti-inflammatory drugs (such as diclofenac and ibuprofen); antiepileptic drugs (such as carbamazepine and primidone); blood lipid regulators (such as clofibrate and gemfibrozil); β-blockers (such as metoprolol and propanolol); and contrast media (such as iopromide and diatrizoate) (Heberer, 2002). For the groups of personal care products, triclosan and triclocarban are the two typical antimicrobial agents frequently detected in wastewater. The synthetic musks include nitro musks (mainly musk xylene and musk ketone) and polycyclic musks (mainly galaxolideand toxalide) with more production and application than the nitro group in recent years. N,N-diethyl-m-toluamide (DEET) is the main active ingredient of insect repellents and regularly detected.

The main source of PPCP infusion into the environment is through sewage treatment plants (STPs) (Daughton and Ternes, 1999). The presence of PPCPs in wastewater treatment plants had been reported in different countries all over the world, mostly in the levels of ng/L to μg/L, such as USA (Boyd et al., 2004), United Kingdom (Ashton et al., 2004), Spain (Carballa et al., 2004), Finland (Lindqvist et al., 2005), and Japan (Nakada et al., 2006). After discharging from STPs, PPCPs in sewage would cause subsequent contamination to the receiving water bodies. As a group of novel emerging contaminants, PPCPs show varied properties with the conventional persistent organic pollutants whose sources may have been banned or limited. The input of PPCPs with STPs as the main source is perpetual, resulting in a steady-state concentration in aquatic systems, which has been described as “pseudo-persistent” (Daughton, 2003). Persistent exposure by PPCPs even at low concentration levels can be significant.

China has become a large country with high production and usage volumes of pharmaceuticals as well as a rapid growing rate of personal care product consumption, which may result in significant occurrence of PPCPs in the environment. The pharmaceutical production by China can account for more than 20% of the total production volume of the world (SERI, 2012). More than 1500 kinds of active pharmaceutical ingredients were produced, and more than 6900 pharmaceutical-manufacturing companies were registered in 2007 (Zhou et al., 2010). Besides the huge pharmaceutical production volume, the consumption rate is also remarkable, especially for the severe antibiotic abuse in current China. The average usage of antibiotics by Chinese is 10 times more than the usage by Americans (CAST, 2008). Around 75% of the patients and 80% of the inpatients with seasonal influenza are prescribed antibiotics. China is also among the top three countries with the largest personal care product consumption, together with America and Japan (ChinaIRN, 2012). China possesses the fastest growing rate of personal care product market in the world, which will reach 8% between 2010 and 2013. The production of active pharmaceutical ingredients by China has rapidly increased in recent years, and in fact China has become the largest producer of active pharmaceutical ingredients of the world.

Total concentration of PPCPs in surface water of Tianjin and Jinan was showed in Fig. 4.9. The results clearly showed the level of PPCPs in Jinan was rather higher than that in Tianjin. However, the elevated level of PPCPs was mainly observed in S1 (sewage canal) from Tianjin and Xiaoqing River in Jinan. The sites located in downstream (JN6) showed higheroncentration that in urban center (JN5, JN7 and JN9) and upstream (JN4).

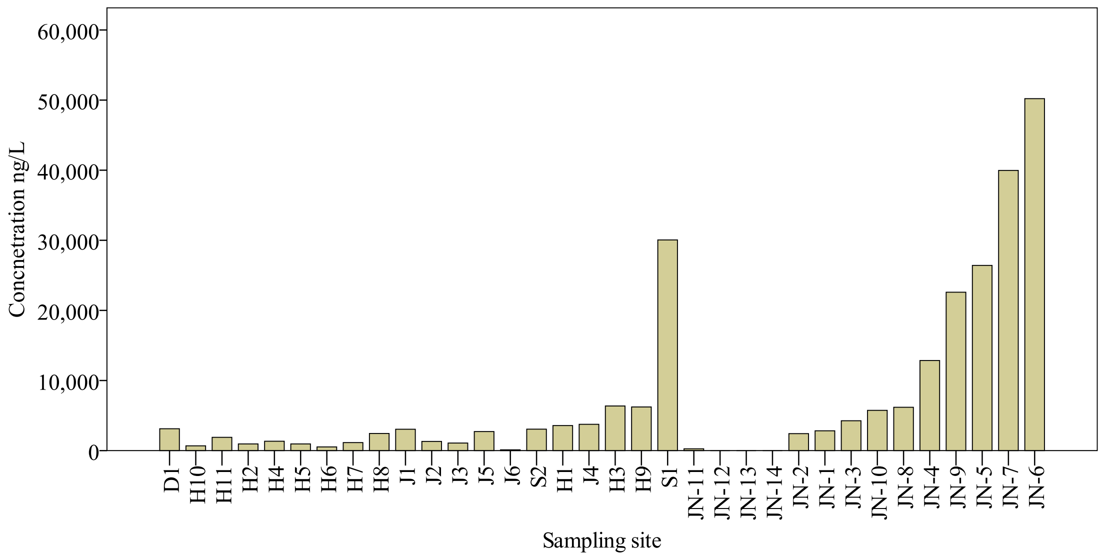


Fig. 4.9 Total concentration of PPCPs in surface water of Tianjin and Jinan

For surface water in Tianjin, antipyrine (non-steroidal anti-inflammatory drug) and lidocaine (a local anesthetic) were detected in all the samples, with a mean concentration of 95 ng/L and 98 ng/L, respectively. The concentration of antipyrine in this study was lower than that reported in sewage plants and rivers from Germany (Ternes, 1998), but slightly higher than that in surface waters from the Netherlands (de Jongh et al., 2012). Antipyrine is an analgesic, a type of medication used to relieve pain. It also functions as an anti-inflammatory medication and an antipyretic, meaning that it can alleviate fevers. This medication is part of a class of drugs called non-steroidal anti-inflammatories (NSAIDs), which include more well-known compounds like ibuprofen and acetaminophen. Often available as a tablet for oral consumption in many countries, it is also found in Europe in the form of ear drops, usually combined with a local anesthetic like lidocaine to treat earaches.

Caffeine, quinoxaline-2-carboxylic acid, metformin and cotinine (a metabolite of nicotine) were observed in more than 90% of samples. Caffeine is of further importance in pharmaceuticals. It enhances the effect of certain analgesics in cough, cold, and headache medicine. Caffeine is used as a cardiac, cerebral, and respiratory stimulant and as a diuretic. Considering its uptake with beverages and foods, caffeine is probably the most widely consumed drug in the world. Pure caffeine is produced commercially as a byproduct from the decaffeination of coffee. It is included on the U.S. EPA list of High Production Volume Chemicals (EPA 2002). Caffeine has been detected in wastewater, surface water, and groundwater worldwide.

Quinoxaline-2-carboxylic acid is used as a marker chemical for carbadox, production and usage of which has been banned in China since 2005. However, quinoxaline-2-carboxylic acid which was observed in the present study are suggestive of recent inputs because its half-life is only 8.5 days and the source of this chemical need further investigation. The anti-diabetic drug metformin was determined at higher concentrations than other PPCPs at several sampling sites, with the highest value observed at S1 (20 μg/L), followed by H3 (2.9 μg/L) and H1 (2.4 μg/L). Site S2 may be impacted by the discharge from metformin production upstream whereas sites H3 and H1 are both located in urban areas and may indicate large amounts usage of this drug within Tianjin's large population. Metformin, an antidiabetic drug with one of the highest consumption rates of all pharmaceuticals worldwide. As one of the most prescribed pharmaceuticals by mass, the antidiabetic drug metformin is still poorly investigated in terms of environmental fate and drinking water relevance. The number of people suffering from diabetes accounts for more than 360 million on a worldwide scale, with about half of them undiagnosed cases. According to the International Diabetes Federation, diabetes caused 4.6 million deaths in 2011 and Type 2 diabetes is increasing in every country (IDF, 2011). In Germany alone prescription rates of metformin almost tripled in the last 10 years to 547 million defined daily doses (DDD) of the pure compound accounting for almost 1100 tons in 2010 (WHO, 2012). Metformin is an orally administered drug with an average dose of 2 g per day (WHO, 2012). The compound is not metabolized in humans and the resorbed fraction (about 70%) is excreted unchanged in urine, the rest in feces (Pentikäinen et al., 1979). Based on its pharmacokinetics, it is not surprising that high metformin concentrations in wastewater treatment plant (WWTP).

The other 4 widely detected PPCPs in terms of mean concentration were clarithromycin (frequency of detection (FOD) 75%; 25 ng/L), roxithromycin (FOD, 75%; 57 ng/L), acetaminophen (FOD, 70%; 395 ng/L) and diethyltoluamide (FOD, 70%; 40 ng/L). The high concentration of acetaminophen observed in this study was reasonable because it has been listed as one of the four most often-used anti-inflammatory pharmaceuticals in China (Peng et al., 2008).

For surface water of Jinan, even though high level of PPCPs was found, the predominant compounds were acetaminophen, caffeine, cotine, metformin and sufamethoxazole, which accounted to over 80% of total PPCPs concentration (Fig. 4.10). Acetaminophen is an active ingredient in hundreds of over-the-counter (OTC) and prescription medicines. It relieves pain and fever. And, it is also combined with other active ingredients in medicines that treat allergy, cough, colds, flu, and sleeplessness. In prescription medicines, acetaminophen is found with other active ingredients to treat moderate to severe pain. In addition, metformin was found in Tianjin and Jinan with high concentration. To our best knowledge, this is the first report concerning the occurrence of metformin in surface waters in China, although, similar metformin concentrations have been reported in surface waters and wastewater effluents in Germany (Scheurer et al., 2012).

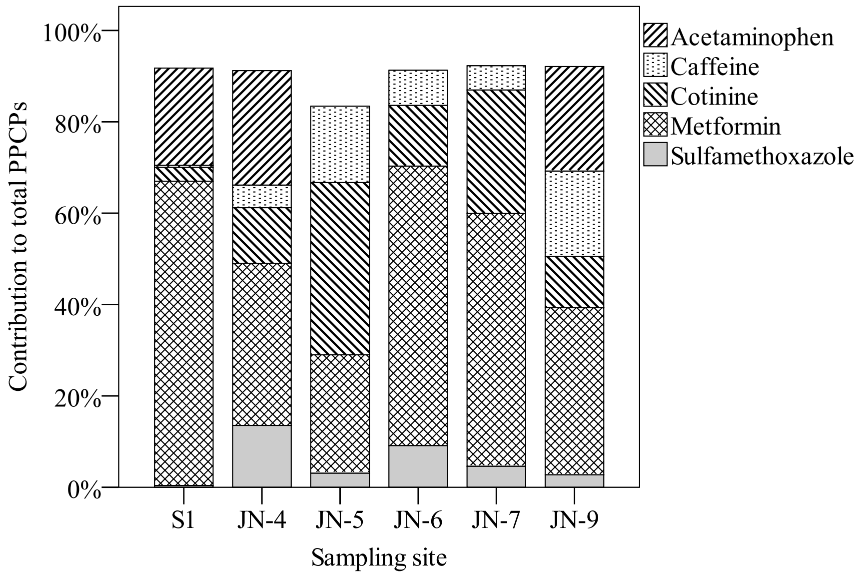


Fig. 4.10 The contribution of dominant PPCPs in surface water

For groundwater in Beijing and Jinan, seven PPCPs were detected at least twice with total concentration in the range of 51.41—1653 ng/L. The 2-phenoxy-ethanol and acetophenone were most frequently quantified in > 85% samples with a maximum concentration of 1328 ng/Land 204 ng/L. Phenoxyethanol is chemical preservative, a glycol ether often used in dermatological products such as skin creams and sunscreen. It is a colorless oily liquid. It is a bactericide (usually used in conjunction with quaternary ammonium compounds), often used in place of sodium azide in biological buffers because phenoxyethanol is less toxic and non-reactive with copper and lead. It is used in many applications such as cosmetics, vaccines and pharmaceuticals as a preservative. As a commonly used preservative in personal care products, Kimura et al. reported the occurrence of 2-phenoxy-ethanol in Japanese rivers with concentration up to 14000 ng/L and suggest that the major sources were cosmetics and household detergents (Kimura et al., 2014). However, most of the groundwater collected in Beijing and Tianjin located in suburban and rural areas, direct household wastewater discharge may be a likely source into groundwater since there is a lack of sewer treatment plant. The maximum concentration of acetophenone observed in this study was one order of magnitude lower than that in groundwater from United States (Barnes et al., 2008). For the plasticizer group, consisting of 5 compounds, the dimethyl phthalate and diethyl phthalate were frequently detected in 20 and 10 samples, respectively. The highest concentration was observed for dimethyl phthalate (1.23 µg/L) in s18, followed by di-n-butyl phthalate (741 ng/L) in S3, and it was far below the New Jersey groundwater quality standard (NJDEP, 2011).

4.5 Pesticides

For surface water in Tianjin 81 pesticides were detected with total concentration ranged from 358 ng/L to 12.6 µg/L. The highest concentration was found in S2, followed by H3 (10.2 µg/L), H9 (2.55 µg/L), J2 (2.46 µg/L), S1 (2.39 µg/L) and J1 (2.39 µg/L), which were mainly located in rural areas and suggested the effects of agricultural runoff. The maximum concentration of pesticides over 1 µg/L were dinoseb (8.39 µg/L), bis (2-chloroisopropyl) ether (3.17 µg/L), myclobutanil (2.25 µg/L), atrazine (1.83 µg/L), acetamiprid (1.64 µg/L), 3-hydroxycarbofuran (1.39 µg/L), 2,5-dichlorophenol (1.38 µg/L) and fenarimol (1.22 µg/L). Dinoseb is an organic solid - yellowish crystals with a pungent odor. Its greatest use is as a contact herbicide for post-emergence weed control in cereals, undersown cereals, seedling lucerne and peas. Dinoseb is also used as a corn yield enhancer and an insecticide and miticide. Dinoseb is degraded slowly by soil bacteria and binds weakly to soil. In water it is mainly broken down by sunlight and not likely to accumulate in aquatic life. The maximum concentration of dinoseb in rivers from Korea was 0.1 µg/L (Cho et al., 2014) which was significantly lower than this study. However, dinoseb was only detected in sewage canal (S2) and the source may be attributed the wastewater discharge from manufacturing and need further investigation. The statistic concentration of frequently detected pesticides in surface water of Tianjin was showed in Table 4.4. The ubiquitous pesticides were related to the OCPs and the maximum concentration was rather low, except for siduron and carbendazim. The widely presence of OCPs was probably due to the historical usage and the persistence of these compounds. Siduron was widely used in north China as herbicide and the source in surface water may be from the storm water runoff. Carbendazim is a popular fungicide in China which has been produced and used in china for more than 30 years.

Table 4.4 Concentration of ubiquitous pesticides in Tianjin

Chemicals	Frequency	Median ng/L	Minimum ng/L	Maximum ng/L
Hexachlorobenzene	100	2.1	0.14	39
p,p'-DDD	100	0.69	0.12	5.5
Siduron	100	198	51	428
a-HCH	90	1.3	ND	32
b-HCH	90	0.9	ND	13
p,p'-DDE	90	0.77	ND	2.3
Carbendazim	90	21	ND	99
o,p'-DDT	85	0.67	ND	2.8
o,p'-DDD	80	1.2	ND	2.6

For surface water in Jinan, 20 pesticides were detected with total concentration ranged from ND (not detected) to 4.68 µg/L. The highest concentration was found in JN6, followed by JN7 (1.53 µg/L) and JN5 (0.89 µg/L). The maximum concentration of pesticides over 1 µg/L was etobenzanid (4.43µg/L). The statistic concentration of frequently detected pesticides in surface water of Jinan was showed in Table 4.5. However, the ubiquitous compounds detected in both cities were quite similar which indicated the preferred pesticides application pattern was similar.

Table 4.5 Concentration of ubiquitous pesticides in surface water in Jinan

Chemicals	Frequency	Median ng/L	Minimum ng/L	Maximum ng/L
Carbendazim	64	12.7	n.d.	204
Siduron	57	79.0	ND	183
Hexachlorobenzene	43	ND	ND	2.95
p,p'-DDT	43	ND	ND	1.79
Endrin	36	ND	ND	3.00
b-HCH	36	ND	ND	1.68
p,p'-DDD	36	ND	ND	2.29
p,p'-DDE	36	ND	ND	1.37
a-HCH	21	ND	ND	1.79

The total concentration of pesticides in surface water of Tianjin and Jinan was showed in Fig 4. 11. Compared to Tianjin, surface water in Jinan was generally less polluted by the pesticides which indicated the intense agricultural activity occurred in Tianjin.

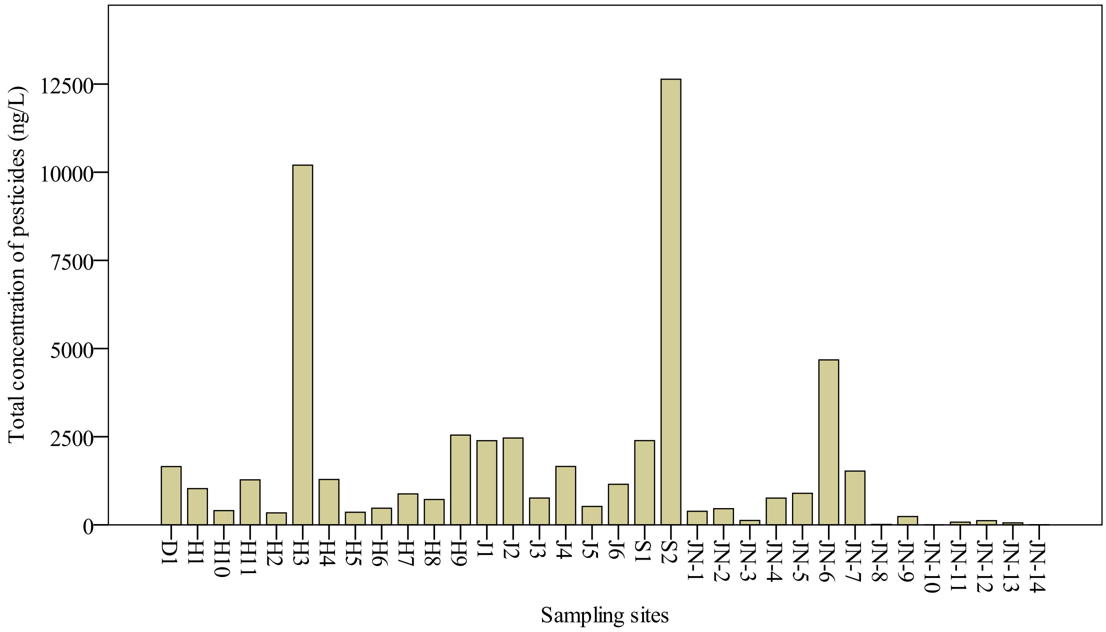


Fig. 4.11 Total concentration of pesticides in surface waters of Tianjin and Jinan

Nineteen out of twenty-seven wells showed positive results for at least one pesticide. Total concentration of pesticides in groundwater of Beijing and Tianjin was showed in Fig. 4.12.

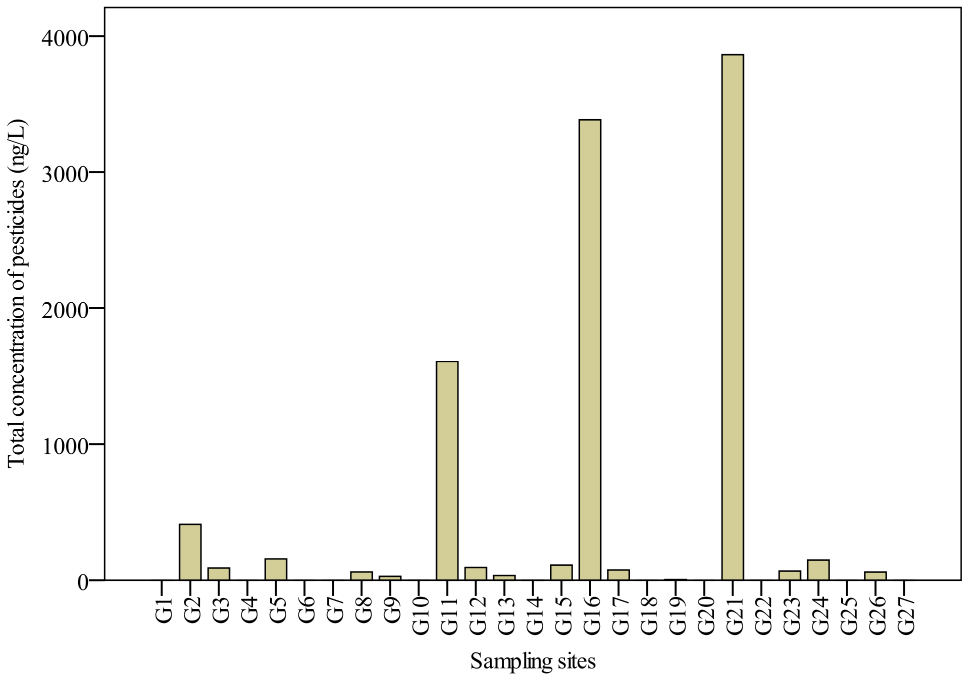


Fig. 4.12 Total concentration of pesticides in groundwater of Beijing and Tianjin

The concentration ranges of pesticides were between ND (not detected) to 1.6 μg/L in Beijing, between ND (not detected) to 3.9 μg/L in Tianjin, with a median value of 14 ng/L and 60 ng/L respectively. It should be noted that only four out of twenty-seven groundwater contained three or more pesticides. However, the maximum level was observed in site G21 where was specially contaminated by 1,4-dichlorobenzene (3.8 μg/L). This contribution may be attributed to the non-point source contamination during sampling process and need further investigation, since 1,4-dichlorobenzene was generally detected in groundwater at trace concentration due to the high log octanol-water partition coefficient (3.4) (Schwarzenbach et al., 1983). The comparable concentration of 1,4-dichlorobenzene were also reported in groundwater collected from United States (Barnes et la., 2008). The maximum number of detected pesticides was observed in site G16 (9) with a total concentration of 3.3 μg/L and the dominant compounds were oxadixyl (805 ng/L), dimethomorph (E) (1472 ng/L) and dimethomorph (Z) (746 ng/L). It was not surprising because this borehole located in the intense greenhouse vegetable cultivation area with a shallow depth (< 4 m) suggesting the potential pesticides leaching to groundwater. As one of the most wildly used fungicide in China, the concentration of oxadixyl in the present study was slightly lower than that detected in groundwater from England and France despite the withdrawal from use in the EU for some years (Lapworth et al., 2015). Also elevated concentration over 1 μg/L was carbendazim found in site 3 (1.61 μg/L). Carbendazim is a popular fungicide which has been produced and used in China for more than 30 years, and the production capacity is 50000 tons per year. The concentration of carbendazim in this monitoring is 2 orders of magnitude lower than that reported in groundwater from Argentina (Loewy et al., 1999). The level of 0.1 μg/L was employed for pesticides maximum residual limits (MRL) in groundwater according to the EU Directive coded 2006/118/EU. Only site 2 with four compounds and other six sits with only one pesticide showed concentrations exceeded the MRL, indicating that most detection are below the levels imposed by the EU for water intended for human consumption.

4.6 Domestic and Industrial Chemicals

For surface water in Tianjin, elevated levels of substances leaching from tires were found in the north sewage canal (S1, 138 μg/L), J1 (66 μg/L) and J5 (10 μg/L) and may again be ascribed to wastewater discharge, in this case from tire manufacturing industries located upstream (Fig. 4.13). It is worth noting that four benzothiazoles (benzothiazole, 2-(methylthio)-benzothiazol, 2(3H)-benzothiazolone and 2-methylbenzothiazole) were prominent and accounted 64%－96% to total concentration of domestic chemicals in these 3 sites.

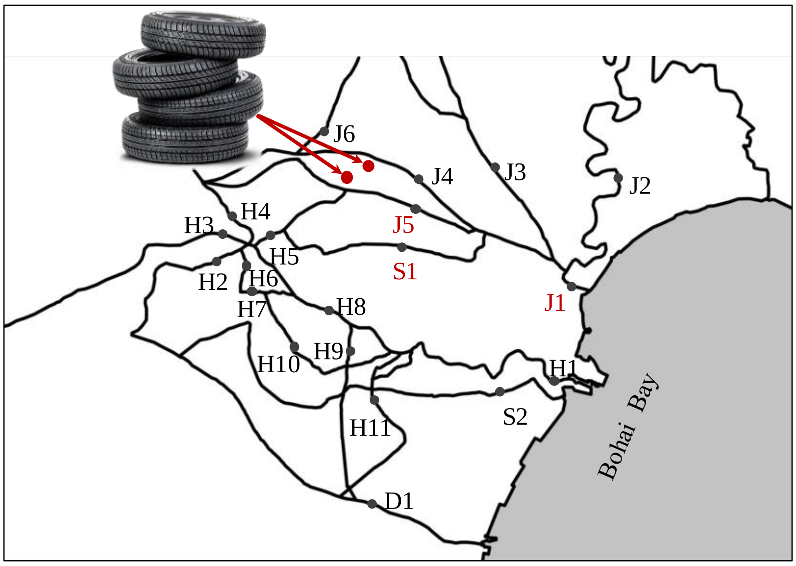


Fig. 4.13 Potential source of elevated level of benzothiazoles

Benzothiazoles are an important class of chemicals with various applications in industry. The largest amount of benzothiazoles has been used as vulcanization accelerator (e.g., 2- morpholinothiobenzothiazole) in rubber production, where they are added in the amounts of over 1%. Among the benzothiazoles, benzothiazole and 2-(4-morpholinyl)benzothiazole are the major components that can leach from rubber and asphalt. Benzothiazoles are added to antifreezes and cooling liquids because of their corrosion-inhibiting properties (Kloepfer et al., 2005). Additionally, benzothiazole has been found to cause eye, skin, and respiratory irritation and skin sensitization (Fishbein, 1990). A previous study of in vivo and in vitro effects of benzothiazole on sheep head minnow indicated that benzothiazole was a gill toxicant and not a neurotoxicant (Evans et al., 1990). Another study (Reemtsma et al., 1995) also suggested that benzothiazole and 2-methylthiobenzothiazole show acute aquatic toxicity in various test systems.

Due to their widespread applications, persistence, and toxicity, benzothiazole derivatives have remained an environmental concern. Several benzothiazoles have been detected in street dust, atmospheric aerosols, surface water, street dust, street runoff, sediment, starry flounder liver, and an industrial effluent from a tire manufacturer (Ni et al., 2008). The occurrence of benzothiazoles was ascribed mainly to the automobile tires and rubber manufacturing industries.

Plasticizers and fire retardants were the major contaminants at sites located in urban areas. Phthalic acid esters (PAEs), potential endocrine disrupting chemicals, are widely used as plasticizers to improve flexibility and workability. Recent investigations have shown that several PAEs are which are toxic and harmful to human health, leading to the instability of internal secretions and procreation ability. Since two phthalate ester plasticizers were even detected in the remote marine atmosphere at Enewetak Atoll in the North Pacific Ocean (Atlas et al., 1981), PAE contamination has become a serious issue arousing much concerning. It was reported that PAE concentrations were 0.1–300 μg/L in surface waters, and they were in the range of 0.1 ng/g to 100 μg/g observed in sediments around the world (Fatoki et al., 2002; Sung et al., 2003). Many researches carried out in China revealed that the maximum levels of di-n-butyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) reached 17 and 76 μg/L in water samples from 10 Hangzhou water plants, respectively; six PAEs, i.e. di-methyl phthalate (DMP), di-ethyl phthalate (DEP), DBP, DEHP, di-n-octyl phthalate (DOP) and butyl-benzyl phthalate (BBP), amounted to 114.166 μg/g in municipal sludge of Beijing (Wang et al., 2008).

In this work, among the six detected PAEs, DEHP and DEP were found in >90% of surface water samples, with a mean concentration of 0.58 μg/L and 0.25 μg/L, respectively, although at relatively low concentrations compared to surface water in USA and Europe (He et al., 2013) (Table 4.6).

Table 4.6 Comparison of DEPand DEHP to other waters (μg/L)

Location	Time	DEP	DEHP
Surface water in Canada	Unknown	0.05–55	0.05–336
Surface water in USA	Unknown	0.01–55	<MDL–137
Surface water in Europe	Unknown	<MDL–4	<MDL–50
Surface water in Netherlands	1999	<MDL–2.3	<MDL–5.0
The Tama River, Japan	1999	<MDL–0.31	<MDL–3.60
The Yellow River, China	2004	0.0115–1.09	0.347–31.8
The Yangtze River, China	2005	<MDL–0.365	0.011–54.73
The Lake Chaohu, China	2010-2011	0.006–0.212	<MDL–0.576
Surface water in Tianjin (this work)	2013	<MDL–0.995	0.085–5.45

Triphenyl phosphate (TPP), as organophosphate flame retardant, was detected in >95% sampling sites, with a mean value of 88 ng/L. TPP is acutely toxic to aquatic organisms and is a suspected neurotoxin (Li et al., 2014); its concentration in the present study is comparable to those reported in river water from Austria (Martínez-Carballo et al., 2007). The chemicals 4-NP and BPA had mean concentrations of 565 ng/L and 25 ng/L, respectively. The high levels of

4-nonylphenol in the present study are in good agreement with a previous report (Jin et al., 2004) and indicate the widespread application of alkylphenol ethoxylates. However, the concentration of 4-nonylphenol in this study was higher than that in surface waters from Germany and comparable to that in other surface waters from China (Table 4.7).

Table 4.7 Comparison of nonylphenol to other waters (ng/L)

Location	Time	Nonylphenol
Pearl River, China	2006	36 – 33231
Yellow River, China	2004	34.2 – 599
Various rivers, Taiwan	2000	<MDL – 5100
Tama River, Japan	2002	51.6 – 147
Han River, Korea	2001	17 – 1530
Kalamazoo River, US	1999	1100
Elbe River, Germany	2001	1.0 – 52
Surface water in Tianjin (this work)	2013	<MDL – 2622

In the last few years, many phenolic xenoestrogens have been reported to have mimic estrogen effects, and may adversely affect the health and reproduction of animals and human. Among them, 4-tert-octylphenol (OP), 4-nonylphenol (NP) and bisphenol A (BPA) deserve particular attention because of their estrogenic activity, widespread application and ubiquity in environment. A recent paper by Hunt et al. (2003), reported that exposure to BPA causes a chromosomal abnormality in the oocytes of female mice, and suggested that this abnormality could lead to reproductive or developmental effects. NP is used as precursors in the manufacture of non-ionic surfactants and is also degradation products of alkylphenol ethoxylates (APEOs), which are used in household detergents, pesticide formulations and other applications (Renner, 1997). Approximately 51% of APEOs is released to the environment in the final form of metabolic products by undergoing mechanical and biological sewage, and sewage sludge treatment (Isobe et al., 2001). In 2001, the amount of NP production was 16 000 t and the total consumption quantity of NP was 24 290 t in China (Jin et al., 2004). BPA was applied mainly as an intermediate to synthesize epoxy resins and polycarbonate plastics. Releases of BPA into the environment are mainly in wastewater from plastics-producing industrial plants and from landfill sites. In 2001, the amount of BPA production in China was 12 200 t and the total consumption quantity of BPA (362 610 t) was contributed mainly by import amount of BPA (94 243 t), epoxy resins (114 000 t) and polycarbonate (211 160 t) (Zhu and Qi, 2003).

A total of 36 industrial compounds were detected in surface waters of Tianjin. Of the chemicals detected in >60% samples were dibenzofuran (85%), biphenyl (75%) and quinoline (70%), with a mean value of 85 ng/L, 85 ng/L and 155 ng/L, respectively. The results reflect that Tianjin is a diversified economic hub in northern China. Tianjin's pillar industries are electronics and information technology, automobiles, bio-tech and pharmaceuticals, metallurgy and petrochemicals industries. Many of these manufacturers could potentially discharge various industrial related pollutants into the environment. Total concentrations of industrial compounds over 1 µg/L was observed at J1, J5, J6, H5, S1, S2 and D1. The maximum concentration of industrial compounds was found in south sewage canal (65 µg/L), which was influenced by high concentrations of 2-naphthol (50.7 µg/L). It was not surprising since Tianjin was an important production base for 2-naphthol. The high concentration of 2-naphthol only found in south sewage canal can be attributed to the wastewater discharge from 2-naphthol manufacturer which was close to our sampling site.

For surface water in Jinan, the frequently domestic and industrial compounds were showed in Table 4.8. The 2,6-di-tert-butyl-4-benzoquinone are the metabolite of the antioxidant butylated hydroxytoluene (BHT) in terms of the literature (Ma et al., 2006). The BHT is a lipophilic organic compound, chemically a derivative of phenol, which is useful for its antioxidant properties. European and U.S. regulations allow small amounts to be used as a food additive. In addition to this use, BHT is widely used to prevent oxidation in fluids (e.g. fuel, oil) and other materials where free radicals must be controlled. The high maximum concentration was observed for hexamethylenetetramine (9.16 µg/L) in JN8, which located in urban areas. The hexamethylenetetramine is highly soluble in water. The dominant use of hexamethylenetetramine is in the production of powdery or liquid preparations of phenolic resins and phenolic resin moulding compounds, where it is added as a hardening component. These products are used as binders, e.g. in brake and clutch linings, abrasive products, non-woven textiles, formed parts produced by moulding processes, and fireproof materials. For our best knowledge, this is the first study reporting the occurrence of hexamethylenetetramine in surface water and the source needs further investigation.

Table 4.8 Concentration of ubiquitous domestic and industrial compounds in Jinan

Chemicals	Frequency	Median ng/L	Minimum ng/L	Maximum ng/L
2,6-Di-tert-butyl-4-benzoquinone	79	123	ND	255
4-tert-Octylphenol	57	24.0	ND	53.5
Anthraquinone	50	29.4	ND	128
Phenol	50	11.0	ND	109
PCB_#60	50	0.20	ND	23.0
2-(Methylthio)-benzothiazol	43	ND	ND	200
Benzyl alcohol	43	ND	ND	1230
Bis(2-ethylhexyl)phthalate	43	ND	ND	2600
Bisphenol A	43	ND	ND	139
alpha-Terpineol	43	ND	ND	1700
PCB_#1	43	ND	ND	0.58

Total concentration of domestic and industrial compounds in surface water from Tianjin and Jinan was showed in Fig 4.14.

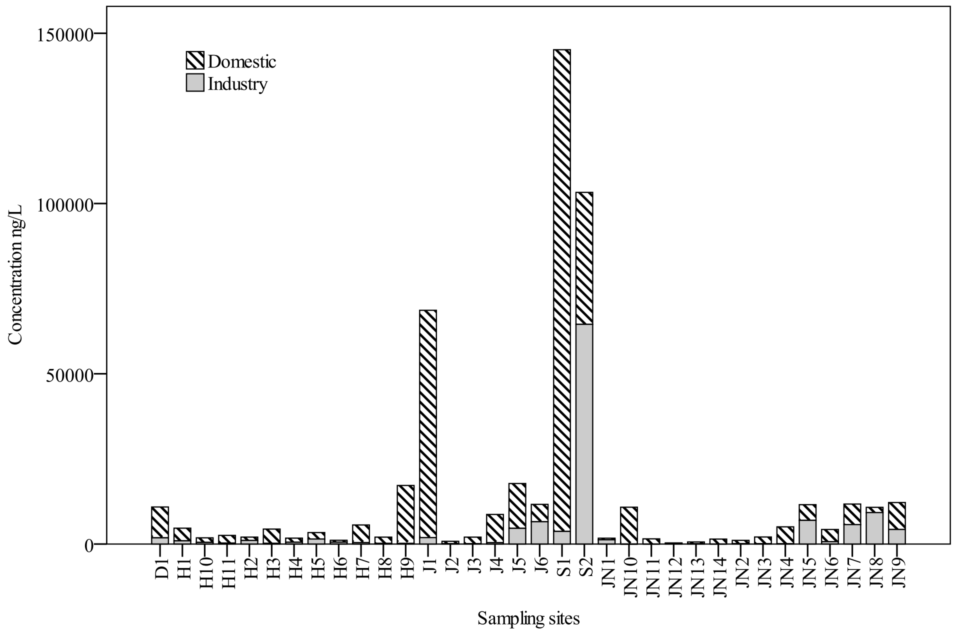


Fig. 4.14 Total concentration of domestic and industrial compounds in surface water from Tianjin and Jinan

The results clearly showed the surface water in Tianjin was more polluted than that in Jinan, which may be impacted by the population and level of industrial development. Although high concentration was found in sewage canal (S1 and S2), S1 was mainly impacted by the benzothaizoles, which come from the waste water discharge from tire manufacturing. The pollution of domestic and industrial compounds in surface water of Jinan was mainly found in Xiaoqing River. However, the total concentration in site JN6, which located in downstream of Xiaoqing River, was low compared to the upstream and tributary which can be ascribed to the dilution from the spring water. The lowest concentration in Jinan was observed in JN12 (330 ng/L; spring water), followed by JN13 (613 ng/L) and JN2 (1081 ng/L).

For ground water in Beijing and Tianjin, the compounds used as intermediate in organic synthesis were more frequently detected and the ubiquitous compound existed in all wells except s30 were 2-ethyl-1-hexanol (2-EH) with an average concentration of 234 ng/L (Table 4.9).

Table 4.9 Ubiquitous domestic and industrial compounds in groundwater

Chemicals	Frequency	Median ng/L	Minimum ng/L	Maximum ng/L
2-Ethyl-1-hexanol	96	151	ND	997
Benzyl alcohol	96	582	ND	1160
Pentamethylbenzene	78	50.6	ND	5050
Nitrobenzene	78	39.8	ND	548
Dimethyl phthalate	74	63.5	ND	1230
3,5-Dimethylphenol	67	41.3	ND	131
2,6-Di-tert-butyl-4-benzo quinone	67	12.1	ND	51.1

It was not surprising since (2-EH) is widely used in the manufacture of ester plasticizers for producing soft polyvinyl chloride, and expected to transport to ground water from applications through soluble and mobile feature. However, the level of 2-EH in this work was far below the ground water quality criterion of 200 μg/L (NJDEP, 2008). Total concentration of domestic and industrial compounds in groundwater from Beijing and Tianjin was showed in Fig. 4.15. The highest total concentration of intermediate was observed in G2 (12.55 μg/L), followed by G23 (7.27 μg/L) and G15 (6.84 μg/L). It should be noted that the diphenylmethane and pentamethylbenzene were predominant compounds in above three sites with concentration up to 5.05 μg/L and 9.52 μg/L, respectively. Since these sites were all located in suburban areas, the leachate from disposal of solid waste may be the possible contribution. The diphenylmethane was also identified in Mexican and Indonesian leachates, and similar concentration of pentamethylbenzene (ranged from 3.0 to 4.4 μg/L) was reported in groundwater near the solid waste landfill in California (A-Mehr Inc., 2012). However, drinking water standards do not exist for these compounds and it is difficult to put the results in a human-health context at this time.

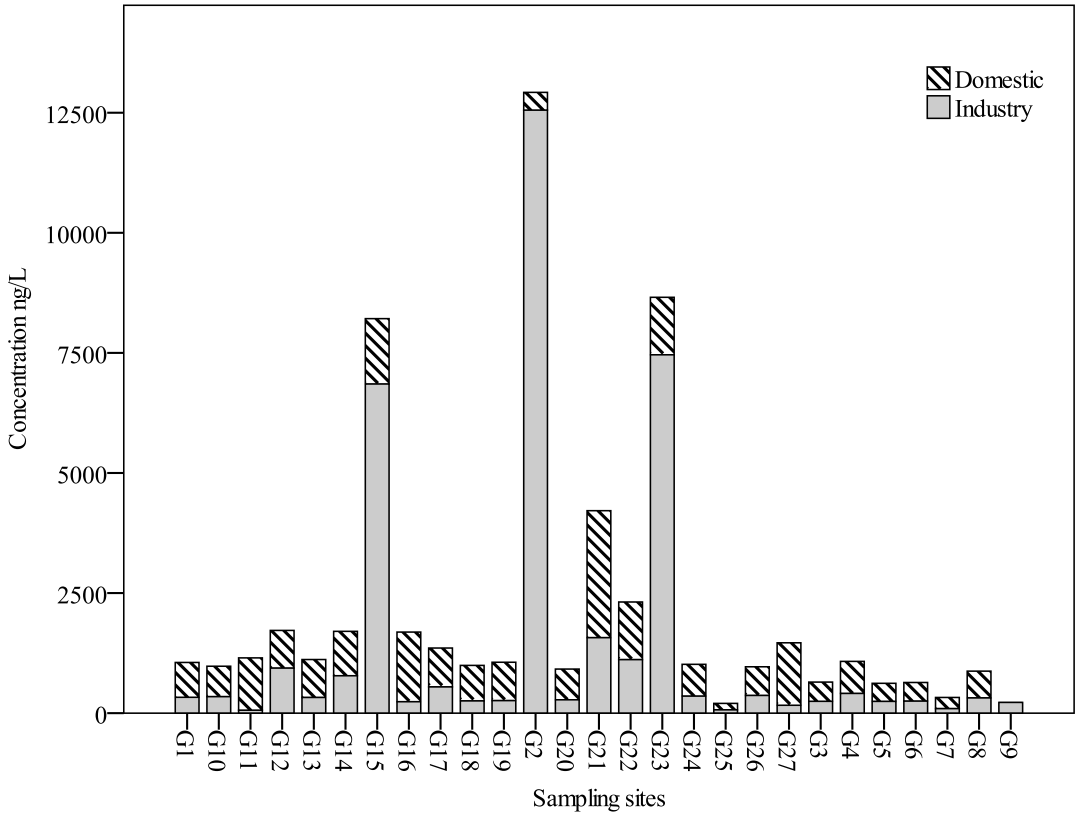


Fig. 4.15 Total concentration of domestic and industrial compounds in groundwater

4.7 Comparison of Groundwater to Surface Water Monitoring and EU-US Groundwater

Data obtained in the groundwater in this work can be quantitatively compared to that in surface water monitoring in Tianjin. The comparison is valid since the same analytical methods were employed for both groundwater and surface water. Overall, the number of compounds detected in in surface water sites was 3 times greater than that quantified in ground water samples, with 67 compounds detected in groundwater also being presented in surface water (Table 4.10). Although most compounds were also observed in surface water monitoring, the frequency of these detections was lower for the groundwater compared to the surface water sites. However, 17 out of 63 compounds shower even higher average concentration in groundwater than that in surface water, which mainly referred to PAHs and pesticides. The total concentration in all groundwater sits was less than 10 µg/L, with over 60% wells having a sum concentration below 2 µg/L, while only one surface water site in Tianjin showed the total concentration lower than 10 µg/L. However, the compounds detected in over 80% of surface water samples with mean concentration exceeding 1 µg/L were not frequently existed in groundwater, such as coprostanol, 2-(methylthio)-benzothiazol and metformin. The compounds with similar average concentration measured in both groundwater and surface water were 2-ethyl-1-hexanol, acetophenone, naphthalene, 2,6-di-tert-butyl-4-benzoquinone, octanol, oleandomycin, acenaphthene and bis(2-ethylhexyl) sebacate.

The number of compounds detected in this work was comparable to that reported in European groundwater, but more than that published in American groundwater. It should be noted the number of target chemicals in our work was approximately 20 times of those reconnaissance in EU and US. The *N*,*N*-diethyltoluamide (DEET), caffeine and bisphenol-A were relatively frequently detected in EU and US, but these compounds were not found in this study. However, the concentration measured in this work was generally great compared to the groundwater in US and EU which indicated the groundwater in Beijing and Tianjin was more polluted and impacted by the intensive industrial and agricultural activities. Although drinking water standards were not available for most compounds analyzed, the elevated concentration observed for some compounds in this work was still below the corresponding health advisory level.

Table 4.10 Concentration of compounds detected in both surface water and groundwater

Compound	Groundwater			Surface water		
	Mean ng/L	Minimum ng/L	Maximum ng/L	Mean ng/L	Minimum ng/L	Maximum ng/L
Benzylalcohol	523	ND	1160	865	ND	15500
Squalane	15.3	ND	142	109	ND	345
Octanol	6.10	ND	55.9	44.6	ND	364
2-Butoxyethanol	31.4	ND	282	63.3	ND	886
Isophorone	2.32	ND	39.4	42.2	ND	156
PCB_#60	0.02	ND	0.21	3.83	ND	23.0
L-Menthol	7.64	ND	153	217	ND	1880
metformin	3.09	ND	45.4	4080	ND	33800
Bis(2-ethylhexyl)sebacate	2.44	ND	33.3	5.50	ND	89.9
Stigmasterol	2.25	ND	32.6	722	ND	4370
Bis(2-ethylhexyl)phthalate	14.2	ND	385	613	ND	5450
4-Cymene	2.52	ND	68.1	36.7	ND	682
Campesterol	0.89	ND	24.0	574	ND	4530
2-tert-Butyl-4-methoxyphenol	0.80	ND	21.5	7.84	ND	110
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	0.48	ND	13.0	5.95	ND	107
p,p'-DDD	0.01	ND	0.28	0.58	ND	5.45
Hexachlorobenzene	0.03	ND	0.51	3.00	ND	39.4
2,6-Di-tert-butyl-4-benzoquinone	10.7	ND	51.1	67.5	ND	255
Cholesterol	73.8	ND	522	5850	ND	40900
beta-Sitosterol	12.1	ND	204	2450	ND	12600

carbendazim	61.8	ND	1610	29.0	ND	204
2-Ethyl-1-hexanol	234	ND	997	217	ND	1154
Ethanol,2-phenoxy-	217	ND	1330	6.81	ND	73.5
Acetophenone	74.5	ND	204	88.5	ND	1430
Pentamethylbenzene	332	ND	5050	26.3	ND	261
Dimethylphthalate	97.2	ND	1230	246	ND	5780
2-Methylnaphthalene	868	ND	9570	86.1	ND	1630
Naphthalene	468	ND	5890	536	ND	5070
3,5-Dimethylphenol	39.1	ND	131	199	ND	3410
1-Methylnaphthalene	634	ND	6200	49.1	ND	815
1,4-Dichlorobenzene	168	ND	3810	37.6	ND	324
Diethylphthalate	12.6	ND	71.5	250.	ND	995
1,3-Dimethylnaphthalene	719	ND	19000	87.9	ND	1610
Carbazole	10.3	ND	59.5	3.10	ND	34.1
1,2-Dimethylnaphthalene	881	ND	14000	3.08	ND	61.6
Diphenylmethane	635	ND	9520	1.30	ND	26.0
Anthraquinone	12.2	ND	219	57.1	ND	293
Phenol	10.8	ND	170	40.1	ND	928
Quinoline	6.98	ND	127	91.8	ND	1870
Dibenzofuran	5.30	ND	51.8	85.2	ND	659
1,4-&2,3-Dimethylnaphthalene	1790	ND	29700	46.7	ND	463
2,6-Dimethylnaphthalene	386	ND	10000	75.0	ND	706
Benzothiazole	11.5	ND	229	945	ND	30900
Phenanthrene	7.16	ND	92.2	196	ND	672
oleandomycin	3.19	ND	39.9	3.55	ND	71.0
2(3H)-Benzothiazolone	3.02	ND	28.9	1690	ND	41100
Di-n-butylphthalate	67.9	ND	741	176	ND	1143
Acenaphthene	23.6	ND	607	17.9	ND	108
2-Nitrophenol	4.53	ND	73.8	54.9	ND	815
Fluorene	4.64	ND	58.3	72.3	ND	288
Phenylethylalcohol	2.96	ND	56.2	14.9	ND	166
Fluoranthene	2.42	ND	40.7	29.0	ND	235
Anthracene	2.64	ND	32.5	23.6	ND	54.7
o,p'-DDD	0.03	ND	0.34	0.60	ND	2.59
diuron	14.0	ND	373	6.95	ND	48.7
atrazine	3.70	ND	56.5	98.0	ND	1830
Tris(2-chloroethyl)phosphate	2.32	ND	32.5	136	ND	544
Longifolene	1.22	ND	20.0	72.0	ND	522
a-HCH	.0356	ND	.53	2.10	ND	31.7
Dimethomorph(E)	54.5	ND	1470	31.3	ND	254
Dimethomorph(z)	27.6	ND	746	16.2	ND	112
Ergosterol	4.32	ND	117	901	ND	4370
Pyrimethanil	3.40	ND	91.8	21.3	ND	412
linuron	1.41	ND	38.1	6.25	ND	125
4,5-Methylene-phenanthrene	1.02	ND	27.6	17.1	ND	105
o,p'-DDT	0.01	ND	0.19	0.76	ND	2.75
p,p'-DDE	0.01	ND	0.10	0.62	ND	2.32

4.8 Conclusion

The surface waters in Tianjin and Jinan are heavily polluted with a large number of OMPs. Generally, the surface water in Tianjin was more polluted compared to that in Jinan, and sewage wastewater discharge was a main source in Jinan. The causes of pollution are industrialization, modernization and urbanization, being experienced by this region and the current management systems for controlling contaminants discharge cannot catch up these the rapid expansion of these factors. In the present study it was confirmed that monitoring for 1300 OMPs provided a much more holistic picture of pollution and revealed that all surface waters in Tianjin were more or less impacted by anthropogenic activities, albeit that the distribution of each chemical class varied among sample locations as a result of population density, geographic condition, level and distribution of industry and agriculture. In contrast to a study on Tokyo Bay (Pan et al., 2014), this study suggests that insufficient treatment efficiency in WWTPs is a major cause of the pollution in the canals. For the three watersheds in Tianjin, chemicals of domestic origin, sterols and pesticides were significant contributors to pollution profiles, even in relatively remote areas; this is consistent with studies in Japan (Pan et al., 2014) and Europe (Loos et al., 2009). Overall, the comprehensive data obtained provides valuable information for refining chemical inventories and technical support for developing sustainable water strategies towards these contaminants.

The occurrence of 1300 organic micro-pollutants in groundwater from Beijing and Tianjin reveals the presence of a wide spectrum of compounds. The groundwater sites with high concentration were mainly contributed by naphthalene and its 7 alkylated derivatives and the potential source was assumed to be the lubricating oils leakage from the well pump. The maximum number of pesticides was observed in the well which located in the intense greenhouse vegetable cultivation area with a shallow depth (< 4 m). The chemicals used as intermediate in organic synthesis were more frequently detected in this work which may be attributed to the improper solid waste disposal. Concerning the occurrence of PPCPs, the direct household wastewater discharge may be the possible contribution to groundwater pollution since most of the groundwater sites located in suburban and rural areas and there is a lack of sewer treatment plant. No obvious relationship was found between previous surface water monitoring and groundwater survey in this study. Compared to the groundwater in US and EU, the groundwater Beijing and Tianjin was more polluted due to the intensive industrial and agricultural activities. However, the novel screening methods provided a useful tool to obtain a detailed picture of pollution and more routine groundwater investigation should be performed to identify the possible pollution spots for protecting human health.

Chapter 5 Multivariate Analysis and Water

5.1 Multivariate Analysis in Surface Water

The application of different multivariate statistical techniques, such as cluster analysis (CA) and principal component analysis (PCA), helps in the interpretation of complex data matrices for better understanding the water quality and ecological status of the studied systems, which allows the identification of possible factors/sources that influence water systems and offers a valuable tool for reliable management of water resources as well as rapid solution to pollution problems. Multivariate statistical techniques have been applied to characterize and evaluate surface and freshwater quality, and those are useful in verifying temporal and spatial variations caused by natural and anthropogenic factors linked to seasonality.

For surface water in Tianjin, the detected 227 compounds were divided into 18 groups (Table S4), and then hierarchical cluster analysis was applied to evaluate the spatial variation of these 18 groups. Squared Euclidean distance was calculated and the dendrogram was rendered in Fig. 5.1.

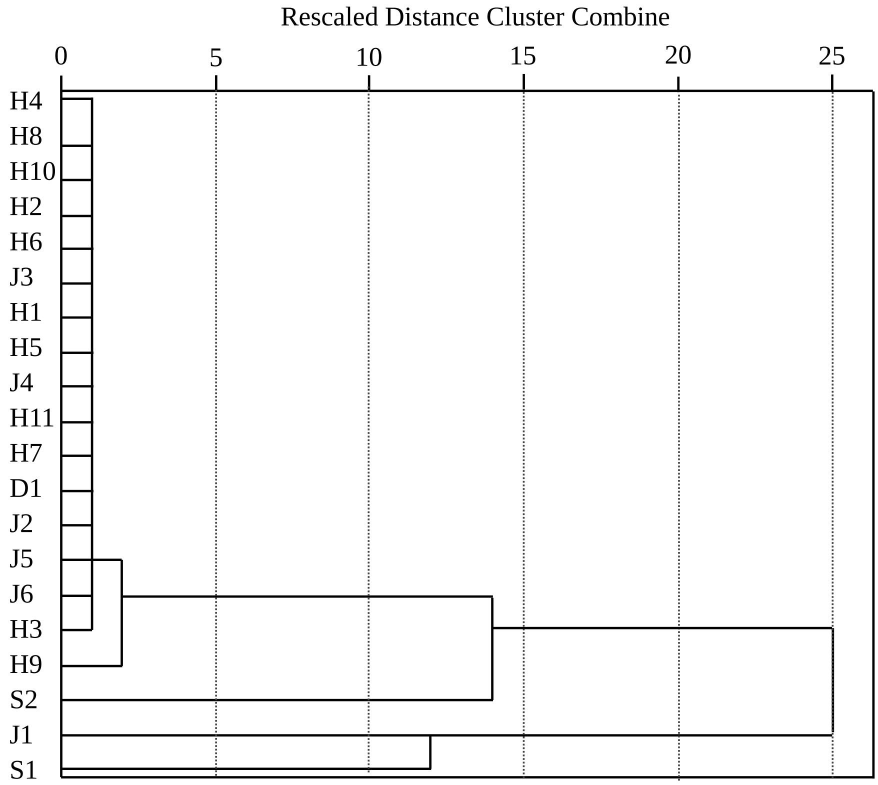


Fig. 5.1 Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for surface water in Tianjin

The results significantly separated J1, north sewage canal (S1) and south sewage canal (S2) from other sampling sites at ($D_{link}/D_{max} \times 25 < 5$). It should be noted that the high concentrations observed at J1 is likely affected by the influx from north sewage canal since this site is located in downstream of the confluence (Fig. 2.2). Sites J1, S1 and S2 represent sites at which the pollution source is wastewater.

PCA on the same data used for spatial cluster analysis renders four varifactors with eigenvalues higher than 1.0 accounting for 78% of total variance (Table 5.1). Varifactor 1 (VF1) explained 31% of total variance and was correlated with (loading>0.7) 6 parameters including intermediates for dyes, chemical intermediates used in organic synthesis, disinfectants, fragrances, fire retardants and pesticides associated with wastewater of industrial, household/business origin and agriculture runoff. VF2 accounting for 20% of total variance showed high correlations (loading>0.8) for leachate from tires, PPCPs and benzothiazoles and this principle component mainly represent the tire manufacture source. Important contributors for VF3 were cholesterol, phytosterol, zoosterol and plasticizers; accounting for 15% of total variance, these chemicals were mainly related to sewage sources. VF4 was dominated by PAHs and intermediates for plastic resins; accounting for 8.6% of total variance, their origins are atmospheric deposition and resin production.

Table 5.1 Principle components loadings matrix for data of surface waters in Tianjin

Variable	PC1	PC2	PC3	PC4
Disinfectant	0.98	-0.01	0.12	-0.03
Intermediate in organic synthesis	0.97	0.02	0.12	0.04
Intermediate for dyes	0.96	-0.02	0.11	0.09
Fragrance	0.94	-0.05	0.06	-0.01
Fire retardant	0.79	0.14	0.22	-0.04
Pesticide	0.72	0.10	0.50	0.00
Leaching from tire	0.05	0.97	0.03	0.03
PPCPs	-0.04	0.96	0.21	-0.01
Benzothiazole	-0.09	0.88	-0.05	-0.05
Antioxidant	0.53	0.60	-0.25	-0.02
Phytosetrol	0.02	-0.24	0.84	-0.18
Cholesterol	0.13	0.33	0.79	-0.10
Plasticizer	0.43	-0.05	0.67	0.03
Zoosterol	0.35	0.49	0.63	-0.05
Intermediate for resin	-0.09	0.08	0.01	0.94
PAH	0.11	-0.16	-0.22	0.91
Fatty acid methy ester	0.00	-0.12	-0.05	-0.05
Industry	0.28	0.25	-0.04	0.35
Eigenvalues	6.3	3.5	2.7	1.6
% Variance explained	31	20	15	8.6

% Cumulative variance	35	54	70	78

For surface water in Jinan, the detected 108 compounds were divided into seven groups which included coprostanol, sterols, PAHs, pesticides, PPCPs, domestic and industrial compounds. Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for surface water in Jinan was showed in Fig. 5.2 as below.

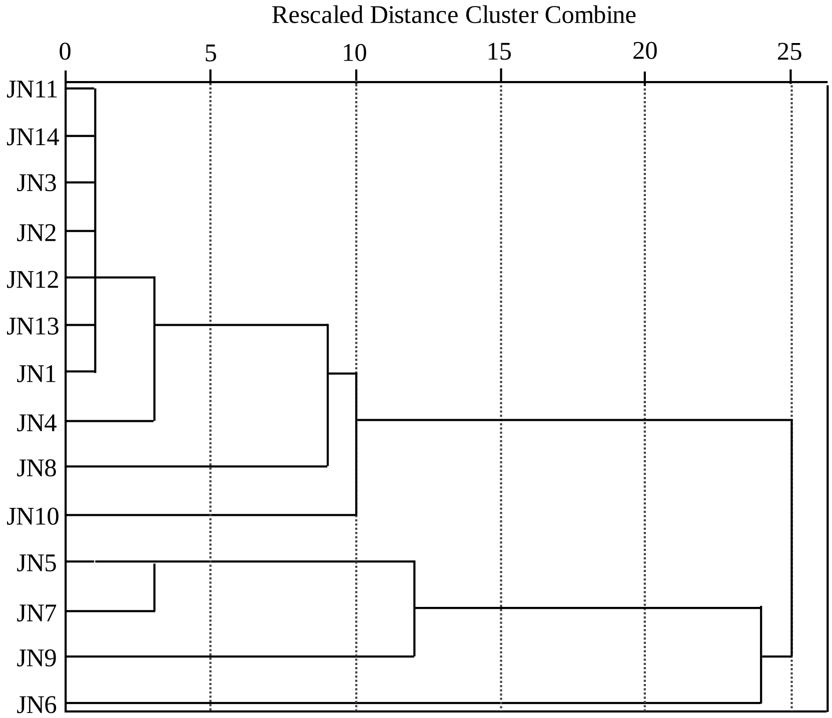


Fig. 5.2 Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for surface water in Jinan

The results separated three groups at (Dlink/Dmax×25 < 15), which can be defined as less polluted (LP), medium polluted (MP), highly polluted (HP). J6 was the only site in HP group, which was reasonable because it located in downstream of Xiaoqing River and surrounded by agricultural areas. JN5, JN7 and JN9 were belonged to the MP group, which all located in Xiaoqing River. The LP group mainly included the Yellow River, spring water and two reservoirs, which are used as drinking water source for the habitants in Jinan.

5.2 Multivariate Analysis in Groundwater

For groundwater in Beijing and Tianjin, the detected 78 compounds were divided into six groups, which included sterols, PAHs, pesticides, PPCPs, domestic and industrial compounds. Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for groundwater was showed in Fig. 5.3.

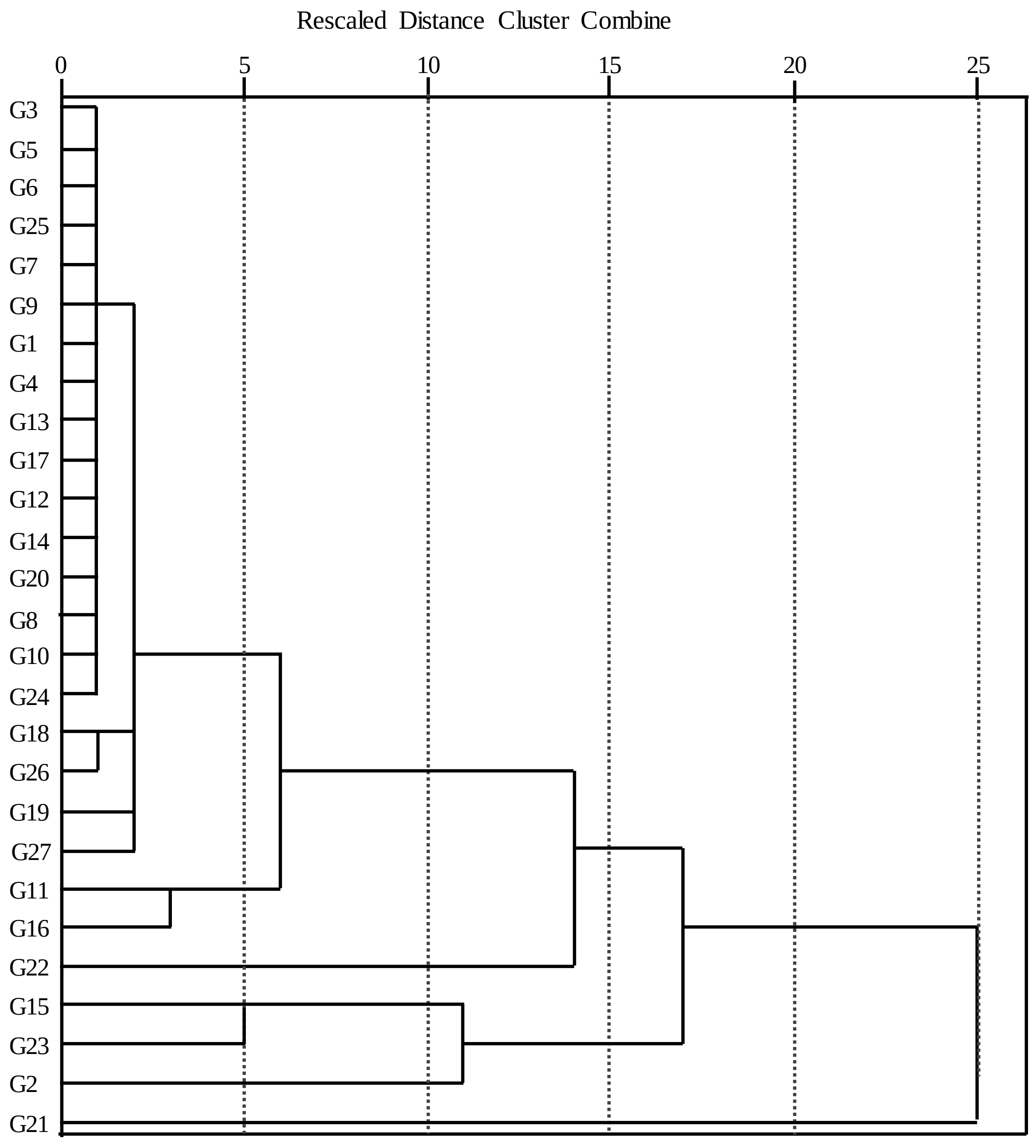


Fig. 5.3 Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for groundwater

The results separated three groups at (Dlink/Dmax×25 < 15), which can be defined as less polluted (LP), medium polluted (MP), highly polluted (HP). G21 was the only site in HP group, where was polluted by multiple sources. G2, G15 and G23 were belonged to the MP group, where were mainly impacted by high concentration of PAHs. PCA on the same data used for spatial cluster analysis renders two varifactors with eigenvalues higher than 1.0 accounting for 75% of total variance (Table 5.2).

Table 5.2 Principle components loadings matrix for data of groundwater

Variable	PC1	PC2
Domestic chemicals	0.93	0.14
PPCPs	0.74	-0.06
Pesticides	0.71	-0.10
Sterols	0.71	0.49
PAH	0.03	0.97
Industrial compounds	-0.02	0.93
Eigenvalues	2.7	1.8
% Variance explained	40	35
% Cumulative variance	40	75

Varifactor 1 (VF1) explained 40% of total variance and was correlated with (loading>0.7) 4 parameters including domestic chemicals, PPCPs, pesticides and sterols which was associated with surface water leakage. VF2 accounting for 35% of total variance showed high correlations (loading>0.9) for PAHs and industrial compounds which was associated from the non-point source and leachate of solid waste.

5.3 Conclusion

The PCA multivariate statistical analysis rendered four principle components for the pollution of surface water of Tianjin, which corresponded to industrial wastewater, domestic discharge, tire production and atmospheric deposition, accounting for 78% of the total variance. The cluster analysis helped to group the twenty sampling sites into three clusters of similar characteristics. The sewage canal was heavily polluted than other watersheds which were not surprising. For surface water in Jinan, Xiaoqing River was seriously polluted which can be ascribed to the domestic wastewater discharge. For groundwater in Tianjin and Beijing, the PCA analysis rendered two components corresponding to the leakage from the surface water and solid waste disposal.

Chapter 6 Water Quality Assessment

6.1 Surface Water Quality Assessment

The environmental risk posed by certain contaminants on aquatic ecosystems was assessed through the calculation of risk quotients (RQ) as described previously (European Agency for the Evaluation of Medicinal Products, 2006; Tauxe-Wuersch et al., 2005). RQ values for aquatic organisms were calculated from the measured environmental concentration (MEC) and the predicted no effect concentration (PNEC) of the target compound. The maximum concentration observed in surface water of this work was used as MEC. A commonly used risk ranking criteria was applied: RQ<0.1 means minimal risk, 0.1≤RQ<1 means median risk, and RQ≥1 means high risk. The results of water risk assessment were presented in Table 6.1.

Table 6.1 Risk assessment in surface water of Tianjin and Jinan

Compounds	MEC (ng/L)		PNEC (μg/L)	RQ	
	Tianjin	Jinan		Tianjin	Jinan
1,3-Dimethylnaphthalene	1611	292	2	0.81	0.15
2,6-Diisopropylnaphthalene	100	84.1	2	0.05	0.04
2-Methylnaphthalene	1631	79.1	2	0.82	0.04
1-Methylnaphthalene	815	56.1	2	0.41	0.03
2-Methylphenanthrene	54	33.7	1.3	0.04	0.03
Acenaphthylene	124	30.3	1.3	0.10	0.02
3-Methylphenanthrene	48	28.9	1.3	0.04	0.02
Fluoranthene	235	29.4	0.01	23.46	2.94
Pyrene	136	23.1	0.0046	29.63	5.02
4-tert-Octylphenol	138	53.5	0.48	0.29	0.11
Caffeine	1434	6090	87	0.02	0.07
Diethyltoluamide	87	56.5	43	2.02E-03	1.31E-03
Ibuprofen	612	697	7.1	0.09	0.10
Nicotine	390	998	2.4	0.16	0.42
Acetaminophen	6402	6810	9.2	0.70	0.74
Clarithromycin	166	159	0.13	1.28	1.22
Cotinine	911	13700	589.5	1.55E-03	0.02
Lidocaine	218	28.8	106	2.05E-03	2.72E-04
Lincomycin	1791	762	379	4.73E-03	2.01E-03
Metformin	20015	33800	511	0.04	0.07
Sulfamethoxazole	173	5000	0.15	1.16	33.33
Atrazine	1829	31.1	1.9	0.96	0.02
Simetryn	237	31.2	1.1	0.22	0.03
Hexachlorobenzene	39	2.95	0.37	0.11	0.01
a-HCH	32	1.79	0.02	1.58	0.09
b-HCH	13	1.68	0.02	0.65	0.08

g-HCH	20	0.83	0.02	0.98	0.04
o,p'-DDD	2.6	1.04	0.00064	4.05	1.63
p,p'-DDE	2.3	1.37	0.0006	3.87	2.28
p,p'-DDT	0.82	1.79	0.002	0.41	0.90
Carbofuran	111	57.9	0.4	0.28	0.14
Dimethoate	225	9.66	1.1	0.20	0.01
Carbendazim	99	204	2.6	0.04	0.08
2(3H)-Benzothiazolone	41083	112	16.1	2.55	0.01
2-(Methylthio)-benzothiazol	31765	200	3.4	9.34	0.06
Benzothiazole	30867	80.8	8.1	3.81	0.01
Tributyl phosphate	2610	250	21	0.12	0.01
Tris(2-chloroethyl) phosphate	544	283	100	0.01	0.00
Bis(2-ethylhexyl) phthalate	5454	2600	0.77	7.08	3.38
Butyl benzyl phthalate	20	9760	2.1	0.01	4.65
Dimethyl phthalate	5785	1670	96	0.06	0.02
Di-n-butyl phthalate	1143	684	4	0.29	0.17
Octanol	155	364	10	0.02	0.04
Benzyl alcohol	15537	1230	1	15.54	1.23
Anthraquinone	293	128	6.6	0.04	0.02
Phenol	928	109	7.7	0.12	0.01
3- & 4-tert-Butylphenol	530	423	0.64	0.83	0.66
Bisphenol A	151	139	1.6	0.09	0.09
Biphenyl	742	536	0.072	10.30	7.44
Isophorone	139	156	990	1.40E-04	1.58E-04
1,2-Dichlorobenzene	128	187	1100	1.16E-04	1.70E-04
e-Caprolactam	147	1480	130	1.13E-03	0.01
Quinoline	1874	111	4.4	0.43	0.03
2-Methyl-2,4-pentandiol	ND	123	4300		2.86E-05
Hexamethylenetetramine	ND	9160	3000		3.05E-03
PCB_#28	ND	0.51	0.000032		15.94
2-Butoxyethanol	ND	886	8.8		0.10
2-tert-Butylphenol	ND	262	0.64		0.41
3,4-Dichloroaniline	ND	164	0.2		0.82
Dicyclohexylamine	ND	466	0.2		2.33
Endrin	ND	3.00	0.01		0.30
Dieldrin	ND	2.47	0.01		0.25
DDVP	ND	75.7	0.00077		98.29
Trimethoprim	ND	74.6	5.1		0.01
Erythromycin	ND	90.6	0.2		0.45
Azithromycin	ND	291	0.09		3.23
Triclosan	ND	63.1	1.55		0.04
1,2-Dimethylnaphthalene	62	ND	2	0.03	
1,4-&2,3-Dimethylnaphthalene	463	ND	2	0.23	
2,6-Dimethylnaphthalene	706	ND	2	0.35	
Naphthalene	5067	ND	2	2.53	
Acenaphthene	108	ND	3.8	0.03	
Anthracene	55	ND	0.1	0.55	
Fluorene	288	ND	2.5	0.12	

Phenanthrene	672	ND	1.3	0.52
9-Methylphenanthrene	26	ND	1.3	0.02
Benzo(a)anthracene	147	ND	0.012	12.28
Chrysene & Triphenylene	77	ND	0.07	1.10
Benzo(a)pyrene	79	ND	0.022	3.60
Benzo(j&b)fluoranthene	227	ND	0.017	13.35
Benzo(ghi)perylene	65	ND	0.0082	7.96
Indeno(1,2,3-cd)pyrene	68	ND	0.00017	402.47
Atenolol	15	ND	148	1.00E-04
Cimetidine	90	ND	100	9.02E-04
Salinomycin	438	ND	1.14	0.38
Acetochlor	166	ND	3.6	0.05
Prometryn	651	ND	0.04	16.28
1,4-Dichlorobenzene	324	ND	20	0.02
Acetamiprid	1639	ND	0.5	3.28
Bendiocarb	117	ND	0.088	1.32
Dinoseb	8394	ND	0.11	76.31
Fenobucarb	68	ND	0.003	22.77
2,5-Dichlorophenol	1382	ND	0.2	6.91
d-HCH	5.9	ND	0.02	0.29
Alachlor	160	ND	0.77	0.21
Carbaryl	18	ND	0.12	0.15
Cyanazine	77	ND	0.012	6.38
Diuron	49	ND	0.2	0.24
Linuron	125	ND	0.9	0.14
Pirimicarb	16	ND	0.6	0.03
Propoxur	22	ND	0.64	0.03
Quizalofop-ethyl	22	ND	0.57	0.04
Simazine	17	ND	1	0.02
Tebufenpyrad	4.9	ND	0.073	0.07
Isoprothiolane	36	ND	40	8.92E-04
Myclobutanil	2252	ND	20	0.11
Pyrimethanil	412	ND	18.8	0.02
Tebuconazole	961	ND	1	0.96
Azoxystrobin	32	ND	0.95	0.03
Cyprodinil	45	ND	0.18	0.25
Dimethomorph(E)	254	ND	0.2	1.27
Dimethomorph(Z)	112	ND	0.2	0.56
Thiabendazole	27	ND	1.2	0.02
2-Methylbenzothiazole	7904	ND	29.8	0.27
4-Methyl-2,6-di-t-butylphenol	163	ND	0.64	0.26
Methyl palmitate	80	ND	0.007	11.48
Tris(2-ethylhexyl) phosphate	77	ND	1.3	0.06
Triphenyl phosphate	712	ND	3.7	0.19
Di(2-ethylhexyl)adipate	597	ND	0.52	1.15
Diethyl phthalate	995	ND	12	0.08
Di-iso-butyl phthalate	8804	ND	3.7	2.38
4-nonylphenol	2622	ND	0.21	12.49
3-&4-Methylphenol	491	ND	7.7	0.06

Acetamide, N-phenyl-	258	ND	135	1.91E-03
Dicyclopentadiene	984	ND	32	0.03
1,2,4-Trichlorobenzene	34	ND	3	0.01
2,4,6-Trichlorophenol	144	ND	57	2.52E-03
2,4-Dichloroaniline	670	ND	0.54	1.24
1,3-Dichloro-2-propanol	577	ND	63	0.01
Trimethyl phosphate	3927	ND	3200	1.23E-03
2-Anisidine	1333	ND	2.5	0.53
2-Chloroaniline	145	ND	0.32	0.45
2-Methylaniline	82	ND	0.13	0.63
N,N-Dimethylaniline	338	ND	23	0.01
N-Ethylaniline	39	ND	43	9.14E-04
Diphenylamine	259	ND	2	0.13
2,5-Dimethylaniline	43	ND	180	2.38E-04
2,4-Dimethylphenol	440	ND	7.7	0.06
3,5-Dimethylphenol	3410	ND	7.7	0.44
4-Chloronitrobenzene	458	ND	2.8	0.16
4-Nitroaniline	3733	ND	210	0.02
N-Methylaniline	209	ND	2.1	0.10
2-Ethyl-1-hexanol	1154	ND	17	0.07
Aniline	757	ND	1.5	0.50
Acetophenone	1426	ND	86.4	0.02

The PNEC information was not available for all compounds. The value of RQ for most detected compounds in Tianjin and Jinan was lowers than 1. However, 33 out of 131 compounds in Tianjin and 13 of 64 chemicals in Jinan showed the MEC higher than their corresponding PNEC. Ten chemicals were observed in surface water of Tianjin with RQ exceeding 10 including fluoranthene, pyrene, benzyl alcohol, biphenyl, indeno(1,2,3-cd)pyrene, dinoseb, fenobucarb, methyl palmitate and 4-nonylphenol. For surface water of Jinan, only sulfamethoxazole and DDVP (dichlorvos) were found with RQ over 10 which indicated the surface water of Tianjin was more pollutated than that in Jinan.

Although direct acute ecological effects have not been reported in the aquatic environment, precautionary measures should be taken to reduce the risks to aquatic organisms due to potential subtle chronic changes in the surface waters of Tianjin and Jinan. Although most studies have looked at the risk of individual compound to organisms, in the aquatic environment chemicals are present as complex mixtures. For example, pharmaceuticals in a mixture showed toxic effects at concentrations lower than the NOEC (No Observed Effect Concentration) for each substance if acting alone (Cleuvers, 2004; Quinn et al., 2008). The combination effect can result from concentration addition where compounds have a similar mode of action, or independent action where the effect of each compound is independent of the others. Nonsteroidal anti-inflammatory drugs in a mixture showed additive effects as they have the same mode of action. Since all compounds investigated in the present study have different chemical structures, the mixture effects were difficult to evaluate.

6.2 Groundwater Quality Assessment

Although the groundwater sampled in Beijing and Tianjin is mainly used for laundry, bathing and kitchen use, oral ingestion exposure is still an important human exposure route and is used to assess groundwater quality. Since drinking water standards are not available for most of the detected compounds, human health impact values were calculated (Table 1). Although few pesticides were observed at concentrations over 0.1 μg L−1, seven compounds including 6 pesticides and diphenylmethane were observed with RQ exceeding 1 at sites G2, G11, G16 and G24. In that context, G16 located in an area of intensive greenhouse vegetable cultivation and since well water is used for only for irrigation purposes, there appears to be little human health risk. Diphenylmethane and diuron concentrations in G2, a sub-urban area, had RQ values of 1.4 and 3.7, respectively, suggesting they may pose a human health risk. Carbendazim was observed at concentrations with the highest RQ (16) in G11, which is located in a rural area and the source may be attributed to the leakage from the pesticides application in agricultural area. Since the CHIVs set in this study assumed that adverse health effects may appear when people drink the groundwater for 70 years, these seems to be little likelihood of immediate adverse effects on human health immediately. To prevent adverse effects, however, further detailed survey on these substances is needed.

Table 6.2 Calculated human health impact values for groundwater

No.	Compounds	Maximum concentration (ng/L)	Threshold value (μg/kg bw/day)	CHIVs (μg/L)	RQ
1	Cholesterol	522	30 [a]	7 [b]	0.075
2	Beta-Sitosterol	204	30 [a]	7 [b]	0.029
3	Ergosterol	117	30 [a]	7 [b]	0.017
4	Stigmasterol	33	30 [a]	7 [b]	0.005
5	Campesterol	24	30 [a]	7 [b]	0.003
6	1,4-&2,3-Dimethylnaphthalene	65000		70 [c]	0.929
7	1,2-Dimethylnaphthalene				
8	2-Methylnaphthalene				
9	1,3-Dimethylnaphthalene				

10	1-Methylnaphthalene				
11	Naphthalene				
12	2,6-Dimethylnaphthalene				
13	Acenaphthene	607	60 [d, e]	210	0.003
14	Phenanthrene	92	40 [f]	140 [b]	0.001
15	Fluorene	58	40 [d, e]	140	0.000
16	Anthracene	33	300 [d, e]	1050	0.000
17	Fluoranthene	41	40 [d, e]	140	0.000
18	4,5-Methylene-phenanthrene	28	1.5 [a]	0.35 [b]	0.079
19	Acetophenone	204	0.1	350	0.001
20	Ethanol, 2-phenoxy-	1328	80000 [g, h]	280	0.005
21	Metformin	45	500 [i]	250 [j]	0.0002
22	Oleandomycin	40	1000 [i]	500 [j]	0.0001
23	Squalane	142	30 [a]	7 [b]	0.020
24	L-Menthol	153	30 [a]	7 [b]	0.022
25	1,1,1-Trichloro-2-methyl-2-propanol	61	30 [a]	7 [b]	0.009
26	Pyrimethanil	92		0.1 [k]	0.918
27	1,4-Dichlorobenzene	3811	10000 [g, t]	35	0.109
28	Oxadixyl	805		0.1 [k]	8.047
29	Diflubenzuron	148		0.1 [k]	1.482
30	Iprodione	61		0.1 [k]	0.608
31	Atrazine	57		0.1 [k]	0.565
32	2-Phenylphenol (OPP)	19		0.1 [k]	0.193
33	Carbendazim	1607		0.1 [k]	16.074
34	Prochloraz	81		0.1 [k]	0.810
35	Dimethomorph(E)	1472		0.1 [k]	14.719
36	Dimethomorph(z)	746		0.1 [k]	7.463
37	Fenhexamid	67		0.1 [k]	0.665
38	Diuron	373		0.1 [k]	3.727
39	Linuron	38		0.1 [k]	0.381
40	Isouron	33		0.1 [k]	0.332
41	Hexachlorobenzene	0.51		0.1 [k]	0.005
42	a-HCH	0.53		0.1 [k]	0.005
43	p,p'-DDE	0.10		0.1 [k]	0.001
44	o,p'-DDD	0.34		0.1 [k]	0.003
45	p,p'-DDD	0.28		0.1 [k]	0.003
46	o,p'-DDT	0.19		0.1 [k]	0.002
47	2,6-Di-tert-butyl-4-benzoquinone	51	9 [a]	2 [b]	0.026
48	2-tert-Butyl-4-methoxyphenol	21	9 [a]	2 [b]	0.011
49	Phenol	170		150 [b]	0.001
50	Cis-5,8,11,14,17-Eicosapentaenoic acid,	396	9 [a]	2 [b]	0.198
51	Tris(2-chloroethyl) phosphate	33	22000 [g, l]	77	0.000
52	Benzyl alcohol	1155	550000 [g, m]	1925	0.001
53	Anthraquinone	219	30 [a]	7 [b]	0.031
54	Octanol	56	1.5 [a]	0.35 [b]	0.160
55	Phenylethyl alcohol	56	70000 [g, n]	245	0.000
56	4-Cymene	68	1.5 [a]	0.35 [b]	0.195
57	Benzothiazole	229	1.5 [a]	0.35 [b]	0.655

58	2(3H)-Benzothiazolone	29	1.5 [a]	0.35 [b]	0.083
59	Dibenzothiophene	13	1.5 [a]	0.35 [b]	0.037
60	Dimethyl phthalate	1230	30 [a]	7 [b]	0.176
61	Di-n-butyl phthalate	741	10 [f]	35 [b]	0.021
62	Bis(2-ethylhexyl)phthalate	385		8 [o]	0.048
63	Diethyl phthalate	71	80 [d, e]	280	0.000
64	Bis(2-ethylhexyl) sebacate	33	1.5 [a]	0.35 [b]	0.095
65	2-Butoxyethanol	282	70 [p, q]	245	0.001
66	Dibenzofuran	52	1.5 [a]	0.35 [b]	0.148
67	Isophorone	39	200 [d, e]	700	0.000
68	Longifolene	20	9 [a]	2 [b]	0.010
69	PCB_#60	0.21	1.5 [a]	0.35 [b]	0.001
70	Pentamethylbenzene	5050	30 [a]	7 [b]	0.721
71	2-Ethyl-1-hexanol	997	35.7 [d, r]	200 [r]	0.005
72	Nitrobenzene	548	2 [d, e]	7	0.078
73	3,5-Dimethylphenol	131	1.5 [a]	0.35 [b]	0.374
74	Carbazole	60	1.5 [a]	0.35 [b]	0.170
75	Quinoline	127	1.5 [a]	0.35 [b]	0.363
76	2-Nitrophenol	74		290 [s]	0.000
77	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	13	9 [a]	2 [b]	0.006
78	Diphenylmethane	9524	30 [a]	7 [b]	1.361

[a] Reported as TTC (Thresholds of toxicological concern) from EPHC–NHMRC–NRMMC, 2008

[b] Reported from EPHC–NHMRC–NRMMC, 2008

[c] Reported from U.S. EPA. 2012e

[d] Reported as RfD (Reference does)

[e] Reported from US-EPA, IRIS

[f] Reported as TDI (Tolerable daily intake) or ADI (Acceptable daily intake)

[g] Reported as NOEL (No observed effect level)

[h] Reported from CEPA (California Environment Protection Agency), 2010

[i] Reported as LDTD (Lowest daily oral therapeutic dose for an adult) from MIMS

[j] The P (proportion from water) was set to 1.

[k] Pesticides, Reported from EC (European Commission), 2006

[l] Reported from WHO, 1998

[m] Reported from EC, 2002.

[n] Reported from Politano et al., 2013

[o] Reported from WHO (Edition, 2011)

[p] Reported as MRL (Minimal risk level)

[q] Reported from ATSDR (Agency for Toxic Substances and Disease Registry), 1998

[r] Reported from NJDEP, 2008

[s] Reported from ATSDR, 1992.

[t] Reported from EC, 2004

6.3 Conclusion

For suface water in Tianjin and Jinan, the toxicological information of PNEC was not available for all the compounds. However, most compounds showed no adverse effects on aquatic organism. However, thirty-three compounds found in Tianjin and thirteen chemicals observed in Jian showed the MEC higher than their corresponding PNEC, which indicated the potential threat to ecosystem. The source of these high concentrations was unknown and need further inveatigation. Calculated human health impact values were set for all detected compounds and it was found that seven compounds were observed at concentrations that may cause adverse human health effect; therefore detailed investigation is needed on these substances to prevent adverse effects.

Chapter 7 General Conclusion and Future Study

7.1 General Conclusion

This work provides important data about the existence of PCB #11 in foodstuffs in China, which accounts for a large proportion of total PCB concentration. The potential source of PCB #11 is important from a toxicity standpoint and its ubiquity as an environmental pollutant. The origin of non-Aroclor PCB #11 was estimated to be its production as a by-product during the production of diarylide yellow pigments. However, the concentrations of ∑209PCBs were relatively low compared to concentrations reported from Russia and Sweden. This difference can be explained by the lower background levels in marine sediments surrounding the Shandong Peninsula. Among the OCPs, HCH and DDTs were the dominant compounds. The highest concentration of HCHs was found in peanut oil, but the level was lower than concentrations reported from India and Vietnam. The composition of HCH reflected the historical use of technical HCH and recent inputs of lindane. The concentrations of DDTs in our study were similar to those from other coastal regions of China. The composition of the DDTs indicated a recent input of DDT into the marine environment. The potential source of DDT may be antifouling paints on the fishing fleet. Daily exposure was somewhat lower than the non-carcinogenic RfD value and cancer benchmark concentration. The results implied that intake of OCPs has no impact on human health in Shandong Peninsula.

The surface waters in Tianjin and Jinan are heavily polluted with a large number of OMPs. The causes of pollution are industrialization, modernization and urbanization, being experienced by this region and the current management systems for controlling contaminants discharge cannot catch up these the rapid expansion of these factors. The groundwater was much less polluted than the surface water. The risk assessments indicated seven of 1300 OMPs screened in groundwater showed the potential human health impacts.

In the present study it was confirmed that monitoring for 1300 OMPs provided a much more holistic picture of pollution and revealed that all surface waters in were more or less impacted by anthropogenic activities, albeit that the distribution of each chemical class varied among sample locations as a result of population density, geographic condition, level and distribution of industry and agriculture. In contrast to a study on Tokyo Bay, this study suggests that insufficient treatment efficiency in sewage treatment plants is a major cause of the pollution in the canals. However, chemicals of domestic origin, sterols and pesticides were significant contributors to pollution profiles, even in relatively remote areas; this is consistent with studies in Japan and Europe. Overall, the comprehensive data obtained provides valuable information for refining chemical inventories and technical support for developing sustainable water strategies towards these contaminants.

This study also provided the baseline information on the occurrence of 1300 OMPs in groundwater from Beijing and Tianjin, which reveals the presence of a wide spectrum of compounds. The groundwater sites with high concentration were mainly contributed by naphthalene and its 7 alkylated derivatives and the potential source was assumed to be the lubricating oils leakage from the well pump. The maximum number of pesticides was observed in the well which located in the intense greenhouse vegetable cultivation area with a shallow depth (< 4 m). The chemicals used as intermediate in organic synthesis were more frequently detected in this work which may be attributed to the improper solid waste disposal. Concerning the occurrence of PPCPs, the direct household wastewater discharge may be the possible contribution to groundwater pollution since most of the groundwater sites located in suburban and rural areas and there is a lack of sewer treatment plant. No obvious relationship was found between previous surface water monitoring and groundwater survey in this study. Compared to the groundwater in US and EU, the groundwater Beijing and Tianjin was more polluted due to the intensive industrial and agricultural activities.

Most compounds showed no adverse effects on aquatic organism and human health, although the toxicity information was not available for many chemicals. However, the exposure to multiple chemical was still a big concern and unknown.

7.2 Future Study

1. This work fist reported the occurrence of PCB #11 in China. Considering the high toxicity and elevated level, a more detailed survey is required on the source, distribution and toxicity information.

2. The monitoring study identified some particular compounds which were observed in elevated level and received less attention, such as metformin, benzothaizoles and naphthalene. An attempt is needed for the emission sources investigation.

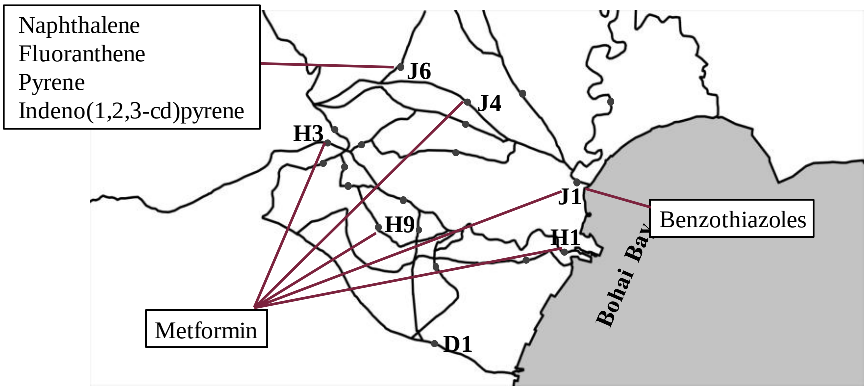


Fig. 7.1 Priority pollutants in surface water of Tianjin

The priority pollutants in surface water of Tianjin were showed in Fig 7.1. The high concentration of PAHs was observed in J6 which was used as drinking purpose. Sine J6 was strictly protected to ensure the water quality, the source is approximately come from the point source. High level of metformin was widely detected in five sites including H3, J4, H9, J1 and H1, and the corresponding measures, such as effective waste water treanment methods, should be undertaken to protect the aquatic environment.

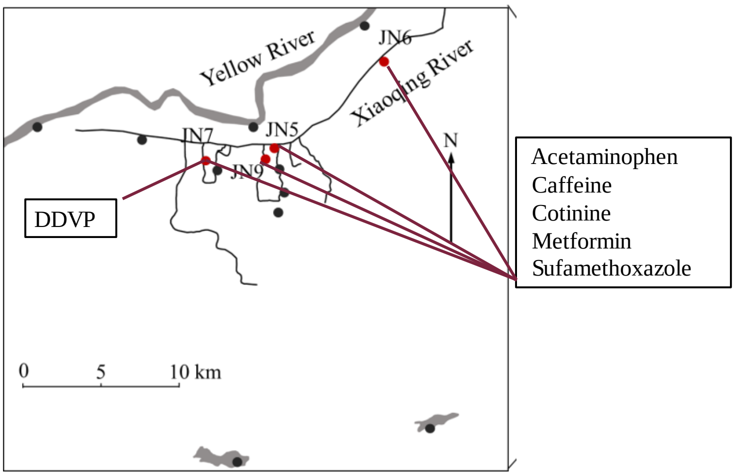


Fig. 7.2 Priority pollutants in surface water of Jinan

The priority pollutants in surface water of Tianjin were showed in Fig. 7.2. The results clearly showed the PPCPs including acetaminophen, caffeine, cotinine, metformin and sulfomethoxazole was dominant compounds. However, considering the elevated level of coprostnaol, the doestical chemicals accounted for a large proportion to the surface water pollution. These pollutants were manily found in Xiaoqing River, where was dominated by the discharge of the sewage waste water and/or the point source. The ability and efficiency of sewer treatment plant may be not enough and should be improved.

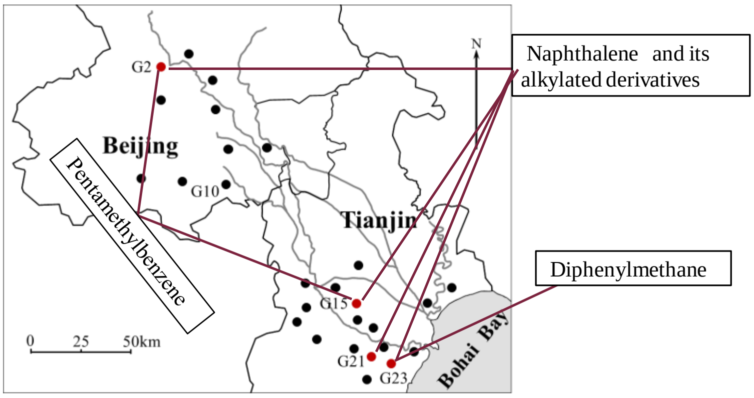


Fig. 7.3 Priority pollutants in surface water of Jinan

The priority pollutants in groundwater of Beijing and Tianjin were showed in Fig. 7.3. Although naphthalene and alkylated naphthalene showed no health risk through oral consumption of groundwater, the elevated level is still a big concern and the source in four sites (G2, G15, G21 and G23; Fig. 7.2) need further investigation. It is estimated that the point source may be the possible contribution. Since pentamethylbenzene and biphenylmethane showed the concentration in some wells over the health risk values. These groundwater sites were not recommended for drinking purpose. Future works will forcus on the souce identificaiton ans removal methods to protect human health.

3. The novel comprehensive methods for monitoring 1300 OMPs have been confirmed to be a useful tool to provide a complete pollution picture. However, some metabolite of PPCPs was found with same or more toxicity than parent compounds, and received increasing attention. The development of database was needed to involve these substances.

4. The work demonstrated the surface water and groundwater were polluted by a large number of wide spectrum chemicals, including sterols, antioxidants, pharmaceuticals and personal care products (PPCPs), PAHs, organophosphate ester flame retardants, plasticizers, and pesticides as well as other industrial chemicals. To develop appropriate strategies for water sources management and water pollution controls approaches is needed to protect the ecosystem and human health.

5. Considering the limited number of sampling events and sites, a systematic sampling should be carried out on the occurrence, distribution and fate of OMPs in aquatic environment as well as a full exposure to multiple chemicals.

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1. **Kong, L.**, Kadokami, K., Wang, S., Duong, H.T., Chau, H.T.C. Monitoring of 1300 organic micro-pollutants in surface waters from Tianjin, North China, Chemosphere, 122: 125–130, 2015.

2. **Kong L**, Kadokami K, Fujita H., Watanabe I., Honda K. Occurrence of Organochlorine Pesticides and Polychlorinated Biphenyls in Foodstuffs from Shandong Peninsula, China, 環境化学= Journal of environmental chemistry, 24(4): 125–134, 2014.

3. Duong, H.T., Kadokami, K., Shirasaka, H., Hidaka, R., Chau, H.T.C., **Kong, L.**, Nguyen, T.Q., Nguyen, T.T. Occurrence of perfluoroalkyl acids in environmental waters in Vietnam, Chemosphere, 122: 115–124, 2015.

4. Chau, H.T.C., Kadokami, K., Duong, H.T., **Kong, L.**, Nguyen, T.T., Nguyen, T.Q., Ito, Y. Occurrence of 1153 organic micropollutants in the aquatic environment of Vietnam, Environmental Science and Pollution Research, 1–10, 2015.

5. Duong, H.T., Kadokami, K., Chau, H.T.C., Nguyen, T.Q., Nguyen, T.T., **Kong, L.** Groundwater screening for 940 organic micro-pollutants in Hanoi and Ho Chi Minh City, Vietnam, Environmental Science and Pollution Research, 1–13, 2015.

Conference Participation

International conference

1. Lingxiao Kong, Kiwao Kadokami, Duong Thi Hanh, Chau Thi Cam Hong,·Monitoring of semi-volatile organic contaminants in surface waters from Tianjin, North China 9th SETAC Asia/Pacific 2014 Conference, Adelaide, Australia; 09/2014

2. **L. Kong,** K. Kadokami, Monitoring of 1300 organic micro-pollutants in surface waters from Tianjin and Jinan, Northern China, SETAC North America 36th Annual Meeting, Salt Lake City, USA, 11/2015

3. Hanh Thi Duong,Hanako Shirasaka, Kiwao Kadokami, Rento Hidaka, Hong Thi Cam Chau, **Lingxiao Kong**, Trung Quang Nguyen and Thao Thanh Nguyen. Detailed Survey on Pollution by Perfluorinated Compounds in Environmental Waters in Vietnam, 2014. 9th SETAC Asia/Pacific 2014 Conference, 14-17 September 2014, Adelaide, Australia, PT9.7.

Domectic conference

1. **Lingxiao Kong**, Kiwao Kadokami, Shaopo Wang, Hanh Thi Duong, Hong Thi Cam Chau. Monitoring of 1300 organic micro-pollutants in surface waters from Tianjin, Northern China. 24th Symposium on Environmental Chemistry, 24-26 June 2015, Sapporo, Japan, 1C-01.

Appendices

Table S1. Chemicals analyzed by comprehensive analysis using GC/MS

No.	Compound	Formula	CAS RN	MW	m/z (Quantitation ion)
1	n-C10H22	C10H22	124-18-5	142	85
2	n-C11H24	C11H24	1120-21-4	156	85
3	n-C12H26	C12H26	112-40-3	170	85
4	n-C13H28	C13H28	629-50-5	184	85
5	n-C14H30	C14H30	629-59-4	198	85
6	n-C15H32	C15H32	629-62-9	212	85
7	n-C16H34	C16H34	544-76-3	226	85
8	n-C17H36	C17H36	629-78-7	240	85
9	n-C18H38	C18H38	593-45-3	254	85
10	n-C19H40	C19H40	629-92-5	268	85
11	n-C20H42	C20H42	112-95-8	282	85
12	n-C21H44	C21H44	629-94-7	296	85
13	n-C22H46	C22H46	629-97-0	310	85
14	n-C23H48	C23H48	638-67-5	324	85
15	n-C24H50	C24H50	646-31-1	338	85
16	n-C25H52	C25H52	629-99-2	352	85
17	n-C26H54	C26H54	630-01-3	366	85
18	n-C27H56	C27H56	593-49-7	380	85
19	n-C28H58	C28H58	630-02-4	394	85
20	n-C29H60	C29H60	630-03-5	408	85
21	n-C30H62	C30H62	638-68-6	422	85
22	n-C31H64	C31H64	630-04-6	437	85
23	n-C32H66	C32H66	4981-99-1	451	85
24	n-C33H68	C33H68	630-05-7	465	85
25	n-C9H20	C9H20	111-84-2	128	85
26	Squalane	C30H62	111-01-3	422	85
27	1,2-Dibromo-3-chloropropane	C3H5Br2Cl	96-12-8	234	157
28	Hexachlorobutadiene	C4Cl6	87-68-3	258	225
29	Hexachloroethane	C2Cl6	67-72-1	234	201
30	Hexachloropropylene	C3Cl6	1888-71-7	246	213
31	Pentachloroethane	C2HCl5	197-61-7	200	167
32	4-Cymene	C10H14	99-87-6	134	119
33	Pentamethylbenzene	C11H16	700-12-9	148	133
34	1,2,3-Trichlorobenzene	C6H3Cl3	87-61-6	180	180
35	1,2,4,5-Tetrabromobenzene	C6H2Br4	636-28-2	390	394
36	1,2,4,5-Tetrachlorobenzene	C6H2Cl4	95-94-3	214	216
37	1,2,4-Trichlorobenzene	C6H3Cl3	120-82-1	180	180
38	1,2-Dichlorobenzene	C6H4Cl2	95-50-1	146	146
39	1,3,5-Trichlorobenzene	C6H3Cl3	108-70-3	180	182
40	1,3-Dichlorobenzene	C6H4Cl2	541-73-1	146	146
41	1,4-Dichlorobenzene	C6H4Cl2	106-46-7	146	146
42	2-Bromochlorobenzene	C6H4BrCl	694-80-4	190	192
43	3-Bromochlorobenzene	C6H4BrCl	108-37-2	190	192
44	Benzyl chloride	C7H7Cl	100-44-7	126	91
45	Pentachlorobenzene	C6HCl5	608-93-5	248	250
46	1-Methylnaphthalene	C11H10	90-12-0	142	142
47	3-Methylphenanthrene	C15H12	832-71-3	192	192
48	9-Methylphenanthrene	C15H13	883-20-5	192	192
50	1,2-Dimethylnaphthalene	C12H12	573-98-8	156	141
51	1,3-Dimethylnaphthalene	C12H12	575-41-7	156	156
52	1,4-&2,3-Dimethylnaphthalene	C12H12	571-58-4&581-40-8	156	156
53	1,8-Dimethylnaphthalene	C12H12	569-41-5	156	156

54	1-Methylphenanthrene	C15H12	832-69-9	192	192
55	1-Phenylnaphthalene	C16H12	605-02-7	204	204
56	2,3-Benzofluorene	C17H12	243-17-4	216	216
57	2,6-Diisopropylnaphthalene	C16H20	24157-81-1	212	197
58	2,6-Dimethylnaphthalene	C12H12	581-42-0	156	156
59	2-Isopropylnaphthalene	C13H14	2027-17-0	170	155
60	2-Methylnaphthalene	C11H10	91-57-6	142	142
61	2-Methylphenanthrene	C15H12	2531-84-2	192	192
62	2-Phenylnaphthalene	C16H12	612-94-2	204	204
63	3,6-Dimethylphenanthrene	C16H14	1576-67-6	206	206
64	3-Methylcholanthrene	C21H16	56-49-5	268	268
65	4,5-Methylene-phenanthrene	C15H10	203-64-5	190	189
66	7,12-Dimethylbenz(a)anthracene	C20H16	57-97-6	256	256
67	Acenaphthene	C12H10	83-32-9	154	153
68	Acenaphthylene	C12H8	208-96-8	152	152
69	Anthracene	C14H10	120-12-7	178	178
70	Benzo(a)anthracene	C18H12	56-55-3	228	228
71	Benzo(a)pyrene	C20H12	50-32-8	252	252
72	Benzo(c)phenanthrene	C18H12	195-19-7	228	228
73	Benzo(e)pyrene	C20H12	192-97-2	252	252
74	Benzo(ghi)perylene	C22H12	191-24-2	276	276
75	Benzo(j&b)fluoranthene	C20H12	205-82-3&205-99-2	252	252
76	Benzo(k)fluoranthene	C20H12	207-08-9	252	252
77	Biphenyl	C12H10	92-52-4	154	154
78	Chrysene & Triphenylene	C18H12	218-01-9&217-59-4	228	228
79	Dibenzo(a,h)anthracene	C22H14	53-70-3	278	278
80	Diphenylmethane	C13H12	101-81-5	168	167
81	Fluoranthene	C16H10	206-44-0	202	202
82	Fluorene	C13H10	86-73-7	166	166
83	Indeno(1,2,3-cd)pyrene	C22H12	193-39-5	276	276
84	m-Terphenyl	C18H14	92-06-8	230	230
85	Naphthalene	C10H8	91-20-3	128	128
86	o-Terphenyl	C18H14	84-15-1	230	230
87	Perylene	C20H12	198-55-0	252	252
88	Phenanthrene	C14H10	85-01-8	178	178
89	p-Terphenyl	C18H14	92-94-4	230	230
90	Pyrene	C16H10	129-00-0	202	202
91	Triphenylmethane	C19H16	519-73-3	244	244
92	1,2,3,4,5,6,7-Heptachloronaphthalene	C10HCl7		366	368
93	1,2,3,4,5,6,8-Heptachloronaphthalene	C10HCl7	58863-15-3	366	368
94	1,2,3,4,5,8-Hexachloronaphthalene	C10H2Cl6		332	334
95	1,2,3,4,6,7-Hexachloronaphthalene	C10H2Cl6	103426-96-6	332	334
96	1,2,3,5,7,8-Hexachloronaphthalene	C10H2Cl6		332	334
97	1,2,3,5,7-Pentachloronaphthalene	C10H3Cl5	53555-65-0	298	300
98	1,2,3,5,8-&1,2,3,6,8-Pentachloronaphthalene	C10H3Cl5		298	300
99	1,2,3,5-Tetrachloronaphthalene	C10H4Cl4	53555-63-8	264	266
100	1,2,3-Trichloronaphthalene	C10H5Cl3	50402-52-3	230	230
101	1,2,4,5,6,8-&1,2,4,5,7,8-Hexachloronaphthalene	C10H2Cl6		332	334
102	1,2,4,5,6-Pentachloronaphthalene	C10H3Cl5		298	300
103	1,2,4,5,8-Pentachloronaphthalene	C10H3Cl5		298	300
104	1,2,4,6,8-Pentachloronaphthalene	C10H3Cl5		298	300
105	1,2,4,7,8-Pentachloronaphthalene	C10H3Cl5		298	300
106	1,2,5,7-&1,2,4,6-&1,2,4,7-Tetrachloronaphthalene	C10H4Cl4	67922-23-0&51570-45-7&67922-21-8	264	266
107	1,2,5,8-&1,2,6,8-Tetrachloronaphthalene	C10H4Cl4	67922-24-1	264	266

108	1,3,7-&1,4,6-Trichloronaphthalene	C10H5Cl3	55720-37-1&2737-54-9	230	230
109	1,4-&1,6-Dichloronaphthalene	C10H6Cl2	1825-31-6&2050-72-8	196	196
110	1,4,5,8-Tetrachloronaphthalene	C10H4Cl4	3432-57-3	264	266
111	1,4,5-Trichloronaphthalene	C10H5Cl3	2437-55-0	230	230
112	1,4,6,7-Tetrachloronaphthalene	C10H4Cl4	55720-43-9	264	266
113	1,5-Dichloronaphthalene	C10H6Cl2	1825-30-5	196	196
114	1-Chloronaphthalene	C10H7Cl	90-13-1	162	162
115	2,3,4,5,6-Pentachloro-p-terphenyl	C18H9Cl5		400	402
116	2,3,5,6-Tetrachloro-p-terphenyl	C18H10Cl4		366	368
117	2,3,6,7-&1,2,4,8-Tetrachloronaphthalene	C10H4Cl4		264	266
118	2,4-&2,5-Dichloro-p-terphenyl	C18H12Cl2		298	298
119	2,4,4',6-Tetrachloro-p-terphenyl	C18H10Cl4		366	368
120	2,4,6-Trichloro-p-terphenyl	C18H11Cl3		332	332
121	2,5-Dichloro-o-terphenyl	C18H12Cl2		298	228
122	2,6-&1,7-Dichloronaphthalene	C10H6Cl2	2065-70-5&2050-73-9	196	196
123	2-Chloronaphthalene	C10H7Cl	91-58-7	162	162
124	4-Chloro-o-terphenyl	C18H13Cl		264	229
125	4-Chloro-p-terphenyl	C18H13Cl		264	264
126	Octachloronaphthalene	C10Cl8	2234-13-1	400	404
127	Tris(4-chlorophenyl)methane	C19H13Cl3	27575-78-6	348	311
128	PCB #1	2-	2051-60-7	188	188
129	PCB #101	22'455'-	37680-73-2	324	326
130	PCB #104	22'466'-	56558-16-8	324	326
131	PCB #105	233'44'-	32598-14-4	324	326
132	PCB #110	233'4'6-	38380-03-9	324	326
133	PCB #114	2344'5-	74472-37-0	324	326
134	PCB #118	23'44'5-	31508-00-6	324	326
135	PCB #119	23'44'6-	56558-17-9	324	326
136	PCB #123	2'344'5-	65510-44-3	324	326
137	PCB #126	33'44'5-	57465-28-8	324	326
138	PCB #128	2,2',3,3',4,4'-	38380-07-3	358	360
139	PCB #138&158	22'344'5'-&233'44'6-	35065-28-2&74472-42-7	358	360
140	PCB #149	22'34'5'6-	38380-04-0	358	360
141	PCB #15	44'-	2050-68-2	222	222
142	PCB #151	22'355'6-	52663-63-5	358	360
143	PCB #153&168	22'44'55'-&23'44'5'6	35065-27-1&41411-63-6	358	360
144	PCB #155	22'44'66'-	33979-03-2	358	360
145	PCB #156	233'44'5-	38380-08-4	358	360
146	PCB #157	233'44'5'-	69782-90-7	358	360
147	PCB #167	23'44'55'-	52663-72-6	358	360
148	PCB #169	33'44'55'-	32774-16-6	358	360
149	PCB #170	22'33'44'5-	35065-30-6	392	324
150	PCB #171	22'33'44'6-	52663-71-5	392	394
151	PCB #177	22'33'4'56-	52663-70-4	392	324
152	PCB #178	22'33'55'6-	52663-67-9	392	394
153	PCB #18	22'5-	37680-65-2	256	256
154	PCB #180	22'344'55'-	35065-29-3	392	324
155	PCB #183	22'344'5'6-	52663-69-1	392	394
156	PCB #187	22'34'55'6-	52663-68-0	392	394
157	PCB #188	22'34'566'-	74487-85-7	392	394
158	PCB #189	233'44'55'-	36935-31-9	392	394
159	PCB #19	22'6-	38444-73-4	256	256
160	PCB #191	233'44'5'6-	74472-50-7	392	394
161	PCB #194	22'33'44'55'-	35694-08-7	426	358
162	PCB #199	22'33'455'6'-	52663-75-9	426	358
163	PCB #201	22'33'45'66'-	40186-71-8	426	430

164	PCB #202	22'33'55'66'-	2136-99-4	426	430
165	PCB #205	233'44'55'6-	74472-53-0	426	358
166	PCB #206	22'33'44'55'6-	40186-72-9	460	392
167	PCB #208	22'33'455'66'-	52663-77-1	460	392
168	PCB #209	22'33'44'55'66'-	2051-24-3	494	498
169	PCB #22	234'-	38444-85-8	256	256
170	PCB #28	244'-	7012-37-5	256	256
171	PCB #3	4-	2051-62-9	188	188
172	PCB #33	2'34-	38444-86-9	256	256
173	PCB #37	344'-	38444-90-5	256	258
174	PCB #4&10	22'-&26-	13029-08-8&33146-45-1	222	222
175	PCB #44	22'35'-	41464-39-5	290	292
176	PCB #49	22'45'-	41464-40-8	290	292
177	PCB #52	22'55'-	35693-99-3	290	292
178	PCB #54	22'66'-	15968-05-5	290	292
179	PCB #70	23'4'5-	32598-11-1	290	292
180	PCB #74	244'5-	32690-93-0	290	292
181	PCB #77	33'44'-	32598-13-3	290	292
182	PCB #8	24'-	34883-43-7	222	222
183	PCB #81	344'5-	70362-50-4	290	292
184	PCB #87	22'345'-	38380-02-8	324	326
185	PCB #95	22'35'6-	38379-99-6	324	326
186	PCB #99	22'44'5-	38380-01-7	324	326
187	Dicyclopentadiene	C10H12	77-73-6	132	66
188	Longifolene	C15H24	475-20-7	204	161
189	*trans*-Decahydronaphthalene	C10H18	493-02-7	138	138
190	1,2,5,6,9,10-Hexabromocyclododecane	C12H18Br6	3194-55-6	636	239
191	2,2',4,4',5,5'-Hexabromobiphenyl (BB-153)	C12H4Br6	59080-40-9	622	308
192	2,2',5,5'-Tetrabromobiphenyl (BB-52)	C12H6Br4		466	310
193	2,2'-Dibromobiphenyl (BB-4)	C12H8Br2	59080-37-4	310	312
194	Hexachlorocyclopentadiene	C5Cl6	77-47-4	270	237
195	1,2,3-Trimethoxybenzene	C9H12O3	634-36-6	168	168
196	Dibenzyl ether	C14H14O	103-50-4	198	91
197	Diphenyl ether	C12H10O	101-84-8	170	170
198	2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	C12H4Br6O		638	484
199	2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	C12H6Br4O		482	326
200	2,4-Dibromodiphenyl ether (BDE-7)	C12H8Br2O		326	328
201	4-Bromophenylphenyl ether	C12H9BrO	101-55-3	248	248
202	4-Chlorophenylphenyl ether	C12H9ClO	7005-72-3	204	204
203	Bis(2-chloroethoxy)methane	C5H10Cl2O2	111-91-1	172	93
204	Bis(2-chloroethyl)ether	C4H8Cl2O	111-44-4	142	93
205	Bis(2-chloroisopropyl)ether	C6H12Cl2O	108-60-1	170	121
206	2,6-Di-tert-butyl-4-benzoquinone	C14H20O2	719-22-2	220	177
207	Acetophenone	C8H8O	98-86-2	120	105
208	Anthraquinone	C14H8O2	84-65-1	208	208
209	Benzanthrone	C17H10O	82-05-3	230	230
210	Cyclopentanone, 2-methyl-	C6H10O	1120-72-5	98	98
211	Isophorone	C9H14O	78-59-1	138	82
212	1-Naphthol	C10H8O	90-15-3	144	144
213	2,4,6-Tri-tert-butylphenol	C18H30O	732-26-3	262	247
214	2,4-Dimethylphenol	C8H10O	105-67-9	122	107
215	2,6-Dimethylphenol	C8H10O	576-26-1	122	122
216	2,6-Di-t-butyl-4-ethylphenol	C16H26O	4130-42-1	234	219
217	2-Methoxyphenol	C7H8O2	90-05-1	124	109
218	2-Methylphenol	C7H8O	95-48-7	108	108
219	2-Naphthol	C10H8O	135-19-3	144	144

220	2-sec-Butylphenol	C10H14O	89-72-5	150	121
221	2-tert-Butyl-4-methoxyphenol	C11H16O2	121-00-6	180	165
222	2-tert-Butylphenol	C10H14O	88-18-6	150	135
223	3- & 4-tert-Butylphenol	C10H14O	585-34-2&98-54-4	150	135
224	3-&4-Methylphenol	C7H8O	108-39-4&106-44-5	108	107
225	3,5-Dimethylphenol	C8H10O	108-68-9	122	122
226	4-Methyl-2,6-di-t-butylphenol	C15H24O	128-37-0	220	220
227	4-n-Butylphenol	C10H14O	1638-22-8	150	107
228	4-n-Heptylphenol	C13H20O	1987-50-4	192	107
229	4-n-Hexylphenol	C12H18O	2446-69-7	178	107
230	4-n-Nonylphenol	C15H24O	104-40-5	220	107
231	4-n-Octylphenol	C14H22O	1806-26-4	206	107
232	4-Nonylphenol	C15H24O	25154-52-3	220	135
233	4-n-Pentylphenol	C11H16O	14938-35-3	164	107
234	4-Phenylphenol	C12H10O	92-69-3	170	170
235	4-sec-Butylphenol	C10H14O	99-71-8	150	121
236	4-tert-Octylphenol	C14H22O	140-66-9	206	135
237	Bisphenol A	C15H16O2	80-05-7	228	213
238	Phenol	C6H6O	108-95-2	94	94
239	Phenol, 2,6-dimethoxy-	C8H10O3	91-10-1	154	154
240	2,3,4,6-Tetrachlorophenol	C6H2Cl4O	58-90-2	230	232
241	2,3,4-Trichlorophenol	C6H3Cl3O	15950-66-0	196	196
242	2,3,5,6-&2,3,4,5-Tetrachlorophenol	C6H2Cl4O	935-95-5&4901-51-3	230	232
243	2,3,5-Trichlorophenol	C6H3Cl3O	933-78-8	196	196
244	2,3,6-Trichlorophenol	C6H3Cl3O	933-75-5	196	196
245	2,3-Dichlorophenol	C6H4Cl2O	576-24-9	162	162
246	2,4,5-Trichlorophenol	C6H3Cl3O	95-95-4	196	196
247	2,4,6-Tribromophenol	C6H3Br3O	118-79-6	328	332
248	2,4,6-Trichlorophenol	C6H3Cl3O	88-06-2	196	196
249	2,4-Dichlorophenol	C6H4Cl2O	120-83-2	162	162
250	2,5-Dichlorophenol	C6H4Cl2O	583-78-8	162	162
251	2,6-Dichlorophenol	C6H4Cl2O	87-65-0	162	162
252	2-Chlorophenol	C6H5ClO	95-57-8	128	128
253	3-&4-Chlorophenol	C6H5ClO	108-43-0&106-48-9	128	128
254	3,4,5-Trichlorophenol	C6H3Cl3O	609-19-8	196	196
255	3,4-Dichlorophenol	C6H4Cl2O	95-77-2	162	162
256	3,5-Dichlorophenol	C6H4Cl2O	591-35-5	162	162
257	4-Bromophenol	C6H5BrO	106-41-2	172	172
258	4-Chloro-3-methylphenol	C7H7ClO	59-50-7	142	142
259	Pentachlorophenol	C6HCl5O	87-86-5	264	266
260	Triclosan	C12H7Cl3O2	3380-34-5	288	290
261	Bis(2-ethylhexyl) phthalate	C24H38O4	117-81-7	390	149
262	Butyl benzyl phtalate	C19H20O4	85-68-7	312	149
263	Dicyclohexyl phthalate	C20H26O4	84-61-7	330	149
264	Diethyl phthalate	C14H14O4	84-66-2	246	149
265	Di-iso-butyl phthalate	C16H22O4	84-69-5	278	149
266	Dimethyl phthalate	C10H10O4	131-11-3	194	163
267	Dimethylterephthalate	C10H10O4	120-61-6	194	163
268	Di-n-butyl phthalate	C16H22O4	84-74-2	278	149
269	Di-n-hexyl phthalate	C20H30O4	84-75-3	334	149
270	Di-n-octyl phthalate	C24H38O4	117-84-0	390	149
271	Di-n-pentyl phthalate	C18H26O4	131-18-0	306	149
272	Di-n-propyl phthalate	C14H18O4	131-16-8	250	149
273	(10Z)-pentadecenoic acid, methyl ester	C16H30O2	90176-52-6	254	222
274	(9Z)-9-Tetradecenoic acid, methyl ester	C15H28O2	56219-06-8	240	96
275	Arachidic acid methyl ester	C21H42O2	1120-28-1	326	326
276	Arachidonic acid methyl ester	C21H34O2	2566-89-4	318	150
277	Behenic acid methyl ester	C23H46O2	929-77-1	354	354
278	*cis*-10-Heptadecenoic acid methyl	C18H32O2	75190-82-8	282	250

	ester				
279	*cis*-11,14,17-Eicosatrienoic acid methyl ester	C21H36O2	55682-88-7	320	95
280	*cis*-11,14-Eicosadienoic acid methyl ester	C21H38O2	2463-02-7	322	322
281	*cis*-11-Eicosenoic acid methyl ester	C21H40O2	2390-09-2	324	292
282	*cis*-13,16-Docosadienoic acid methyl ester	C23H42O2	61012-47-3	350	350
283	*cis*-4,7,10,13,16,19-Docosahexaenoic acid methyl ester	C23H34O2	301-01-9	342	119
284	*cis*-5,8,11,14,17-Eicosapentaenoic acid, methyl ester	C21H32O2	2734-47-6	316	119
285	*cis*-8,11,14-Eicosatrienoic acid methyl ester	C21H36O2	21061-10-9	320	150
286	Elaidic acid methyl ester	C19H36O2	1937-62-8	296	264
287	Erucic acid methyl ester	C23H44O2	1120-34-9	352	320
288	gamma-Linolenic acid methyl ester	C19H32O2	301-00-8	292	292
289	Heneicosanoic acid methyl ester	C22H44O2	6064-90-0	340	340
290	Lignoceric acid, methyl ester	C25H50O2	2442-49-1	382	382
291	Linoleic acid methyl ester	C19H34O2	112-63-0	294	294
292	Linolelaidic acid methyl ester	C19H34O2	2566-97-4	294	294
293	Linolenic acid methyl ester	C19H32O2	7361-80-0	292	292
294	Methyl decanoate	C11H22O2	110-42-9	186	87
295	Methyl dodecanoate	C13H26O2	111-82-0	214	87
296	Methyl heptadecanoate	C18H36O2	1731-92-6	284	284
297	Methyl hexanoate	C7H14O2	106-70-7	130	87
298	Methyl myristate	C15H30O2	124-10-7	242	87
299	Methyl octanoate	C9H18O2	111-11-5	158	87
300	Methyl palmitate	C17H34O2	112-39-0	270	270
301	Methyl palmitoleate	C17H32O2	1120-25-8	268	236
302	Methyl pentadecanoate	C16H32O2	7132-64-1	256	87
303	Methyl tridecanoate	C14H28O2	1731-88-0	228	87
304	Methyl undecanoate	C12H24O2	1731-86-8	200	87
305	Nervonic acid methyl ester	C25H48O2	2733-88-2	380	348
306	Oleic acid methyl ester	C19H36O2	112-62-9	296	264
307	Stearic acid methyl ester	C19H38O2	112-61-8	298	298
308	Tricosanoic acid methyl ester	C24H48O2	2433-97-8	368	368
309	1,4-Benzenediol	C6H6O2	123-31-9	110	110
310	1-Acetoxy-2-methoxyethane	C5H10O3	110-49-6	118	58
311	1-Nonanol	C9H20O	143-08-8	144	83
312	24-Ethyl coprostanol	C29H52O	4736-91-8	416	215
313	2-Butoxyethanol	C6H14O2	111-76-2	118	57
314	2-Cyclohexen-1-one	C6H8O	930-68-7	96	96
315	2-Ethyl-1-hexanol	C8H18O	104-76-7	130	83
316	2-Heptanol	C7H16O	543-49-7	116	45
317	2-Hydroxy-4-methoxy-4'-methyl-benzophenone	C15H14O4		258	241
318	2-Methyl-2,4-pentandiol	C6H14O2	107-41-5	118	59
319	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	C15H22O2	1620-98-0	234	219
320	3-Hexanol, 4-ethyl-	C8H18O	19780-44-0	130	59
321	3-Methoxy-1-butyl acetate	C7H14O3	4435-53-4	146	71
322	alpha-Terpineol	C10H18O	10482-56-1	154	136
323	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	C9H10O4	134-96-3	182	182
324	Benzyl alcohol	C7H8O	100-51-6	108	108
325	beta-Sitosterol	C29H50O	83-46-5	414	414
326	Bis(2-ethylhexyl) sebacate	C26H50O4	122-62-3	426	185
327	Butanoic acid, butyl ester	C8H16O2	109-21-7	136	89
328	Campesterol	C28H48O	474-62-4	400	400
329	Cholestane	C27H48	481-21-0	372	217

330	Cholestanol	C27H48O	80-97-7	388	215
331	Cholesterol	C27H46O	57-88-5	386	301
332	Coprostanol	C27H48O	360-68-9	388	373
333	Coprostanone	C27H46O	15600-08-5	386	316
334	Cyclohexanol	C6H12O	108-93-0	100	82
335	Di(2-ethylhexyl)adipate	C22H42O4	103-23-1	370	129
336	Dibenzofuran	C12H8O	132-64-9	168	168
337	Epicoprostanol	C27H48O	516-92-7	388.6 7	370
338	Ergosterol	C28H44O	57-87-4	396	363
339	Ethanol, 2-phenoxy-	C8H10O2	122-99-6	138	94
340	Fucosterol	C29H48O	17605-67-3	412	314
341	Isosafrole	C10H10O2	120-58-1	162	162
342	n-Butylacrylate	C7H12O2	141-32-2	128	73
343	Octanol	C8H18O	111-87-5	130	56
344	Phenylethyl alcohol	C8H10O	60-12-8	122	122
345	Propanoic acid, 2-methyl-, 2-methylpropyl ester	C8H16O2	97-85-8	144	71
346	Safrole	C10H10O2	94-59-7	162	162
347	Stigmastanol	C29H52O	83-45-4	416	215
348	Stigmasterol	C29H48O	83-48-7	412	412
349	1,1,1-Trichloro-2-methyl-2-propa nol	C4H7Cl3O	57-15-8	176	125
350	1,3-Dichloro-2-propanol	C3H6Cl2O	96-23-1	128	79
351	2-Chloro-6-methylphenol	C7H7ClO	87-64-9	142	107
352	Tris(4-chlorophenyl)methanol	C19H13Cl3O	3010-80-8	364	251
353	1-Naphthylamine	C10H9N	134-32-7	143	143
354	2,3-&3,4-Dimethylaniline	C8H11N	87-59-2&95-64-7	121	121
355	2,5-Dimethylaniline	C8H11N	95-78-3	121	121
356	2,6-Diaminotoluene	C7H10N2	823-40-5	122	122
357	2,6-Dimethylaniline	C8H11N	87-62-7	121	121
358	2-Acetylaminofluorene	C15H13NO	53-96-3	223	181
359	2-Anisidine	C7H9NO	90-04-0	123	123
360	2-Methylaniline	C7H9N	95-53-4	107	106
361	2-Naphthylamine	C10H9N	91-59-8	143	143
362	3-Anisidine	C7H9NO	536-90-3	123	123
363	3-Toluidine	C7H9N	108-44-1	107	106
364	4-Aminobiphenyl	C12H11N	92-67-1	169	169
365	4-Anisidine	C7H9NO	104-94-9	123	108
366	4-Dimethylaminoazobenzene	C14H15N3	60-11-7	225	225
367	Acetamide, N-phenyl-	C8H9NO	103-84-4	135	135
368	Aniline	C6H7N	62-53-3	93	93
369	Benzamide, N-phenyl-	C13H11NO	93-98-1	197	197
370	Benzidine	C12H12N2	92-87-5	184	184
371	Diphenylamine	C12H11N	122-39-4	169	169
372	m-Aminophenol	C6H7NO	591-27-5	109	109
373	m-Phenylenediamine	C6H8N2	108-45-2	108	108
374	N,N-Dimethylaniline	C8H11N	121-69-7	121	120
375	N-Ethylaniline	C8H11N	103-69-5	121	106
376	N-Methylaniline	C7H9N	100-61-8	107	106
377	N-Phenyl-1-naphthylamine	C16H13N	90-30-2	219	219
378	N-Phenyl-2-naphthylamine	C16H13N	135-88-6	219	219
379	Phenacetin	C10H13NO2	62-44-2	179	179
380	Phenol, 4-(phenylamino)-	C12H11NO	122-37-2	185	185
381	p-Phenylenediamine	C6H8N2	106-50-3	108	108
382	2,3-Dichloroaniline	C6H5Cl2N	608-27-5	161	161
383	2,4,6-Tribromoaniline	C6H4Br3N	147-82-0	327	331
384	2,4,6-Trichloroaniline	C6H4Cl3N	634-93-5	195	195
385	2,4-Dichloroaniline	C6H5Cl2N	554-00-7	161	161
386	2,6-Dibromo-4-chloroaniline	C6H4Br2ClN	874-17-9	283	285
387	2-Bromo-4,6-dichloroaniline	C6H4BrCl2N	697-86-9	239	241
388	2-Chloroaniline	C6H6cLN	95-51-2	127	127

389	3,3'-Dichlorobenzidine	C12H10Cl2N2	91-94-1	252	252
390	3,4-Dichloroaniline	C6H5Cl2N	95-76-1	161	161
391	3,5-Dimethylaniline	C8H11N	108-69-0	121	121
392	4,4'-Methylene-bis(2-chloroanilin e)	C13H12Cl2N2	101-14-4	266	266
393	4-Bromo-2,6-dichloroaniline	C6H4BrCl2N	697-86-9	239	241
394	4-Chloroaniline	C6H6ClN	106-47-8	127	127
395	5-Chloro-2-methyl aniline	C7H8ClN	95-79-4	141	106
396	N-Nitroquinoline-N-oxide	C9H6N2O3	56-57-5	190	190
397	Quinoline	C9H7N	91-22-5	129	129
398	Quinoline, 2,7-dimethyl-	C11H11N	93-37-8	287	157
399	1,3,5-Trinitrobenzene	C6H3N3O6	99-35-4	213	213
400	1,3-Dinitrobenzene	C6H4N2O4	99-65-0	168	168
401	1,4-Dinitrobenzene	C6H4N2O4	100-25-4	168	168
402	1-Nitronaphthalene	C10H7NO2	86-57-7	173	173
403	1-Nitropyrene	C16H9NO2	5522-43-0	247	247
404	2,4,6-Trinitrotoluene	C7H5N3O6	118-96-7	227	210
405	2,4-Diamino-6-nitrotoluene	C7H9N3O2	6629-29-4	167	167
406	2,4-Dinitroaniline	C6H5N3O4	97-02-9	183	183
407	2,4-Dinitrotoluene	C7H6N2O4	121-14-2	182	165
408	2,6-Diamino-4-nitrotoluene	C7H9N3O2	59229-75-3	167	167
409	2,6-Dinitrotoluene	C7H6N2O4	606-20-2	182	165
410	2-Amino-4,6-dinitrotoluene	C7H7N3O4	35572-78-2	197	180
411	2-Amino-6-nitrotoluene	C7H8N2O2	603-83-8	152	152
412	2-Nitroaniline	C6H6N2O2	88-74-4	138	138
413	2-Nitroanisole	C7H7NO3	91-23-6	153	123
414	2-Nitronaphthalene	C10H7NO2	581-89-5	173	173
415	2-Nitrotoluene	C7H7NO2	88-72-2	137	120
416	3-&4-Nitroanisole	C7H7NO3	555-03-3&100-17-4	153	153
417	3-Nitroaniline	C6H6N2O2	99-09-2	138	138
418	3-Nitrofluoranthene	C16H9NO2	892-21-7	247	247
419	3-Nitrophenanthrene	C14H9NO2	17024-19-0	223	223
420	3-Nitrotoluene	C7H7NO2	99-08-1	137	137
421	4-Amino-2,6-dinitrotoluene	C7H7N3O4	19406-51-0	197	180
422	4-Amino-2-nitrotoluene	C7H8N2O2	119-32-4	152	152
423	4-Methyl-3-nitrophenol	C7H7NO3	2042-14-0	153	136
424	4-Nitroaniline	C6H6N2O2	100-01-6	138	138
425	4-Nitrophenanthrene	C14H9NO2	82064-15-1	223	223
426	4-Nitrotoluene	C7H7NO2	99-99-0	137	137
427	5-Nitro-o-toluidine	C7H8N2O2	99-55-8	152	152
428	6-Nitrochrysene	C18H11NO2	7496-02-8	273	273
429	7-Nitrobenz(a)anthracene	C18H11NO2	20268-51-3	273	273
430	9-Nitroanthracene	C14H9NO2	602-60-8	223	223
431	9-Nitrophenanthrene	C14H9NO2	954-46-1	223	165
432	Nitrobenzene	C6H5NO2	98-95-3	123	123
433	Tetryl	C7H5N5O8	479-45-8	287	194
434	2,3-Dichloronitrobenzene	C6H3Cl2NO2	3209-22-1	191	191
435	2,4-Dichloronitrobenzene	C6H3Cl2NO2	611-06-3	191	191
436	2,5-Dichloronitrobenzene	C6H3Cl2NO2	89-61-2	191	191
437	2,6-Dichloro-4-nitroaniline	C6H4Cl2N2O2	99-30-9	206	206
438	3-Chloronitrobenzene	C6H4ClNO2	121-73-3	157	157
439	4-Chloro-2-nitroaniline	C6H5ClN2O2	89-63-4	172	172
440	4-Chloronitrobenzene	C6H4ClNO2	100-00-5	157	157
441	N-Nitrosodiethylamine	C4H10N2O	55-18-5	102	102
442	N-Nitroso-di-n-butylamine	C8H18N2O	924-16-3	158	84
443	N-Nitrosomorpholine	C4H8N2O2	59-89-2	116	116
444	N-Nitrosopiperidine	C5H10N2O	100-75-4	114	114
445	N-Nitrosopyrrolidine	C4H8N2O	930-55-2	100	100
446	1,3-Dicyclohexylurea	C13H24N2O	2387-23-7	224	224
447	2,4-Dinitrophenol	C6H4N2O5	51-28-5	184	184
448	2-Methyl-4,6-dinitrophenol	C7H6N2O5	534-52-1	198	198
449	2-Nitrophenol	C6H5NO3	88-75-5	139	139
450	3-Methylpyridine	C6H7N	108-99-6	93	93

451	4-Nitrophenol	C6H5NO3	100-02-7	139	139
452	Acetamide, N-(2-phenylethyl)-	C10H13NO	877-95-2	163	104
453	Carbazole	C12H9N	86-74-8	167	167
454	Cyclohexanamine, N-cyclohexyl-	C12H23N	101-83-7	181	138
455	Dibutylamine	C8H19N	111-92-2	129	86
456	e-Caprolactam	C6H11NO	105-60-2	113	113
457	Ethylcarbamate	C3H7NO2	51-79-6	89	62
458	Formamide, N-cyclohexyl-	C7H13NO	766-93-8	127	84
459	N-Ethylmorpholine	C6H13NO	100-74-3	115	100
460	Nicotinonitrile	C6H4N2	100-54-9	104	104
461	Phenazine	C12H8N2	92-82-0	180	180
462	Phenoxazine	C12H9NO	135-67-1	183	183
463	Phthalimide	C8H5NO2	85-41-6	147	147
464	Urea, N,N-diethyl-	C5H12N2O	634-95-7	116	116
465	5-Bromoindole	C8H6BrN	10075-50-0	195	195
466	2(3H)-Benzothiazolone	C7H5NOS	934-34-9	151	151
467	2-(Methylthio)-benzothiazol	C8H7NS2	615-22-5	181	181
468	2-Acetyl-5-methylthiophene	C7H8OS	13679-74-8	140	125
469	2-Mercaptobenzothiazole	C7H5NS2	149-30-4	167	167
470	2-Methylbenzothiazole	C8H7NS	120-75-2	149	149
471	Benzothiazole	C7H5NS	95-16-9	135	135
472	Dibenzothiophene	C12H8S	132-65-0	184	184
473	Diphenyldisulfide	C12H10S2	882-33-7	218	218
474	Ethyl methanesulfonate	C3H8O3S	62-50-0	124	109
475	Phenothiazine	C12H9NS	92-84-2	199	199
476	Phenoxathiin	C12H8OS	262-20-4	200	200
477	Methapyrilene	C14H19N3S	91-80-5	297	97
478	Diethyl-p-nitrophenyl phosphate	C10H14NO6P	311-45-5	275	109
479	Tributyl phosphate	C12H27O4P	126-73-8	266	99
480	Tricresyl phosphate	C21H21O4P	1330-78-5	368	368
481	Trimethyl phosphate	C3H9O4P	512-56-1	140	110
482	Tris(2-ethylhexyl) phosphate	C24H51O4P	78-42-2	434	99
483	Tris(1,3-dichloro-2-propyl) phosphate	C9H15Cl6O4P	13674-87-8	428	381
484	Tris(2-chloroethyl) phosphate	C6H12Cl3O4P	115-96-8	284	249
485	Tris(2-chloroethyl)phosphite	C6H12Cl3O3P	140-08-9	268	233
486	Aspirin	C9H8O4	50-78-2	180	120
487	Caffeine	C8H10N4O2	58-08-2	194	194
488	Carbamazepine	C15H12N2O	298-46-4	236	193
489	Crotamiton	C13H17NO	483-63-6	203	69
490	Diethyltoluamide	C12H17NO	134-62-3	191	119
491	Ethenzamide	C9H11NO2	738-73-8	165	120
492	Fenoprofen	C15H14O3	31879-05-7	242	197
493	Ibuprofen	C13H18O2	15687-27-1	206	161
494	L-Menthol	C10H20O	2216-51-5	156	95
495	Mefenamic Acid	C15H15NO2	61-68-7	241	223
496	Naproxen	C14H14O3	22204-53-1	230	185
497	Nicotine	C10H14N2	54-11-5	162	84
498	Propyphenazone	C14H18N2O	479-92-5	230	215
499	Thymol	C10H14O	89-83-8	150	135
500	3-Hydroxycarbofuran 1	C12H15NO4	16655-82-6	237	137
501	3-Hydroxycarbofuran 2	C12H15NO4	16655-82-6	237	137
502	Acephate	C4H10NO3PS	30560-19-1	183	136
503	Acetamiprid	C10H11ClN4	135410-20-7	222	152
504	a-HCH	C6H6Cl6	319-84-6	288	219
505	Aldoxycarb deg.	C7H14N2O4S	1646-88-4	222	68
506	Aldrin	C12H8Cl6	309-00-2	362	263
507	Allethrin 1	C19H26O3	584-79-2	302	123
508	Allethrin 2 & Bioallethrin 1	C19H26O3	584-79-2	302	123
509	Azamethiphos	C9H10ClN2O5 PS	35575-96-3	324	215
510	Azinphos-ethyl	C12H16N3O3P	2642-71-9	345	132

		S2			
511	Azinphos-methyl	C10H12N3O3PS2	86-50-0	317	160
512	Bendiocarb	C11H13NO4	22781-23-3	223	151
513	b-HCH	C6H6Cl6	319-85-7	288	219
514	Bifenazate	C17H20N2O3	149877-41-8	300	258
515	Bifenthrin	C23H22ClF3O2	82657-04-3	422	181
516	Bioresmethrin	C22H26O3	28434-01-7	338	123
517	Bromophos	C8H8BrCl2O3PS	2104-96-3	364	331
518	Buprofezin	C16H23N3OS	69327-76-0	305	105
519	Cadusafos	C10H23O2PS2	95465-99-9	270	159
520	Carbaryl	C12H11NO2	63-25-2	201	144
521	Carbofuran	C12H15NO3	1563-66-2	221	164
522	Carbophenothion	C11H16ClO2PS3	786-19-6	342	121
523	Chlorethoxyfos	C6H11Cl4O3PS	54593-83-8	334	153
524	Chlorfenapyr	C15H11BrClF3N2O	122453-73-0	406	59
525	Chlorfenson	C12H8Cl2O3S	80-33-1	302	175
526	Chlorfenvinphos E	C12H14Cl3O4P	18708-86-6	358	267
527	Chlorfenvinphos Z	C12H14Cl3O4P	18708-87-7	358	267
528	Chlormephos	C5H12ClO2PS2	24934-91-6	235	234
529	Chlorpropylate	C17H16Cl2O3	5836-10-2	338	251
530	Chlorpyrifos	C9H11Cl3NO3PS	2921-88-2	349	314
531	Chlorpyrifos-methyl	C7H7Cl3NO3PS	5598-13-0	321	286
532	*cis*-Chlordane	C10H6Cl8	5103-71-9	406	373
533	Coumaphos	C14H16ClO5PS	56-72-4	362	362
534	Crimidine	C7H10ClN3	535-89-7	172	156
535	Cyanofenphos	C15H14NO2PS	13067-93-1	303	169
536	Cyanophos, CYAP	C9H10NO3PS	2636-26-2	243	243
537	Cyfluthrin 1	C22H18Cl2FNO3	68359-37-5	433	163
538	Cyfluthrin 2	C22H18Cl2FNO3	68359-37-5	433	163
539	Cyfluthrin 3	C22H18Cl2FNO3	68359-37-5	433	163
540	Cyfluthrin 4	C22H18Cl2FNO3	68359-37-5	433	163
541	Cyhalothrin 1	C23H19ClF3NO3	68085-85-8	449	181
542	Cyhalothrin 2	C23H19ClF3NO3	68085-85-8	449	181
543	Cypermethrin 1	C22H19Cl2NO3	52315-07-8	415	163
544	Cypermethrin 2	C22H19Cl2NO3	52315-07-8	415	163
545	Cypermethrin 3	C22H19Cl2NO3	52315-07-8	415	163
546	Cypermethrin 4	C22H19Cl2NO3	52315-07-8	415	163
547	Cyromazine	C6H10N6	66215-27-8	166	151
548	DCIP	C6H12Cl2O	108-60-1	171	121
549	DDVP	C4H7Cl2O4P	62-73-7	220	185
550	Deltamethrin	C22H19Br2NO3	52918-63-5	503	181
551	Demeton-S-methyl	C6H15O3PS2	919-86-8	230	142
552	Demeton-S-methylsulphon	C6H15O5PS2	17040-19-6	262	169
553	d-HCH	C6H6Cl6	319-86-8	288	219
554	Dialifos	C14H17cLNO4PS2	10311-84-9	394	208

555	Diazinon	C12H21N2O3PS	333-41-5	304	137
556	Diazinon oxon	C12H21N2O4P	962-58-3	288	273
557	Dichlofenthion, ECP	C10H13Cl2O3PS	97-17-6	314	279
558	Dicrotophos	C8H16NO5P	141-66-2	237	127
559	Dieldrin	C12H8Cl6O	60-57-1	378	79
560	Diflubenzuron	C14H9ClF2N2O2	35367-38-5	310	141
561	Dimethoate	C5H12NO3PS2	60-51-5	229	125
562	Dimetylvinphos 1	C10H10Cl3O4P	2274-67-1	330	295
563	Dimetylvinphos 2	C10H10Cl3O4P	2274-67-1	330	295
564	Dinoseb	C10H12N2O5	88-85-7	240	211
565	Diofenolan 1	C18H20O4	63837-33-2	300	300
566	Diofenolan 2	C18H20O4	63837-33-2	300	300
567	Dioxabenzofos(Salithion)	C8H9O3PS	3811-49-2	216	216
568	Disulfoton	C8H19O2PS3	298-04-4	274	88
569	Endosulfan I	C9H6Cl6O3S	959-98-8	404	241
570	Endosulfan II	C9H6Cl6O3S	33213-65-9	404	195
571	Endosulfan sulfate	C9H6Cl6O4S	1031-07-8	420	272
572	Endrin	C12H8Cl6O	72-20-8	378	263
573	Endrin aldehyde	C12H8Cl6O	7421-93-4	378	345
574	Endrin ketone	C12H8Cl6O	53494-70-5	378	317
575	EPN	C14H14NO4PS	2104-64-5	323	157
576	EPN oxon	C14H14NO5P	2012-00-2	307	141
577	Esfenvalerate 1	C25H22ClNO3	66230-04-4	419	225
578	Esfenvalerate 2	C25H22ClNO3	66230-04-4	419	225
579	Ethiofencarb	C11H15NO2S	29973-13-5	225	107
580	Ethion	C9H22O4P2S4	563-12-2	384	231
581	Ethoprophos	C8H19O2PS2	13194-48-4	242	158
582	Etofenprox	C25H28O3	80844-07-1	376	163
583	Etoxazole metabolite				246
584	Etrimfos	C10H17N2O4PS	38260-54-7	292	292
585	Famphur	C10H16NO5PS2	52-85-7	325	218
586	Fenchlorphos	C8H8Cl3O3PS	299-84-3	320	285
587	Fenitrothion (MEP)	C9H12NO5PS	122-14-5	261	277
588	Fenitrothion oxon	C9H12NO6P	2255-17-6	261	244
589	Fenobucarb	C12H17NO2	3766-81-2	207	150
590	Fenoxycarb	C17H19NO4	72490-01-8	301	116
591	Fenthion	C10H15O3PS2	55-38-9	278	278
592	Fenvalerate 1	C25H22ClNO3	51630-58-1	419	167
593	Fenvalerate 2	C25H22ClNO3	51630-58-1	419	167
594	Fipronil	C12H4Cl2F6N4OS	120068-37-3	436	367
595	Flucythrinate 1	C26H23F2NO4	70124-77-5	451	199
596	Flucythrinate 2	C26H23F2NO4	70124-77-5	451	199
597	Flufenoxuron dec2	C21H11ClF6N2O3	101463-69-8	488	331
598	Flufenoxuron dec3	C21H11ClF6N2O3	101463-69-8	488	305
599	Fluvalinate 1	C26H22ClF3N2O3	69409-94-5	502	250
600	Fluvalinate 2	C26H22ClF3N2O3	69409-94-5	502	250
601	Fonofos	C10H15OPS2	994-22-9	246	246
602	g-HCH	C6H6Cl6	58-89-9	288	219
603	Heptachlor	C10H5Cl7	76-44-8	370	272
604	Heptachlor epoxide (B)	C10H5Cl7O	1024-57-3	386	353
605	Indoxacarb	C22H17ClF3N3O7	144171-61-9	528	150

606	Isazofos	C9H17ClN3O3PS	42509-80-8	313	161
607	Isocarbophos	C11H16NO4PS	24353-61-5	289	136
608	Isofenphos	C15H24NO4PS	25311-71-1	345	213
609	Isofenphos oxon	C15H24NO5P	31120-85-1	329	229
610	Isoprocarb	C11H15NO2	2631-40-5	193	121
611	Isoxathion	C13H16NO4PS	18854-01-8	313	177
612	Isoxathion oxon	C13H16NO5P	32306-29-9	297	161
613	Leptophos	C13H10BrCl2O2PS	21609-90-5	412	377
614	Malathion	C10H19O6PS2	121-75-5	330	173
615	Mecarbam	C10H20NO5PS2	2595-54-2	329	131
616	Methacrifos	C7H13O5PS	30864-28-9	240	208
617	Methamidophos	C2H8NO2PS	10265-92-6	141	94
618	Methidathion	C6H11N2O4PS3	950-37-8	302	145
619	Methiocarb	C11H15NO2S	2032-65-7	225	168
620	Methoprene	C19H34O3	40596-69-8	310	73
621	Methoxychlor	C16H15Cl3O2	72-43-5	344	227
622	Methyl parathion	C8H10NO5PS	298-00-0	263	263
623	Mevinphos 1	C7H13O6P	7786-34-7	224	127
624	Mevinphos 2	C7H13O6P	7786-34-7	224	127
625	Monocrotophos	C7H14NO5P	6923-22-4	223	127
626	Naled	C4H7Br2Cl2O4P	300-76-5	378	109
627	Nereistoxin oxalate deg.				149
628	Novaluron deg.	C17H9ClF8N2O4	116714-46-6	492	335
629	*o,p'*-DDD	C14H10Cl4	53-19-0	318	235
630	*o,p'*-DDE	C14H8Cl4	3424-82-6	316	246
631	*o,p'*-DDT	C14H9Cl5	789-02-6	352	235
632	Omethoate	C5H12NO4PS	1113-02-6	213	156
633	Oxychlordane	C10H4Cl8O	27304-13-8	420	387
634	*p,p'*-DDD	C14H10Cl4	72-54-8	318	235
635	*p,p'*-DDE	C14H8Cl4	72-55-9	316	246
636	*p,p'*-DDT	C14H9Cl5	50-29-3	352	235
637	Parathion	C10H14NO5PS	56-38-2	291	291
638	Permethrin 1	C21H20Cl2O3	52645-53-1	390	183
639	Permethrin 2	C21H20Cl2O3	52645-53-1	390	183
640	Phenothrin 1	C23H26O3	26002-80-2	350	183
641	Phenothrin 2	C23H26O3	26002-80-2	350	183
642	Phenthoate	C12H17O4PS2	2597-03-7	320	274
643	Phorate	C7H17O2PS3	298-02-2	260	260
644	Phosalone	C12H15ClNO4PS2	2310-17-0	367	182
645	Phosmet	C11H12NO4PS2	732-11-6	317	160
646	Phosphamidon	C10H19ClNO5P	13171-21-6	299	127
647	Piperonyl butoxide	C19H30O5	51-03-6	338	176
648	Pirimicarb	C11H18N4O2	23103-98-2	238	166
649	Pirimiphos-methyl	C11H20N3O3PS	29232-93-7	305	290
650	Profenofos	C11H15BrClO3PS	41198-08-7	372	337
651	Propaphos	C13H21O4PS	7292-16-2	304	220
652	Propetamphos	C10H20NO4PS	31218-83-4	281	138
653	Propoxur	C11H15NO3	114-26-1	209	110
654	Prothiofos	C11H15Cl2O2PS2	34643-46-4	344	309
655	Pyraclofos	C14H18ClN2O3PS	77458-01-6	360	360

656	Pyrethrin 1	C21H28O3	8003-34-7	328	123
657	Pyrethrin 2	C22H28O5	8003-34-7	372	123
658	Pyrethrin 3		8003-34-7		123
659	Pyrethrin 4		8003-34-7		107
660	Pyridaben	C19H25ClN2OS	96489-71-3	364	147
661	Pyridaphenthion	C14H17N2O4PS	119-12-0	340	340
662	Pyriproxyfen	C20H19NO3	95737-68-1	321	136
663	Quinalphos	C12H15N2O3PS	13593-03-8	298	146
664	Silafluofen	C25H29FO2Si	105024-66-6	408	179
665	Sulfotep	C8H20O5P2S2	3689-24-5	322	322
666	Sulprofos	C12H19O3PS2	38527-90-1	306	322
667	Tebupirimfos	C13H23N2O3PS	96182-53-5	318	318
668	Tefluthrin	C17H14ClF7O2	79538-32-2	418	177
669	Temephos	C16H20O6P2S3	3383-96-8	466	466
670	Terbufos	C9H21O2PS3	13071-79-9	288	231
671	Tetrachlorvinphos	C10H9Cl4O4P	22248-79-9	364	329
672	Tetramethrin-1		8003-34-7		164
673	Tetramethrin-2		8003-34-7		164
674	Thiamethoxam deg.				212
675	Thiocyclam	C5H11NS3	31895-21-3	181	135
676	Thiometon	C6H15O2PS3	640-15-3	246	88
677	Tolfenpyrad	C21H22ClN3O2	129558-76-5	383	383
678	Tralomethrin deg.	C22H19Br4NO3	66841-25-6	661	253
679	*trans*-Chlordane	C10H6Cl8	5103-74-2	406	373
680	*trans*-Nonachlor	C10H5Cl9	5103-73-1	440	409
681	Triazophos	C12H16N3O3PS	24017-47-8	313	161
682	Trichlorfon	C4H8Cl3O4P	52-68-6	256	109
683	XMC	C10H13NO2	2655-14-3	179	122
684	Xylylcarb	C10H13NO2	2425-10-7	179	122
685	2,6-Dichlorobenzamid	C7H5Cl2NO	2008-58-4	190	173
686	Acetochlor	C14H20ClNO2	34256-82-1	269	223
687	Alachlor	C14H20ClNO2	15972-60-8	269	188
688	Allidochlor	C8H12ClNO	93-71-0	173	138
689	Ametryn	C9H17N5S	834-12-8	227	227
690	Amino-chlornitrofen	C12H8Cl3NO	26306-61-6	287	289
691	Anilofos	C13H19ClNO3PS2	64249-01-0	367	226
692	Atrazine	C8H14cLN5	1912-24-9	215	200
693	Benfluralin	C13H16F3N3O4	1861-40-1	335	292
694	Benfuresate	C12H16O4S	68505-69-1	256	163
695	Benoxacor	C11H11Cl2NO2	98730-04-2	259	120
696	Bensulide	C14H24NO4PS3	741-58-2	397	77
697	Bentazone	C10H12N2O3S	25057-89-0	240	198
698	Bifenox	C14H9Cl2NO5	42576-02-3	340	341
699	Bromacil	C9H13BrN2O2	314-40-9	260	205
700	Bromobutide	C15H22BrNO	74712-19-9	311	119
701	Butachlor	C17H26ClNO2	23184-66-9	311	176
702	Butafenacil	C20H18ClF3N2O6	134605-64-4	475	331
703	Butamifos	C13H21N2O4PS	36335-67-8	332	286

704	Butylate	C11H23NOS	2008-41-5	217	146
705	Cafenstrole	C16H22N4O3S	125306-83-4	350	100
706	Captan	C9H8Cl3NO2S	133-06-2	299	79
707	Carbetamide	C12H16N2O3	16118-49-3	236	119
708	Carfentrazone-ethyl	C15H14Cl2F3N3O3	128639-02-1	411	312
709	Chloridazon	C10H8ClN3O	1698-60-8	221	221
710	Chlorimuron-ethyl	C15H15ClN4O6S	99283-00-8	414	159
711	Chlornitrofen (CNP)	C12H6Cl3NO3	1836-77-7	317	317
712	Chlorpropham	C10H12ClNO2	101-21-3	213	213
713	Chlorsulfuron	C12H12ClN5O4S	64902-72-3	357	140
714	Chlorthal-dimethyl	C10H6Cl4O4	1861-32-1	330	301
715	Cinmethylin	C18H26O2	87818-31-3	274	105
716	Clomazone	C12H14ClNO2	81777-89-1	239	204
717	Clomeprop	C16H15Cl2NO2	84496-56-0	324	288
718	Cyanazine	C9H13ClN6	21725-46-2	240	225
719	Cycloate	C11H21NOS	1134-23-2	215	154
720	Cyhalofop Butyl	C20H20FNO4	122008-85-9	357	256
721	Desmedipham	C16H16N2O4	13684-56-5	300	181
722	Dichlobenil	C7H3Cl2N	1194-65-6	171	171
723	Diclofop-methyl	C16H14Cl2O4	51338-27-3	340	340
724	Diclosulam	C13H10Cl2FN5O3S	145701-21-9	405	342
725	Difenzoquat metilsulfate	C18H20N2O4S	43222-48-6	360	234
726	Diflufenican	C19H11F5N2O2	83164-33-4	394	266
727	Dimepiperate	C15H21NOS	61432-55-1	263	119
728	Dimethametryn	C11H21N5S	22936-75-0	255	212
729	Dimethenamid	C12H18ClNO2S	87674-68-8	275	154
730	Dimethipin	C6H10O4S2	55290-64-7	210	54
731	Diphenamid	C16H17NO	957-51-7	239	167
732	Dithiopyr	C15H16F5NO2S2	97886-45-8	401	286
733	EPTC	C9H19NOS	759-94-4	189	128
734	Esprocarb	C15H23NOS	85785-20-2	265	222
735	Ethalfluralin	C13H14F3N3O4	55283-68-6	333	316
736	Ethofumesate	C13H18O5S	26225-79-6	286	286
737	Etobenzanid	C16H15Cl2NO3	79540-50-4	339	179
738	Fenoxaprop-ethyl	C18H16ClNO5	66441-23-4	361	288
739	Flamprop-methyl	C17H15ClFNO3	52756-25-9	335	105
740	Flumiclorac-pentyl	C21H23ClFNO5	87546-18-7	423	423
741	Flumioxazin	C19H15FN2O4	103361-09-7	354	354
742	Fluridone	C19H14F3NO	59756-60-4	329	328
743	Fluthiacet-methyl	C15H15ClFN3O3S2	117337-19-6	403	403
744	Furilazole	C11H13Cl2NO3	121776-33-8	277	220
745	Hexazinone	C12H20N4O2	51235-04-2	252	171
746	Imazamethabenz-methyl	C16H20N2O3	81405-85-8	288	256
747	Indanofan	C20H17ClO3	133220-30-1	340	174
748	Isopropalin	C15H23N3O4	33820-53-0	309	280
749	Isoxadifen-ethyl	C18H17NO3	163520-33-0	295	182
750	Lenacil	C13H18N2O2	2164-08-1	234	153
751	MCPA-thioethyl (Phenothiol)	C11H13ClO2S	25319-90-8	244	244
752	MCPB-ethyl	C13H17ClO3	10443-70-6	256	115

753	Mefenacet	C16H14N2O2S	73250-68-7	298	192
754	Mefenpyr-diethyl	C16H18Cl2N2O4	135590-91-9	372	253
755	Methyl dymron	C17H20N2O	42609-73-4	268	107
756	Metolachlor	C15H22ClNO2	51218-45-2	283	162
757	Metribuzin	C8H14N4OS	21087-64-9	214	198
758	Metribuzin DA	C8H13N3OS	35045-02-4	199	199
759	Metribuzin DADK	C8H14N4OS	21087-64-9	214	154
760	Metribuzin DK	C8H14N4OS	21087-64-9	214	168
761	Molinate	C9H17NOS	2212-67-1	187	126
762	Nitralin	C13H19N3O6S	4726-14-1	345	316
763	Nitrofen (NIP)	C12H7Cl2NO3	1836-75-5	283	283
764	Norflurazon	C12H9ClF3N3O	27314-13-2	303	303
765	Oryzalin	C12H18N4O6S	19044-88-3	346	317
766	Oxabetrinil	C12H12N2O3	74782-23-3	232	73
767	Oxadiazon	C15H18Cl2N2O3	19666-30-9	344	258
768	Oxyfluorfen	C15H11ClF3NO4	42874-03-3	361	252
769	Pebulate	C10H21NOS	1114-71-2	203	128
770	Pendimethalin	C13H19N3O4	40487-42-1	281	252
771	Pentoxazone	C17H17ClFNO4	110956-75-7	353	285
772	Phenmedipham deg.				167
773	Picolinafen	C19H12F4N2O2	137641-05-5	376	376
774	Piperophos	C14H28NO3PS2	24151-93-7	353	320
775	Pretilachlor	C17H26ClNO2	51218-49-6	311	162
776	Prometryn	C10H19N5S	7287-19-6	241	241
777	Propachlor	C11H14ClNO	1918-16-7	211	120
778	Propanil	C9H9Cl2NO	709-98-8	217	161
779	Propazine	C9H16ClN5	139-40-2	229	214
780	Propham	C10H13NO2	122-42-9	179	179
781	Propyzamide	C12H11Cl2NO	23950-58-5	255	173
782	Pyraflufen ethyl	C15H13Cl2F3N2O4	129630-17-7	412	412
783	Pyrazoxyfen	C20H16Cl2N2O3	71561-11-0	402	105
784	Pyributicarb	C18H22N2O2S	88678-67-5	330	165
785	Pyridate	C19H23ClN2O2S	55512-33-9	378	207
786	Pyriminobac-methyl E	C17H19N3O6	136191-64-5	361	302
787	Pyriminobac-methyl Z	C17H19N3O6	136191-64-5	361	302
788	Quinoclamine	C10H6ClNO2	2797-51-5	207	172
789	Quizalofop-ethyl	C19H17ClN2O4	76578-14-8	372	299
790	Simazine (CAT)	C7H12ClN5	122-34-9	201	201
791	Simetryn	C8H15N5S	1014-70-6	213	213
792	Sulfentrazone	C11H10Cl2F2N4O3S	122836-35-5	386	307
793	Swep	C8H7Cl2NO2	1918-18-9	219	187
794	Terbacil	C9H13ClN2O2	5902-51-2	216	161
795	Terbcarb (MBPMC)	C17H27NO2	1918-11-2	277	205
796	Terbutryn	C10H19N5S	886-50-0	241	226
797	Thenylchlor	C16H18ClNO2S	96491-05-3	323	127
798	Thiobencarb	C12H16ClNOS	28249-77-6	257	100
799	Tri-allate	C10H16Cl3NOS	2303-17-5	303	268
800	Tribenuron-methyl	C15H17N5O6S	101200-48-0	395	154

801	Triclopyr	C7H4Cl3NO3	55335-06-3	255	212
802	Trifluralin	C13H16F3N3O4	1582-09-8	335	306
803	2-Phenylphenol (OPP)	C12H10O	90-43-7	170	170
804	Azaconazole	C12H11Cl2N3O2	60207-31-0	299	217
805	Azoxystrobin	C22H17N3O5	131860-33-8	403	344
806	Benalaxyl	C20H23NO3	71626-11-4	325	148
807	Bitertanol	C20H23N3O2	55179-31-2	337	170
808	Bromuconazole-1	C13H12BrCl2N3O	116255-48-2	375	173
809	Bromuconazole-2	C13H12BrCl2N3O	116255-48-2	375	173
810	Bupirimate	C13H24N4O3S	41483-43-6	316	273
811	Captafol	C10H9Cl4NO2S	2425-06-1	347	79
812	Carboxin	C12H13NO2S	5234-68-4	235	235
813	Chinomethionat	C10H6N2OS2	2439-01-2	234	206
814	Chloroneb	C8H8Cl2O2	2675-77-6	206	191
815	Chlorothalonil (TPN)	C8Cl4N2	1897-45-6	264	266
816	Cyflufenamid	C20H17F5N2O2	180409-60-3	412	91
817	Cyproconazole	C15H18ClN3O	113096-99-4	291	222
818	Cyprodinil	C14H15N3	121552-61-2	225	224
819	Dichlofluanid	C9H11Cl2FN2O2S2	1085-98-9	332	224
820	Dichlofluanid metabolite				200
821	Dichlone	C10H4Cl2O2	117-80-6	226	226
822	Diclobutrazol	C15H19Cl2N3O	75736-33-3	327	270
823	Diclocymet 1	C15H18Cl2N2O	139920-32-4	312	277
824	Diclocymet 2	C15H18Cl2N2O	139920-32-4	312	277
825	Diclomezine	C11H8Cl2N2O	62865-36-5	254	254
826	Dicloran	C6H4Cl2N2O2	99-30-9	206	206
827	Diethofencarb	C14H21NO4	87130-20-9	267	225
828	Difenoconazole 1	C19H17Cl2N3O3	119446-68-3	405	265
829	Difenoconazole 2	C19H17Cl2N3O3	119446-68-3	405	265
830	Dimethomorph E	C21H22ClNO4	110488-70-5	387	301
831	Dimethomorph Z	C21H22ClNO4	110488-70-5	387	301
832	Diniconazole	C15H17Cl2N3O2	83657-24-3	325	268
833	Ditalimfos	C12H14NO4PS	5131-24-8	299	130
834	Edifenphos	C14H15O2PS2	17109-49-8	310	173
835	Ethoxyquin	C14H19NO	91-53-2	217	202
836	Etridiazole (Echlomezol)	C5H5Cl3N2OS	2593-15-9	246	211
837	Famoxadone	C22H18N2O4	131807-57-3	374	330
838	Fenamidone	C17H17N3OS	161326-34-7	311	238
839	Fenarimol	C17H12Cl2N2O	60168-88-9	330	219
840	Fenbuconazole	C19H17ClN4	114369-43-6	336	198
841	Fenbuconazole lactone A	C19H17ClN4	114369-43-6	337	145
842	Fenbuconazole lactone B	C19H17ClN4	114369-43-6	337	256
843	Fenoxanil	C15H18Cl2N2O2	115852-48-7	328	293
844	Fenpropimorph	C20H33NO	67306-03-0	303	128
845	Ferimzone	C15H18N4	89269-64-7	254	239
846	Fluazinam	C13H4Cl2F6N4O4	79622-59-6	464	372
847	Fludioxonil	C12H6F2N2O2	131341-86-1	248	248

848	Fluquinconazole	C16H8Cl2FN5O	136426-54-5	375	340
849	Flusilazole	C16H15F2N3Si	85509-19-9	315	233
850	Flusilazole metabolite				235
851	Flusulfamide	C13H7Cl2F3N2O4S	106917-52-6	414	179
852	Flutolanil	C17H16F3NO2	66332-96-5	323	173
853	Flutriafol	C16H13F2N3O	76674-21-0	301	219
854	Folpet	C9H4Cl3NO2S	133-07-3	295	260
855	Fthalide	C8H2Cl4O2	27355-22-2	270	243
856	Furametpyr	C17H20ClN3O2	123572-88-3	333	157
857	Furametpyr metabolite				296
858	Hexachlorobenzene	C6Cl6	118-74-1	282	284
859	Hexaconazole	C14H17Cl2N3O	79983-71-4	313	214
860	Hymexazol	C4H5NO2	10004-44-1	99	99
861	Imazalil	C14H14Cl2N2O	35554-44-0	296	215
862	Imibenconazole	C17H13Cl3N4S	86598-92-7	410	125
863	Iprobenfos (IBP)	C13H21O3PS	26087-47-8	288	204
864	Iprodione	C13H13Cl2N3O3	36734-19-7	329	314
865	Iprodione metabolite				142
866	Isoprothiolane	C12H18O4S2	50512-35-1	290	118
867	Kresoxim methyl	C18H19NO4	143390-89-0	313	116
868	Mefenoxam	C15H21NO4	70630-17-0	279	206
869	Mepanipyrim	C14H13N3	110235-47-7	223	222
870	Mepronil	C17H19NO2	55814-41-0	269	119
871	Metalaxyl	C15H21NO4	57837-19-1	279	206
872	Metominostrobin E	C16H16N2O3	133408-50-1	284	191
873	Metominostrobin Z	C16H16N2O3	133408-50-1	284	191
874	Myclobutanil	C15H17ClN4	88671-89-0	288	179
875	Napropamide	C17H21NO2	15299-99-7	271	128
876	Nitrothal-isopropyl	C14H17NO6	10552-74-6	295	236
877	Oxadixyl	C14H18N2O4	77732-09-3	278	163
878	Oxpoconazole-formyl	C17H23ClN2O3		338	114
879	Oxpoconazole-fumalate	C23H28ClN3O6	174212-12-5	478	294
880	Penconazole	C13H15Cl2N3	66246-88-6	283	248
881	Pencycron	C19H21ClN2O	66063-05-6	328	125
882	Pentachloronitrobenzene (Quintozene)	C6Cl5NO2	82-68-8	293	237
883	Prochloraz	C15H16Cl3N3O2	67747-09-5	375	180
884	Procymidone	C13H11Cl2NO2	32809-16-8	283	283
885	Propamocarb	C9H20N2O2	25606-41-1	188	58
886	Propiconazole 1	C15H17Cl2N3O2	60207-90-1	341	259
887	Propiconazole 2	C15H17Cl2N3O2	60207-90-1	341	259
888	Pyraclostrobin	C19H18ClN3O4	175013-18-0	388	132
889	Pyrazophos	C14H20N3O5PS	13457-18-6	373	221
890	Pyrifenox E	C14H12Cl2N2O	88283-41-4	294	262
891	Pyrifenox Z	C14H12Cl2N2O	88283-41-4	294	262
892	Pyrimethanil	C12H13N3	53112-28-0	199	198

893	Pyroquilon	C11H11NO	57369-32-1	173	130
894	Quinoxyfen	C15H8Cl2FNO	124495-18-7	307	237
895	Simeconazole	C14H20FN3OSi	149508-90-7	293	121
896	Spiroxamine 1	C18H35NO2	118134-30-8	297	100
897	Spiroxamine 2	C18H35NO2	118134-30-8	297	100
898	TCMTB	C9H6N2S3	21564-17-0	238	180
899	Tebuconazole	C16H22ClN3O	107534-96-3	307	250
900	Tecnazene	C6HCl4NO2	117-18-0	259	261
901	Tetraconazole	C13H11Cl2F4N3O	112281-77-3	371	336
902	Thiabendazole	C10H7N3S	148-79-8	201	201
903	Thifluzamide	C13H6Br2F6N2O2S	130000-40-7	526	194
904	Tolclofos-methyl	C9H11Cl2O3PS	57018-04-9	301	265
905	Tolylfluanid	C10H13Cl2FN2O2S2	731-27-1	346	238
906	Tolylfluanid metabolite				214
907	Triadimefon	C14H16ClN3O2	43121-43-3	293	208
908	Triadimenol 1	C14H18ClN3O2	89482-17-7	295	168
909	Triadimenol 2	C14H18ClN3O2	82200-72-4	295	168
910	Trichlamid	C13H16Cl3NO3	70193-21-4	339	148
911	Tricyclazole	C9H7N3S	41814-78-2	189	189
912	Tridemorph	C19H39NO	81412-43-3	297	153
913	Trifloxystrobin	C20H19F3N2O4	141517-21-7	408	116
914	Triflumizole	C15H15ClF3N3O	99387-89-0	345	278
915	Vinclozolin	C12H9Cl2NO3	50471-44-8	285	285
916	Zoxamide	C14H16Cl3NO2	156052-68-5	335	187
917	6-Benzylaminopurine	C12H11N5	1214-39-7	225	225
918	Acrinathrin	C26H21F6NO5	101007-06-1	541	181
919	Amitraz	C19H23N3	33089-61-1	293	293
920	Amitraz deg.				162
921	Bromopropylate	C17H16Br2O3	18181-80-1	426	341
922	Chlorobenzilate	C16H14Cl2O3	510-15-6	324	251
923	Clofentezine	C14H8Cl2N4	74115-24-5	302	137
924	Dicofol	C14H9Cl5O	115-32-2	368	139
925	Dicofol deg.	C14H9Cl5O	115-32-2	368	139
926	Ethychlozate	C11H11ClN2O2	27512-72-7	238	165
927	Etoxazole	C21H23F2NO2	153233-91-1	359	204
928	Fenamiphos	C13H22NO3PS	22224-92-6	303	303
929	Fenothiocarb	C13H19NO2S	62850-32-2	253	160
930	Fenpropathrin	C22H23NO3	39515-41-8	349	181
931	Fensulfothion	C11H17O4PS2	115-90-2	308	293
932	Fluacrypyrim	C20H21F3N2O5	229977-93-9	426	204
933	Fosthiazate 1	C9H18NO3PS2	98886-44-3	283	195
934	Fosthiazate 2	C9H18NO3PS2	98886-44-3	283	195
935	Halfenprox	C24H23BrF2O3	111872-58-3	476	263
936	Hexythiazox	C17H21ClN2O2S	78587-05-0	352	227
937	Methomyl oxime	C5H11N3O2S	13749-94-5	105	105
938	Paclobutrazol	C15H20ClN3O	76738-62-0	293	236
939	Probenazole	C10H9NO3S	27605-76-1	223	130
940	Prohydrojasmon	C15H26O3	158474-72-7	254	153
941	Propargite 1	C19H26O4S	2312-35-8	350	135

942	Propargite 2	C19H26O4S	2312-35-8	350	135
943	Pyrimidifen	C20H28ClN3O2	105779-78-0	377	184
944	Spirodiclofen	C21H24Cl2O4	148477-71-8	410	71
945	Tebufenpyrad	C18H24ClN3O	119168-77-3	333	171
946	Tecloftalam	C14H5Cl6NO3	76280-91-6	473	394
947	Tetradifon	C12H6Cl4O2S	116-29-0	354	356
948	Tribufos	C12H27OSP3	78-48-8	314	169
949	Uniconazole P	C15H18ClN3O	83657-17-4	291	234
	4-Chlorotoluene-d4			130	130
	1,4-Dichlorobenzene-d4			150	150
	Naphthalene-d8			136	136
	Acenaphthene-d10	Internal standards		164	164
	Phenanthrene-d10			188	188
	Fluoranthene-d10			212	212
	Chrysene-d12			240	240
	Perylene-d12			264	264

Table S2. Precursor and product ions of SRM for GC-MS/MS

No.	Compound	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
1	PCB #1	188.04	153.03	20	17.48	18.48
		190.04	153.03	20	17.48	18.48
2	Pentachlorobenzene	247.85	141.92	25	17.62	18.62
		247.85	212.87	25	17.62	18.62
		249.85	179.89	20	17.62	18.62
3	PCB #3	188.04	153.03	20	18.75	19.75
		190.04	153.03	20	18.75	19.75
4	PCB #4&10	222	152	20	19.26	20.26
		224	152	20	19.26	20.26
5	α-HCH	180.91	108.95	25	20.38	21.38
		180.91	144.93	10	20.38	21.38
		182.91	146.93	15	20.38	21.38
		218.89	144.93	25	20.38	21.38
		218.89	180.91	5	20.38	21.38
		218.89	182.91	15	20.38	21.38
6	Hexachlorobenzene	248.84	213.86	20	20.45	21.45
		262.83	116.92	20	20.45	21.45
		264.82	116.92	20	20.45	21.45
		283.81	213.86	20	20.45	21.45
		283.81	248.84	14	20.45	21.45
		285.81	250.83	20	20.45	21.45
7	PCB #8	222	152	20	20.47	21.47
		224	152	20	20.47	21.47
8	PCB #19	255.96	185.97	20	20.95	21.95
		257.96	185.97	20	20.95	21.95
9	β-HCH	180.91	108.95	25	21.06	22.06
		180.91	144.93	10	21.06	22.06
		182.91	146.93	15	21.06	22.06
		218.89	144.93	25	21.06	22.06
		218.89	180.91	5	21.06	22.06
		218.89	182.91	15	21.06	22.06
10	γ-HCH	180.91	108.95	25	21.28	22.28
		180.91	144.93	10	21.28	22.28
		182.91	146.93	15	21.28	22.28
		218.89	144.93	25	21.28	22.28
		218.89	180.91	5	21.28	22.28
		218.89	182.91	15	21.28	22.28
11	PCB #18	255.96	185.97	20	21.58	22.58
		257.96	185.97	20	21.58	22.58
12	PCB #15	222	152	20	21.73	22.73

		224	152	20	21.73	22.73
13	*δ*-HCH	180.91	108.95	25	22.04	23.04
		180.91	144.93	10	22.04	23.04
		182.91	146.93	15	22.04	23.04
		218.89	144.93	25	22.04	23.04
		218.89	180.91	5	22.04	23.04
		218.89	182.91	15	22.04	23.04
14	PCB #54	289.92	219.94	20	22.4	23.4
		291.92	219.94	20	22.4	23.4
15	PCB #28	255.96	185.97	20	22.83	23.83
		257.96	185.97	20	22.83	23.83
16	PCB #33	255.96	185.97	20	23.03	24.03
		257.96	185.97	20	23.03	24.03
17	Heptachlor	236.89	142.93	28	23.16	24.16
		269.87	234.89	12	23.16	24.16
		271.87	236.89	13	23.16	24.16
		273.87	238.88	8	23.16	24.16
		334.84	301.85	12	23.16	24.16
		336.84	265.87	15	23.16	24.16
		336.84	301.85	15	23.16	24.16
		336.84	301.85	12	23.16	24.16
		338.84	265.87	15	23.16	24.16
		338.84	267.87	15	23.16	24.16
		338.84	303.85	15	23.16	24.16
18	PCB #22	255.96	185.97	20	23.23	24.23
		257.96	185.97	20	23.23	24.23
19	PCB #52	289.92	219.94	20	23.69	24.69
		291.92	219.94	20	23.69	24.69
20	PCB #49	289.92	219.94	20	23.78	24.78
		291.92	219.94	20	23.78	24.78
21	PCB #104	323.88	253.91	20	24.02	25.02
		325.88	255.91	20	24.02	25.02
22	Aldrin	262.91	192.93	24	24.06	25.06
		262.91	227.92	26	24.06	25.06
		264.91	229.92	26	24.06	25.06
		292.9	222.92	20	24.06	25.06
		292.9	257.91	10	24.06	25.06
23	PCB #44	289.92	219.94	20	24.15	25.15
		291.92	219.94	20	24.15	25.15
24	PCB #37	255.96	185.97	20	24.31	25.31
		257.96	185.97	20	24.31	25.31
25	Heptachlor epoxide (B)	352.83	262.87	14	25.03	26.03
		354.83	264.87	15	25.03	26.03
		386.79	262.86	15	25.03	26.03
26	Oxychlordane	386.79	322.83	15	25.03	26.03
27	PCB #74	289.92	219.94	20	25.05	26.05
		291.92	219.94	20	25.05	26.05
28	PCB #70	289.92	219.94	20	25.16	26.16
		291.92	219.94	20	25.16	26.16
29	PCB #95	323.88	253.91	20	25.2	26.2
		325.88	255.91	20	25.2	26.2
30	PCB #155	357.84	287.88	25	25.51	26.51
		359.84	289.87	25	25.51	26.51
31	*trans*-Chlordane	372.81	265.87	13	25.6	26.6
32	*o,p'*-DDE	246.95	175.97	25	25.68	26.68
		246.95	175.97	20	25.68	26.68
		317.94	245.95	15	25.68	26.68
33	PCB #101	323.88	253.91	20	25.78	26.78
		325.88	255.91	20	25.78	26.78
34	PCB #99	323.88	253.91	20	25.88	26.88
		325.88	255.91	20	25.88	26.88
35	*cis*-Chlordane	372.81	265.87	13	25.91	26.91
		409.8	374.81	5	25.91	26.91

36	*trans*-Nonachlor	406.78	299.94	20	25.99	26.99
		408.78	301.83	20	25.99	26.99
37	PCB #119	323.88	253.91	20	26.01	27.01
		325.88	255.91	20	26.01	27.01
38	PCB #87	323.88	253.91	20	26.39	27.39
		325.88	255.91	20	26.39	27.39
39	PCB #81	289.92	219.94	20	26.43	27.43
		291.92	219.94	20	26.43	27.43
40	*p,p'*-DDE	245.95	175.97	25	26.46	27.46
		247.95	175.97	20	26.46	27.46
		317.94	245.95	20	26.46	27.46
		317.94	247.95	20	26.46	27.46
41	Dieldrin	262.91	192.93	25	26.58	27.58
		262.91	227.92	5	26.58	27.58
		276.91	204.93	20	26.58	27.58
		276.91	206.93	20	26.58	27.58
		276.91	240.92	10	26.58	27.58
		278.9	242.92	15	26.58	27.58
		379.87	344.88	7	26.58	27.58
42	PCB #110	323.88	253.91	20	26.6	27.6
		325.88	255.91	20	26.6	27.6
43	*o,p'*-DDD	234.97	164.98	17	26.61	27.61
		236.97	164.98	20	26.61	27.61
44	PCB #77	289.92	219.94	20	26.67	27.67
		291.92	219.94	20	26.67	27.67
45	PCB #151	357.84	287.88	25	26.86	27.86
		359.84	289.87	25	26.86	27.86
46	Endrin	262.91	190.93	25	27.07	28.07
		262.91	192.93	26	27.07	28.07
		280.9	244.92	5	27.07	28.07
		280.9	244.92	12	27.07	28.07
		344.88	280.9	8	27.07	28.07
47	PCB #149	357.84	287.88	25	27.15	28.15
		359.84	289.87	25	27.15	28.15
48	PCB #123	323.88	253.91	20	27.16	28.16
		325.88	255.91	20	27.16	28.16
49	PCB #118	323.88	253.91	20	27.25	28.25
		325.88	255.91	20	27.25	28.25
50	*cis*-Nonachlor	406.78	299.84	20	27.44	28.44
		408.78	301.83	20	27.44	28.44
51	*p,p'*-DDD	234.94	164.96	16	27.45	28.45
		234.97	164.98	17	27.45	28.45
		234.97	198.97	18	27.45	28.45
52	*o,p'*-DDT	236.94	164.96	20	27.45	28.45
		236.97	164.98	20	27.45	28.45
		317.92	245.94	20	27.45	28.45
53	PCB #114	323.88	253.91	20	27.48	28.48
		325.88	255.91	20	27.48	28.48
54	PCB #188	391.81	321.84	25	27.52	28.52
		393.8	323.84	25	27.52	28.52
55	PCB #153&168	357.84	287.88	25	27.74	28.74
		359.84	289.87	25	27.74	28.74
56	PCB #105	323.88	253.91	20	27.83	28.83
		325.88	255.91	20	27.83	28.83
57	*p,p'*-DDT	234.94	164.96	16	28.34	29.34
		234.94	198.95	15	28.34	29.34
58	PCB #138&158	357.84	287.88	25	28.38	29.38
		359.84	289.87	25	28.38	29.38
59	PCB #178	391.81	321.84	25	28.49	29.49
		393.8	323.84	25	28.49	29.49
60	PCB #126	323.88	253.91	25	28.6	29.6
		325.88	255.91	25	28.6	29.6

61	PCB #187	391.81	321.84	25	28.69	29.69
		393.8	323.84	25	28.69	29.69
62	PCB #183	391.81	321.84	25	28.82	29.82
		393.8	323.84	25	28.82	29.82
63	PCB #128	357.84	287.88	25	28.95	29.95
		359.84	289.87	25	28.95	29.95
64	PCB #167	357.84	287.88	25	29.02	30.02
		359.84	289.87	25	29.02	30.02
65	PCB #177	391.81	321.84	25	29.33	30.33
		393.8	323.84	25	29.33	30.33
66	PCB #202	427.77	357.8	25	29.39	30.39
		429.76	357.8	25	29.39	30.39
67	PCB #171	391.81	321.84	25	29.45	30.45
		393.8	323.84	25	29.45	30.45
68	PCB #156	357.84	287.88	25	29.52	30.52
		359.84	289.87	25	29.52	30.52
69	PCB #201	427.77	357.8	25	29.57	30.57
		429.76	357.8	25	29.57	30.57
70	PCB #157	357.84	287.88	25	29.62	30.62
		359.84	289.87	25	29.62	30.62
71	PCB #180	391.81	321.84	25	29.87	30.87
		393.8	323.84	25	29.87	30.87
72	PCB #191	391.81	321.84	25	29.98	30.98
		393.8	323.84	25	29.98	30.98
73	PCB #169	357.84	287.88	25	30.37	31.37
		359.84	289.87	25	30.37	31.37
74	PCB #170	391.81	321.84	25	30.5	31.5
		393.8	323.84	25	30.5	31.5
75	PCB #199	427.77	357.8	25	30.65	31.65
		429.76	357.8	25	30.65	31.65
76	PCB #189	391.81	321.84	25	31.16	32.16
		393.8	323.84	25	31.16	32.16
77	PCB #208	461.73	391.77	25	31.39	32.39
		463.73	393.77	25	31.39	32.39
78	PCB #194	427.77	357.8	25	31.89	32.89
		429.76	357.8	25	31.89	32.89
79	PCB #205	427.77	357.8	25	31.98	32.98
		429.76	357.8	25	31.98	32.98
80	PCB #206	461.73	391.77	25	32.65	33.65
		463.73	393.77	25	32.65	33.65
81	PCB #209	495.69	425.73	25	33.28	34.28
		497.69	427.73	25	33.28	34.28
Internal standards	Naphthalene-d_8	136.11	136.11	15	10.53	14.53
	Acenaphthene-d_{10}	82.07	82.07	15	17.18	18.18
		164.14	164.14	15	17.18	18.18
		165.14	165.14	15	17.18	18.18
	Phenanthrene-d_{10}	94.07	94.07	15	21.61	22.61
		188.14	188.14	15	21.61	22.61
		189.14	189.14	15	21.61	22.61
	Fluoranthene-d_{10}	106.07	106.07	15	25.17	26.17
		212.14	212.14	15	25.17	26.17
		213.14	213.14	15	25.17	26.17
	Chrysene-d_{12}	120.09	120.09	15	29.52	30.52
		240.17	240.17	15	29.52	30.52
		241.17	241.17	15	29.52	30.52
	Perylene-d_{12}	132.09	132.09	15	33.45	34.45
		264.17	264.17	15	33.45	34.45
		265.17	265.17	15	33.45	34.45

Table S3. Target compounds analyzed by LC/TOF/MS

No.	Compound	Formula	CAS RN	MW	m/z (Quantitation ion)	m/z (Qualifier ion)
1	4,4'-Oxybis-benzenamine	C12H12N2O	101-80-4	200.095	201.10224	
2	Dicyclohexylamine	C12H23N	101-83-7	181.183	182.19033	
3	3,3-Dimethoxybenzidine	C14H16N2O2	119-90-4	244.1211	245.12845	
4	4,4'-Methylenebis(N,N-dimethylaniline)	C17H22N2	101-61-1	254.1783	255.18558	
5	Adenochrome semicarbazone/Carbazochrome	C10H12N4O3	69-81-8	236.0909	237.09822	
6	Hexaconazole	C14H17Cl2N3O	79983-71-4	313.0749	314.08214	316.0729
7	Cafenstrole	C16H22N4O3S	125306-83-4	350.1413	351.14854	353.1443
8	Fenarimol	C17H12Cl2N2O	60168-88-9	330.0327	331.03994	333.037
9	Testosterone	C19H28O2	58-22-0	288.2089	289.21621	
10	Phenacetin	C10H13NO2	62-44-2	179.0946	180.10191	
11	Metformin	C4H11N5	657-24-9	129.1014	130.10872	
12	Sulfanilamide	C6H8N2O2S	63-74-1	172.0306	190.06447	192.0603
13	Quinoxaline-2-carboxylic acid	C9H6N2O2	879-65-2	174.0429	192.07675	
14	Sulfamethizole	C9H10N4O2S2	144-82-1	270.0245	271.03179	273.0276
15	Sulfamethoxazole	C10H11N3O3S	723-46-6	253.0521	254.05939	256.0552
16	Cefotaxime	C16H17N5O7S2	63527-52-6	455.0569	456.06422	458.06
17	Cotinine	C10H12N2O	486-56-6	176.095	177.10224	
18	Cimetidine	C10H16N6S	51481-61-9	252.1157	253.12299	255.1188
19	Antipyrine	C11H12N2O	60-80-0	188.095	189.10224	
20	Losartan	C22H23ClN6O	114798-26-4	422.1622	423.16946	425.1665
21	Tilmicosin	C46H80N2O13	108050-54-0	868.566	869.57332	
22	Roxithromycin	C41H76N2O15	80214-83-1	836.5246	837.53185	
23	Chlorpromazine	C17H19ClN2S	50-53-3	318.0957	319.10302	321.1001
24	Salinomycin	C42H70O11	53003-10-4	750.4918	768.52564	
25	Sulfadiazine	C10H10N4O2S	68-35-9	250.0524	251.05972	253.0555
26	Terbutaline	C12H19NO3	23031-25-6	225.1365	226.14377	
27	Atenolol	C14H22N2O3	29122-68-7	266.163	267.17032	
28	Theophylline	C7H8N4O2	58-55-9	180.0647	203.05395	
29	Sulfamerazine	C11H12N4O2S	127-79-7	264.0681	265.07537	267.0712
30	Thiamphenicol	C12H15NO5Cl2S	15318-45-3	355.0048	373.03862	375.0357
31	Sulfamonomethoxine	C11H12N4O3S	1220-83-3	280.063	281.07029	283.0661
32	Ranitidine	C13H22N4O3S	66357-35-5	314.1413	315.14854	317.1443

33	2-(Di-n-butylamino)ethanol	C10H23NO	102-81-8	173.1779	174.18524	
34	Ormetoprim	C14H18N4O2	6981-18-6	274.143	275.15025	
35	4,4'-Diaminodiphenyl-methane	C13H14N2	101-77-9	198.1157	199.12297	
36	Bezafibrate	C19H20NO4Cl	41859-67-0	361.1080858	362.11536	364.1124
37	Propranolol	C16H21NO2	525-66-6	259.1572	260.16451	
38	Pyriminobac-methyl(E)	C17H19N3O6	147411-69-6	361.1274	362.13466	
39	Alachlor	C14H20O2NCl	15972-60-8	269.1183	270.12553	272.1226
40	Triphenylphosphate	C18H15O4P	115-86-6	326.0708	327.07807	
41	Flumequine	C14H12FNO3	42835-25-6	261.0801	262.0874	
42	Enrofloxacin	C19H22N3O3F	93106-60-6	359.1645	360.1718	
43	Esprocarb	C15H23NOS	85785-20-2	265.15	266.15731	268.1531
44	Monocrotophos	C7H14NO5P	6923-22-4	223.0609591	241.09478	
45	Clenbuterol	C12H18Cl2N2O	37148-27-9	276.0796186	277.0869	279.0839
46	Lincomycin	C18H34N2O6S	154-21-2	406.2137575	407.22103	409.2168
47	Salbutamol	C13H21NO3	18559-94-9	239.1521435	240.15942	
48	Tylosin	C46H77NO17	1401-69-0	915.5191501	916.52643	
49	Tribenuron methyl	C15H17N5O6S	101200-48-0	395.089954	396.09723	398.093
50	Aldicarb	C7H14N2O2S	116-06-3	190.0775984	208.11142	210.1072
51	Aldicarb sulfone	C7H14N2O4S	1646-88-4	222.0674	223.0747	225.0705
52	Aramite	C15H23O4SCl	140-57-8	334.1005576	352.13438	354.1314
53	Boscalid	C18H12N2OCl2	188425-85-6	342.0326684	343.03994	345.037
54	Carbaryl	C12H11O2N	63-25-2	201.0789786	219.1128	
55	Carbofuran	C12H15NO3	1563-66-2	221.1052	222.11247	
56	Clofentezine	C14H8N4Cl2	74115-24-5	302.0126017	303.01988	305.0169
57	Cyprodinil	C14H15N3	121552-61-2	225.1265975	226.13387	
58	Diflubenzuron	C14H9N2O2ClF2	35367-38-5	310.0320617	311.03934	313.0364
59	Dimethomorph(E)	C21H22NO4Cl	110488-70-5(isomer)	387.1237359	388.13101	390.1281
60	Dimethomorph(Z)	C21H22NO4Cl	110488-70-5(isomer)	387.1237359	388.13101	390.1281
61	Diuron	C9H10Cl2N2O	330-54-1	232.0170184	233.02429	235.0213
62	Epoxiconazole	C17H13N3OClF	133855-98-8	329.073118	330.08039	332.0774
63	Fenamidone	C17H17N3OS	161326-34-7	311.1092329	312.11651	314.1123
64	Fenpyroximate	C24H27N3O4	134098-61-6	421.2001564	422.20743	
65	Flufenacet	C14H13N3O2SF4	142459-58-3	363.0664602	364.07374	366.0695
66	Fluridone	C19H14NOF3	59756-60-4	329.1027487	330.11003	
67	Hexythiazox	C17H21N2O2SCl	78587-05-0	352.1012263	353.1085	355.1056
68	Linuron	C9H10N2O2Cl2	330-55-2	248.011933	249.01921	251.0163
69	Monolinuron	C9H11N2O2Cl	1746-81-2	214.0509053	215.05818	217.0552

70	Oxamyl	C7H13N3O3S	23135-22-0	219.067762	237.10159	239.0974
71	Propaquizafop	C22H22N3O5Cl	111479-05-1	443.1247985	444.13207	446.1291
72	Pyraclostrobin	C19H18N3O4Cl	175013-18-0	387.0985838	388.10586	390.1029
73	Tebufenozide	C22H28N2O2	112410-23-8	352.2150782	353.22235	
74	Tebuthiuron	C9H16N4OS	34014-18-1	228.1044818	229.11176	231.1076
75	Triflumuron	C15H10N2O3ClF3	64628-44-0	358.0332045	359.04048	361.0375
76	Thiamethoxam	C8H10N5O3SCl	153719-23-4	291.0192876	292.02656	294.0236
77	Imidacloprid	C9H10N5O2Cl	138261-41-3	255.0523023	256.05958	258.0566
78	Clothianidin	C6H8N5O2SCl	210880-92-5	249.0087229	250.016	252.013
79	Chloridazon	C10H8N3OCl	1698-60-8	221.0355896	222.04287	224.0399
80	Oxycarboxin	C12H13NO4S	5259-88-1	267.0565286	268.06381	270.0596
81	Thiacloprid	C10H9N4SCl	111988-49-9	252.0236447	253.03092	255.028
82	Thiabendazole	C10H7N3S	148-79-8	201.0360679	202.04334	204.0391
83	Azamethiphos	C9H10N2O5PSCl	35575-96-3	323.9736564	324.98093	326.978
84	Dimethirimol	C11H19N3O	5221-53-4	209.1528122	210.16009	
85	Tralkoxydim 1	C20H27NO3	87820-88-0	329.1990937	330.20637	
86	Tralkoxydim 2	C20H27NO3		329.1990937	330.20637	
87	Isoxaflutole	C15H12NO4SF3	141112-29-0	359.0439132	360.05119	362.047
88	Azinphos-methyl	C10H12N3O3PS2	86-50-0	317.0057692	318.01305	320.0088
89	Pyriftalid	C15H14N2O4S	135186-78-6	318.0674276	319.0747	321.0705
90	Ferimzone(E)	C15H18N4	89269-64-7(isomer)	254.1531466	255.16042	
91	Ferimzone(Z)	C15H18N4	89269-64-7(isomer)	254.1531466	255.16042	
92	Methoxyfenozide	C22H28N2O3	161050-58-4	368.2099928	369.21727	
93	Chromafenozide	C24H30N2O3	143807-66-3	394.2256428	395.23292	
94	Butafenacil	C20H18N2O6ClF3	134605-64-4	474.0805486	492.11437	494.1114
95	Iprovalicarb	C18H28N2O3	140923-17-7	320.2099928	321.21727	
96	Simeconazole	C14H20N3OFSi	149508-90-7	293.135967	294.14324	
97	Oryzalin	C12H18N4O6S	19044-88-3	346.094705	347.10198	349.0978
98	Naproanilide	C19H17NO2	52570-16-8	291.1259288	292.13321	
99	Fenoxycarb	C17H19NO4	79127-80-3	301.1314081	302.13868	
100	Anilofos	C13H19NO3PS2Cl	64249-01-0	367.0232491	368.03053	370.0276
101	Cyflufenamid	C20H17N2O2F5	180409-60-3	412.1210188	413.1283	
102	Pyrazolynate/Pyrazolate	C19H16N2O4SCl2	58011-68-0	438.0207831	439.02806	441.0251
103	Indoxacarb	C22H17N3O7ClF3	144171-61-9	527.0707122	528.07799	530.075
104	Benzofenap	C22H20N2O3Cl2	82692-44-2	430.0850979	431.09237	433.0894
105	Quizalofop-ethyl	C19H17N2O4Cl	76578-14-8	372.0876848	373.09496	375.092
106	Lactofen	C19H15NO7ClF3	77501-63-4	461.0489142	479.08274	481.0798

107	Furathiocarb	C18H26N2O5S	65907-30-4	382.1562426	383.16352	385.1593
108	Clomeprop	C16H15NO2Cl2	84496-56-0	323.0479842	324.05526	326.0523
109	Cloquintocet-mexyl	C18H22NO3Cl	99607-70-2	335.1288213	336.1361	338.1331
110	Avermectin B1a	C48H72O14	65195-55-3	872.492207	895.48143	
111	Ethenzamide	C9H11NO2	938-73-8	165.0789786	166.08626	
112	Propyphenazone	C14H18N2O	479-92-5	230.1419	231.14919	
113	Mepirizole	C11H14N4O2	18694-40-1	234.1116757	235.11895	
114	Tolperisone	C16H23NO	728-88-1	245.1779644	246.18524	
115	Sulfapyridine	C11H11N3O2S	144-83-2	249.0571973	250.06447	252.0603
116	Epinastine	C16H15N3	80012-43-7	249.1265975	250.13387	
117	Ketoprofen	C16H14O3	22071-15-4	254.0943	272.12812	
118	Cyclophosphamide	C7H15Cl2N2O2P	50-18-0	260.0248	261.0321	263.0291
119	Tolbutamide	C12H18N2O3S	64-77-7	270.1038	271.11109	273.1069
120	Pentoxifylline	C13H18N4O3	6493-05-6	278.1379	279.14517	
121	Etodolac	C17H21NO3	41340-25-4	287.1521	288.15942	
122	Carazolol	C18H22N2O2	57775-29-8	298.168128	299.1754	
123	Metoclopramide	C14H22N3O2Cl	364-62-5	299.1400547	300.14733	302.1444
124	Scopolamine	C17H21NO4	51-34-3	303.1471	304.15433	
125	Amitriptyline	C20H23N	50-48-6	277.1830497	278.19033	
126	Diphenidol	C21H27NO	972-02-1	309.2092645	310.21654	
127	Sulfadimethoxine	C12H14N4O4S	122-11-2	310.0736	311.08085	313.0766
128	Fluvoxamine	C15H21N2O2F3	54739-18-3	318.1555125	319.16279	
129	Acetohexamide	C15H20N2O4S	968-81-0	324.1143778	325.12165	327.1175
130	Ifenprodil	C21H27NO2	23210-56-2	325.2041791	326.21146	
131	Paroxetine	C19H20NO3F	61869-08-7	329.1427217	330.15	
132	Disopyramide	C21H29N3O	3737-09-5	339.2310626	340.23834	
133	Cefalexin	C16H17N3O4S	15686-71-2	347.0939767	348.10125	350.097
134	Ampicillin	C16H19N3O4S	69-53-4	349.1096	350.1169	352.1127
135	Pirenzepine	C19H21N5O2	28797-61-7	351.1695249	352.1768	
136	Prednisolone	C21H28O5	50-24-8	360.1937	361.20095	
137	Haloperidol	C21H23NO2ClF	52-86-8	375.1401349	376.14741	378.1445
138	Chlorpheniramine maleate	C20H23N2O4Cl	113-92-8	390.1346349	275.13095	277.128
139	Dexamethasone	C22H29O5F	50-02-2	392.1999022	393.20718	
140	Cefuroxime	C16H16N4O8S	55268-75-2	424.0688842	442.10271	444.0985
141	Verapamil	C27H38N2O4	52-53-9	454.2831577	455.29043	
142	Dipyridamole	C24H40N8O4	58-32-2	504.3172518	505.32453	
143	Oleandomycin	C35H61NO12	3922-90-5	687.4193764	688.42665	

144	Erythromycin	C37H67NO13	114-07-8	733.4612	734.46852	
145	Clarithromycin	C38H69NO13	81103-11-9	747.4768913	748.48417	
146	Azithromycin	C38H72N2O12	83905-01-5	748.5085	749.5158	
147	Spiramycin	C43H74N2O14	8025-81-8	842.5140051	?	
148	Acetaminophen	C8H9NO2	103-90-2	151.0633285	152.0706	
149	Dextromethorphan	C18H25NO	125-71-3	271.1936144	272.20089	
150	Diltiazem	C22H26N2O4S	42399-41-7	414.161328	415.1686	417.1644
151	Fenofibrate	C20H21O4Cl	49562-28-9	360.1128369	361.12011	363.1172
152	Fluoxetine	C17H18NOF3	54910-89-3	309.1340488	310.14133	
153	Griseofulvin	C17H17O6Cl	126-07-8	352.071366	353.07864	355.0757
154	Ifosfamide	C7H15N2O2PCl2	3778-73-2	260.0248197	261.0321	363.0291
155	Lidocaine	C14H22N2O	137-58-6	234.1732133	235.18049	
156	Metoprolol	C15H25NO3	37350-58-6	267.1834437	268.19072	
157	Promethazine	C17H20N2S	60-87-7	284.1347193	285.142	
158	Sotalol	C12H20N2O3S	3930-20-9	272.1194632	273.12674	275.1225
159	Sulpiride	C15H23N3O4S	15676-16-1	341.1409269	342.1482	344.144
160	Diclosulam	C13H10Cl2FN5O3S	145701-21-9	404.9865	405.99382	407.9909
161	Thidiazuron	C9H8N4OS	51707-55-2	220.0419	221.04916	223.045
162	Forchlorfenuron	C12H10ClN3O	68157-60-8	247.0512	248.05852	250.0556
163	Fomesafen	C15H10ClF3N2O6S	72178-02-0	437.99	456.02384	458.0209
164	Imazaquin	C17H17N3O3	81335-37-7	311.127	312.13427	
165	Flumetsulam	C12H9F2N5O2S	98967-40-9	325.0445	326.05178	328.0476
166	Methomyl	C5H10N2O2S	16752-77-5	162.0462983	163.05357	165.0494
167	Bendiocarb	C11H13NO4	22781-23-3	223.0844579	224.09173	
168	Thiodicarb	C10H18N4O4S3	59669-26-0	354.0490172	355.05629	357.0521
169	Pirimicarb	C11H18N4O2	23103-98-2	238.1429758	239.15025	
170	Furametpyr	C17H20N3O2Cl	123572-88-3	333.1244046	334.13168	336.1287
171	Methabenzthiazuron	C10H11N3OS	18691-97-9	221.0622827	222.06956	224.0654
172	Azoxystrobin	C22H17N3O5	131860-33-8	403.1168207	404.1241	
173	Fenobucarb	C12H17NO2	3766-81-2	207.1259288	208.13321	
174	Methiocarb	C11H15NO2S	2032-65-7	225.0823494	226.08963	228.0854
175	Dymron	C17H20N2O	42609-52-9	268.1575633	269.16484	
176	Cumyluron	C17H19N2OCl	99485-76-4	302.118591	303.12587	305.1229
177	Chloroxuron	C15H15N2O2Cl	1982-47-4	290.0822054	291.08948	293.0865
178	Mepanipyrim	C14H13N3	110235-47-7	223.1109474	224.11822	
179	Triticonazole	C17H20N3OCl	131983-72-7	317.12949	318.13677	320.1338
180	Indanofan	C20H17O3Cl	133220-30-1	340.0866221	341.0939	343.0909

181	Tetrachlorvinphos	C10H9O4PCl4	22248-79-9	363.8992561	381.93308	383.9301
182	Carpropamid	C15H18NOCl3	104030-54-8	333.0453973	334.05267	336.0497
183	Imazalil	C14H14N2OCl2	35554-44-0	296.0483185	297.05559	299.0526
184	Pencycuron	C19H21N2OCl	66063-05-6	328.134241	329.14152	331.1386
185	Oxaziclomefone	C20H19NO2Cl2	153197-14-9	375.0792843	376.08656	378.0836
186	Fenoxaprop-ethyl	C18H16NO5Cl	66441-23-4(racemate)	361.0717003	362.07898	364.076
187	Spinosyn A	C41H65NO10	131929-60-7	731.4608473	732.46812	
188	Metsulfuron-methyl	C14H15N5O6S	74223-64-6	381.0743039	382.08158	384.0774
189	Thifensulfuron-methyl	C12H13N5O6S2	79277-27-3	387.0307246	388.038	390.0338
190	Azimsulfuron	C13H16N10O5S	120162-55-2	424.1025844	425.10986	427.1057
191	Chlorsulfuron	C12H12N5O4SCl	64902-72-3	357.0298523	358.03713	360.0342
192	Florasulam	C12H8N5O3SF3	145701-23-1	359.0299944	360.03727	362.0331
193	Cinosulfuron	C15H19N5O7S	94593-91-6	413.1005187	414.1078	416.1036
194	Foramsulfuron	C17H20N6O7S	173159-57-4	452.1114177	453.11869	455.1145
195	Sulfosulfuron	C16H18N6O7S2	141776-32-1	470.0678383	471.07511	473.0709
196	Flazasulfuron	C13H12N5O5SF3	104040-78-0	407.0511238	408.05843	410.0542
197	Propoxycarbazone-sodium	C15H17N4O7SNa	181274-15-7	420.0715646	421.07884	423.0746
198	Triasulfuron	C14H16N5O5SCl	82097-50-5	401.0560671	402.06337	404.0604
199	Clofencet	C13H11N2O3Cl	129025-54-3	278.0458199	279.0531	281.0501
200	Mesosulfuron-methyl	C17H21N5O9S2	208465-21-8	503.0780687	504.08535	506.0811
201	Ethametsulfuron-methyl	C15H18N6O6S	97780-06-8	410.100853	411.10813	413.1039
202	Pyrazosulfuron-ethyl	C14H18N6O7S	93697-74-6	414.0957677	415.10304	417.0988
203	Naptalam	C18H13NO3	132-66-1	291.0895433	292.09682	
204	Iodosulfuron-methyl-sodium	C14H13N5O6SINa	144550-36-7	528.9529009	529.96017	531.956
205	Trifloxysulfuron-sodium	C14H13N5O6SF3Na	199119-58-9	459.0436335	460.05091	462.0467
206	Halosulfuron-methyl	C13H15N6O7SCl	100784-20-1	434.0411453	435.04842	437.0455
207	Metosulam	C14H13N5O4SCl2	139528-85-1	417.00653	418.01381	420.0109
208	Penoxsulam	C16H14N5O5SF5	219714-96-2	483.0635803	484.07086	486.0667
209	Chlorimuron-ethyl	C15H15N4O6SCl	90982-32-4	414.0400826	415.04736	417.0444
210	Ethoxysulfuron	C15H18N4O7S	126801-58-9	398.0896196	416.12345	418.1192
211	Sulfentrazone	C11H10N4O3SCl2F2	122836-35-5	385.9818727	404.0157	406.0127
212	Clodinafop	C14H11NO4ClF	114420-56-3	311.0360638	312.04334	314.0404
213	Bensulfuron-methyl	C16H18N4O7S	83055-99-6	410.0896196	411.0969	413.0927
214	Fluazifop	C15H12NO4F3	69335-91-7	327.0718425	328.07912	
215	Cyclosulfamuron	C17H19N5O6S	136849-15-5	421.1056041	422.11288	424.1087
216	Fenhexamid	C14H17NO2Cl2	126833-17-8	301.0636342	302.07091	304.068
217	Asulam	C8H10N2O4S	3337-71-1	230.0361	248.06995	250.0657

218	Bensulide	C14H24NO4PS3	741-58-2	397.0605	398.06778	400.0636
219	Fenthion oxon sulfone	C10H15O6PS	14086-35-2	294.0327	312.06652	314.0623
220	Fenthion oxon sulfoxide	C10H15O5PS	6552-13-2	278.0378	279.04506	281.0409
221	Fenthion sulfone	C10H15O5PS2	3761-42-0	310.0099	328.04368	330.0395
222	Fenthion sulfoxide	C10H15O4PS2	3761-41-9	294.0149	295.02221	297.018
223	Fipronil	C12H4Cl2F6N4OS	120068-37-3	435.9387	453.97253	455.9696
224	Siduron	C14H20N2O	1982-49-6	232.1576	233.16484	
225	Tricyclazole	C9H7N3S	41814-78-2	189.0361	190.04334	192.0391
226	Iprodione	C13H13Cl2N3O3	36734-19-7	329.0334	330.04067	332.0377
227	2,3,5-Trimethacarb	C11H15NO2	12407-86-2	193.1102787	194.11756	
228	Benfuracarb	C20H30N2O5S	82560-54-1	410.1875428	411.19482	413.1906
229	Butocarboxim	C7H14N2O2S	34681-10-2	190.0775984	208.11142	210.1072
230	Butocarboxim sulfoxide	C7H14N2O3S	34681-24-8	206.0725131	207.07979	209.0756
231	Carbosulfan	C20H32N2O3S	55285-14-8	380.2133636	381.22064	383.2164
232	Dioxacarb	C11H13NO4	6988-21-2	223.0844579	224.09173	
233	Ethiofencarb	C11H15NO2S	29973-13-5	225.0823495	226.08963	228.0854
234	Isoprocarb	C11H15NO2	2631-40-5	193.1102787	194.11756	
235	Metolcarb	C9H11NO2	1129-41-5	165.0789786	166.08626	
236	Promecarb	C12H17NO2	2631-37-0	207.1259288	208.13321	
237	Propoxur	C11H15NO3	114-26-1	209.1051934	210.11247	
238	Terbucarb	C17H27NO2	1918-11-2	277.2041791	295.23804	
239	Thiofanox-sulfone	C9H18N2O4S	39184-59-3	250.0987278	268.13255	270.1283
240	Thiofanox-sulfoxide	C9H18N2O3S	39184-27-5	234.1038132	252.13764	254.1334
241	XMC	C10H13NO2	2655-14-3	179.0946287	180.10191	
242	Xylylcarb	C10H13NO2	2425-10-7	179.0946287	180.10191	
243	Acephate	C4H10NO3PS	30560-19-1	183.0119004	184.01918	186.015
244	Benzobicyclon metabolite	C16H15ClO5S		354.0329	372.0667	374.0637
245	Carbendazim	C9H9N3O2	10605-21-7	191.0694766	192.07675	
246	Cyazofamid	C13H13ClN4O2S	120116-88-3	324.0447741	325.05205	327.0491
247	Cycloprothrin	C26H21Cl2NO4	63935-38-6	481.0847636	499.11859	501.1156
248	Mepanipyrim metabolite	C14H17N3O		243.1371622	244.14444	
249	Nitenpyram	C11H15ClN4O2	120738-89-8	270.0883535	271.09563	273.0927
250	Phoxim	C12H15N2O3PS	14816-18-3	298.0540996	299.06138	301.0572
251	Prochloraz	C15H16Cl3N3O2	67747-09-5	375.0308099	376.03809	378.0351
252	Tepraloxydim	C17H24ClNO4	149979-41-9	341.139386	342.14666	344.1437
253	Triflumizole	C15H15ClF3N3O	68694-11-1	345.0855744	346.09285	348.0899
254	Triflumizole metabolite	C12H14ClF3N2O		294.0746754	295.08195	297.079

255	Methamidophos	C2H8NO2PS	10265-92-6	141.0013	142.00861	144.0044
256	Propamocarb	C9H20N2O2	24579-73-5	188.1525	189.15975	
257	Pymetrozin	C10H11N5O	123312-89-0	217.0964	218.10364	
258	Thiabendazole metabolite	C10H7N3OS	948-71-0	217.031	218.03826	220.0341
259	Vamidothion	C8H18NO4PS2	2275-23-2	287.0415	288.04876	290.0446
260	Acetamiprid	C10H11ClN4	135410-20-7	222.0672	223.0745	225.0716
261	Tribenuron methyl	C15H17N5O6S	101200-48-0	395.09	396.09723	398.093
262	Isouron	C10H17N3O2	55861-78-4	211.1321	212.13935	
263	Sethoxydim	C17H29NO3S	74051-80-2	327.1868	328.19409	330.1899
264	Benzobicyclon	C22H19ClO4S2	156963-66-5	446.0413	447.0486	449.0457
265	Ethoxyquin	C14H19NO	91-53-2	217.1467	218.15394	
266	Fentrazamide	C16H20ClN5O2	158237-07-1	349.1306	350.13783	352.1349
267	Imibenconazole	C17H13Cl3N4S	86598-92-7	409.9927	410.99993	412.997
268	Chlorfluazuron	C20H9Cl3F5N3O3	71422-67-8	538.963	539.97024	541.9673
269	Acetazolamide	C4H6N4O3S2	59-66-5	221.9881315	222.99541	224.9912
270	Betaxolol	C18H29NO3	63659-18-7	307.2147438	308.22202	
271	Bisoprolol	C18H31NO4	66722-44-9	325.2253085	326.23258	
272	Candesartan	C24H20N6O3	139481-59-7	440.1596885	441.16697	
273	Diazepam	C16H13N2OCl	439-14-5	284.0716408	285.07892	287.076
274	Imipramine	C19H24N2	50-49-8	280.1939488	281.20123	
275	Naproxen	C14H14O3	22204-53-1	230.0942943	248.12812	
276	Norgestimate	C23H31NO3	35189-28-7	369.2303939	370.23767	
277	Penicillin G	C16H18N2O4S	61-33-6	334.0987	335.106	337.1018
278	Phenytoin	C15H12N2O2	57-41-0	252.0899	253.09715	
279	Primidone	C12H14N2O2	125-33-7	218.2554	219.1128	
280	Virginiamycin M1	C28H35N3O7	21411-53-0	525.2475005	526.25478	
281	Metribuzin	C8H14N4OS	21087-64-9	214.08883	215.09611	217.0919
282	Metominostrobin（E)	C16H16N2O3	133408-50-1	284.11609	285.12337	
283	Cyanazine	C9H13ClN6	21725-46-2	240.08902	241.0963	243.0933
284	Tiadinil	C11H10ClN3OS	223580-51-6	267.02331	268.03059	270.0276
285	Tebuconazole	C16H22ClN3O	107534-96-3	307.14514	308.15242	310.1495
286	Bromacil	C9H13BrN2O2	314-40-9	260.01604	261.02332	263.0213
287	Prometryn	C10H19N5S	7287-19-6	241.13612	242.14339	244.1392
288	Fenvalerate	C25H22ClNO3	51630-58-1	419.12882	437.16265	439.1597
289	Pirimiphos-methyl	C11H20N3O3PS	29232-93-7	305.0963	306.10358	308.0994
290	Inabenfide	C19H15ClN2O2	82211-24-3	338.08221	339.08948	341.0865
291	Imazosulfuron	C14H13ClN6O5S	122548-33-8	412.03567	413.04294	415.04

292	Etobenzanid	C16H15Cl2NO3	79540-50-4	339.0429	340.05018	342.0472
293	Ametryn	C9H17N5S	834-12-8	227.12047	228.12774	230.1235
294	Pyriminobac-methyl（Z)	C17H19N3O6	147411-70-9	361.12739	362.13466	
295	Thifluzamide	C13H6Br2F6N2O2S	130000-40-7	525.84209	526.84937	528.8473
296	Trinexapac-ethyl	C13H16O5	95266-40-3	252.09977	253.10705	
297	Propanil	C9H9Cl2NO	709-98-8	217.00612	218.0134	220.0104
298	Spinosyn A	C41H65NO10	131929-60-7	731.46085	732.46812	
299	Spinosyn D	C42H67NO10	131929-63-0	745.4765	746.48377	
300	Difenoconazole	C19H17Cl2N3O3	119446-68-3	405.0647	406.07197	408.069
301	Tetraconazole	C13H11Cl2F4N3O	112281-77-3	371.02153	372.02881	374.0259
302	Oxadiargyl	C15H14Cl2N2O3	39807-15-3	340.03815	358.07197	360.069
303	Dinotefuran	C7H14N4O3	165252-70-0	202.10659	203.11387	
Internal standards	Methomyl-d3	C7H7D3N2			166.0724	
	Imazalil-d5	C11H12D6N4O2			245.1819	
	Pirimicarb-d6	C14H9D5N2OCl2			302.087	

Table S4 Monitoring results in surface waters from Tianjin (ng/L)

No.	Compounds	Group	J1	J2	J3	J4	J5	J6	H1	H2	H3	H4
1	Cholesterol	Cholesterol	1392	4950	1141	3271	2217	1325	3317	1819	6378	2279
2	beta-Sitosterol	Phytosetrol	764	2381	1091	1933	1033	1204	665	988	3270	1346
3	Stigmasterol		683	984	955	334	1189	ND	ND	499	1002	242
4	Campesterol		ND	627	236	518	301	ND	ND	217	896	304
5	Ergosterol		4370	1872	1367	1952	2649	1192	345	312	259	1895
6	Fucosterol		466	1740	1054	3279	1159	ND	ND	605	1187	ND
7	Stigmastanol		ND	115	ND	ND	61	ND	ND	ND	189	ND
8	Coprostanol	Zoosterol	433	4143	33	302	610	ND	562	846	4450	1509
9	Epicoprostanol		ND	1336	ND	90	203	ND	120	152	1027	384
10	24-Ethyl coprostanol		ND	676	ND	ND	ND	ND	ND	ND	1137	ND
11	Cholestanol		ND	702	210	537	420	492	1373	457	1216	513
12	Coprostanone		77	583	20	71	119	15	105	134	799	302
	Coprostanol/Cholesterol		0.31	0.84	0.03	0.09	0.28	ND	0.17	0.47	0.70	0.66
	$5\beta/(5\beta+5\alpha)$		1.00	0.86	0.13	0.36	0.59	ND	0.29	0.65	0.79	0.75
	Epicoprostanol/Coprostanol		ND	0.32	ND	0.30	0.33	ND	0.21	0.18	0.23	0.25
13	1,2-Dimethylnaphthalene		ND	ND	ND	ND	ND	ND	ND	62	ND	ND
14	1,3-Dimethylnaphthalene		ND	ND	74	ND	220	1611	ND	234	ND	66
15	1,4-&2,3-Dimethylnaphthalene		ND	ND	ND	ND	ND	463	ND	126	ND	ND

16	2,6-Diisopropylnaphthalene	2-Ring PAHs	ND	ND	ND	ND	ND	ND	ND	ND	28	ND
17	2,6-Dimethylnaphthalene		ND	ND	ND	ND	140	706	ND	189	1.6	ND
18	2-Methylnaphthalene		ND	ND	ND	ND	212	1631	ND	359	ND	ND
19	Diphenylmethane		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	Naphthalene		ND	ND	ND	ND	352	5067	ND	740	36	ND
21	1-Methylnaphthalene		ND	ND	ND	ND	97	815	ND	169	ND	ND
22	2-Methylphenanthrene	3-Ring PAHs	ND	ND	16	22	21	54	ND	19	14	28
23	2-Phenylnaphthalene		ND	ND	ND	ND	28	ND	ND	26	ND	37
24	4,5-Methylene-phenanthrene		ND	ND	ND	ND	ND	105	ND	47	29	63
25	Acenaphthene		ND	ND	ND	15	27	81	ND	30	ND	14
26	Acenaphthylene		ND	ND	17	ND	31	ND	ND	74	13	39
27	Anthracene		ND	ND	25	45	41	55	16	31	19	48
28	Fluorene		14	ND	63	77	96	288	16	91	20	84
29	Phenanthrene		35	ND	221	290	275	672	120	231	115	322
30	3-Methylphenanthrene		ND	ND	14	18	17	48	ND	ND	13	22
31	9-Methylphenanthrene		ND	ND	ND	ND	ND	26	ND	ND	ND	12
32	2,3-Benzofluorene	4-Ring PAHs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
33	Benzo(a)anthracene		ND	ND	ND	ND	ND	ND	ND	ND	ND	19
34	Benzo(c)phenanthrene		ND	ND	ND	ND	ND	21	ND	ND	ND	ND
35	Chrysene & Triphenylene		ND	ND	ND	ND	ND	77	ND	ND	ND	21
36	Fluoranthene		27	ND	41	60	49	235	17	54	59	93
37	Pyrene		16	ND	20	29	22	136	15	29	28	52
38	Benzo(a)pyrene	5-Ring PAHs	ND	ND	ND	ND	ND	79	ND	11	ND	25
39	Benzo(e)pyrene		ND	ND	ND	ND	ND	328	ND	35	ND	ND
40	Benzo(j&b)fluoranthene		ND	ND	ND	ND	ND	227	ND	ND	ND	60
41	Benzo(ghi)perylene	6-Ring PAHs	ND	ND	ND	ND	ND	65	ND	ND	ND	17
42	Indeno(1,2,3-cd)pyrene		ND	ND	ND	ND	ND	68	ND	ND	ND	18
	2-3 rings PAHs/Total PAHs		53	ND	88	84	96	90	83	95	77	71
	Anthracene/(Anthracene+Phenathrene)		ND	ND	ND	0.13	0.13	0.08	0.12	0.12	0.14	0.13
	Flurene/(Flurene+Pyrene)		0.62	ND	0.67	0.67	0.69	0.63	0.54	0.65	0.68	0.64
43	4-tert-Octylphenol	PPCPs	ND	ND	ND	44	43	ND	ND	ND	ND	ND
44	Caffeine		411	133	25	281	494	ND	454	264	1434	256
45	Diethyltoluamide		63	25	80	71	65	ND	ND	ND	51	ND
46	Ibuprofen		ND	ND	ND	ND	203	ND	ND	ND	343	ND
47	L-Menthol		194	ND	ND	ND	28	ND	42	18	118	ND
48	Nicotine		ND	ND	ND	ND	ND	ND	ND	ND	ND	221

57	Cotinine		261	598	104	112	159	42	ND	196	477	240
49	Thymol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
50	Quinoxaline-2-carboxylic acid		ND	133	159	375	142	ND	252	43	642	39
51	Acetaminophen		123	41	ND	ND	ND	ND	ND	77	119	143
52	Antipyrine		80	132	176	77	92	13	210	36	46	16
53	Atenolol		ND	15	ND	ND	ND	ND	ND	ND	ND	ND
54	Bezafibrate		ND	ND	ND	ND	ND	ND	ND	42	ND	ND
55	Cimetidine		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
56	Clarithromycin		11	18	ND	ND	15	ND	33	11	24	6.2
58	Lidocaine		15	106	87	218	107	7.5	105	82	107	143
59	Lincomycin		ND	ND	ND	247	ND	ND	ND	ND	ND	ND
60	Losartan		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
61	Metformin		1867	ND	450	2281	796	51	2365	176	2917	260
62	Oleandomycin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
63	Phenacetin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
64	Roxithromycin		24	59	ND	ND	52	ND	76	12	33	15
65	Salinomycin		ND	ND	ND	ND	438	ND	ND	ND	ND	ND
66	Sulfamethoxazole		ND	52	ND	48	87	ND	38	ND	60	ND
67	Acetochlor		ND	ND	ND	ND	ND	ND	ND	ND	166	ND
68	Atrazine		188	102	ND	ND	ND	ND	366	77	1829	ND
69	Clomazone		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	Prometryn		426	ND	425	370	236	ND	340	ND	56	ND
71	Simetryn		ND	37	79	100	ND	ND	ND	ND	ND	ND
72	1,4-Dichlorobenzene		145	ND	ND	ND	10	139	15	ND	43	ND
73	3-Hydroxycarbofuran		ND	1386	ND	ND	ND	ND	ND	ND	ND	932
74	Acetamiprid		ND	ND	ND	ND	ND	ND	ND	ND	1639	ND
75	Bendiocarb		ND	ND	ND	ND	ND	117	ND	ND	ND	ND
76	Bis(2-chloroisopropyl)ether	Pestcide	ND	ND	ND	ND	ND	737	ND	36	ND	ND
77	Dinoseb		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
78	Fenobucarb		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
79	2,5-Dichlorophenol		1382	ND	ND	ND	ND	ND	ND	ND	ND	ND
80	Hexachlorobenzene		1.0	39.4	2.6	2.6	3.3	16.2	0.89	2.9	0.37	3.2
81	a-HCH		3.0	2.5	ND	3.7	1.6	0.7	9.3	0.56	1.4	ND
82	b-HCH		1.1	10.2	0.72	ND	2.0	0.5	7.5	0.58	0.91	0.6
83	d-HCH		5.8	0.46	0.44	ND	ND	ND	2.7	0.76	0.43	ND
84	g-HCH		0.77	ND	ND	0.5	0.4	0.5	1.2	ND	0.68	ND
90	*p,p'*-DDT		0.82	ND	ND	0.79	ND	ND	ND	ND	ND	0.19

89	*p,p'*-DDE		0.82	0.72	0.16	1.7	0.15	0.12	0.15	2.3	1.7	2.2
88	*p,p'*-DDD		1.5	5.4	0.22	0.9	0.36	0.39	2.0	1.0	0.74	1.0
87	*o,p'*-DDT		1.8	ND	0.4	ND	0.58	0.77	2.7	1.3	1.2	ND
86	*o,p'*-DDE		0.5	0.38	ND	1.1	ND	ND	ND	2.2	1.5	2.0
85	*o,p'*-DDD		0.4	1.9	ND	0.8	ND	ND	1.6	1.4	1.8	1.5
91	Alachlor		ND	ND	ND	ND	ND	ND	ND	ND	160	ND
92	Aldicarb sulfone		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
93	Benzofenap		ND	ND	ND	ND	ND	ND	ND	ND	25	ND
94	Butafenacil		ND	ND	ND	ND	ND	ND	ND	ND	13	ND
95	Carbaryl		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
96	Carbofuran		ND	ND	ND	ND	ND	ND	ND	ND	111	ND
97	Chloroxuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
98	Clomeprop		ND	45	ND	40	ND	ND	ND	ND	76	ND
99	Cumyluron	Pestcide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
100	Cyanazine		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
101	Dimethoate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
102	Diuron		ND	ND	4.8	ND	ND	ND	49	ND	ND	5.2
103	Dymron		ND	5.4	ND	ND	ND	ND	ND	ND	19	ND
104	Fenoxaprop-ethyl		ND	ND	ND	ND	ND	ND	ND	ND	26	ND
105	Fenpyroximate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
106	Fenthion Oxon Sulfone		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
107	Fenthion Oxon Sulfoxide		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
108	Fenthion Sulfone		11	ND	ND	28	ND	6.3	ND	ND	54	18
109	Fenthion Sulfoxide		34	ND	ND	64	ND	ND	ND	ND	ND	ND
110	Flufenacet		ND	8.4	ND	12	ND	ND	ND	ND	25	12
111	Fomesafen		ND	ND	ND	ND	ND	ND	ND	ND	595	ND
112	Furathiocarb		ND	ND	ND	ND	ND	ND	ND	ND	25	ND
113	Linuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
114	Mefenacet		116	ND	ND	14	ND	ND	ND	ND	ND	ND
115	Methabenzthiazuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
116	Naproanilide		ND	ND	22	ND	ND	ND	ND	ND	25	ND
117	Naptalam		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
118	Oxaziclomefone		ND	ND	ND	ND	ND	ND	ND	ND	30	ND
119	Pirimicarb		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
120	Propoxur		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
121	Quizalofop-ethyl		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
122	Siduron		70	124	137	428	246	51	191	205	212	294

123	Simazine		ND	ND	11	ND	ND	ND	ND	ND	ND	ND
124	Tebufenpyrad		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
125	Tebuthiuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
126	Tetrachlorvinphos		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
127	Isoprothiolane	Pestcide	ND	36	ND	ND	ND	ND	ND	ND	ND	ND
128	Myclobutanil		ND	ND	ND	ND	ND	ND	ND	ND	2252	ND
129	Pyrimethanil		ND	ND	ND	ND	ND	ND	ND	ND	412	ND
130	Tebuconazole		ND	ND	ND	ND	ND	ND	ND	ND	961	ND
131	Triadimenol 2		ND	123	ND	ND	ND	ND	ND	ND	ND	ND
132	Tricyclazole		ND	515	ND	ND	ND	ND	ND	ND	ND	ND
133	4-Chloro-3-methylphenol		ND	ND	ND	470	ND	ND	ND	ND	ND	ND
134	Azoxystrobin		ND	ND	4.6	ND	ND	ND	ND	ND	32	ND
135	Boscalid		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
136	Carbendazim		ND	20	26	71	22	ND	39	7.9	99	7.5
137	Cyprodinil		ND	ND	ND	23	ND	ND	ND	ND	ND	ND
138	Dimethomorph(E)		ND	ND	32	ND	ND	ND	ND	ND	ND	ND
139	Dimethomorph(Z)		ND	ND	15	ND	ND	ND	ND	ND	42	ND
140	Epoxiconazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	8
141	Ethoxyquin		ND	ND	ND	ND	ND	83	ND	ND	ND	ND
142	Fenarimol		ND	ND	ND	ND	ND	ND	ND	ND	1224	ND
143	Ferimzone(E)	Pesticide	ND	ND	ND	ND	ND	ND	ND	ND	24	ND
144	Ferimzone(Z)		ND	ND	ND	7.1	ND	ND	ND	ND	14	ND
145	Mepanipyrim		ND	ND	ND	17	ND	ND	ND	ND	ND	ND
146	Thiabendazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
147	Triticonazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
148	2-Methylbenzothiazole		766	ND	ND	ND	2013	ND	ND	ND	ND	ND
149	2(3H)-Benzothiazolone	Vulcanisation	41083	ND	ND	2247	5834	ND	ND	ND	ND	ND
150	2-(Methylthio)-benzothiazol	accelerator	13005	ND	79	420	1158	ND	279	26	155	47
151	Benzothiazole		6019	ND	ND	ND	665	42	ND	ND	ND	ND
152	2,6-Di-tert-butyl-4-benzoquinone		25	ND	ND	ND	ND	ND	118	ND	ND	ND
153	4-Methyl-2,6-di-t-butylphenol	Antioxidant	ND	ND	ND	ND	ND	35	ND	30	ND	ND
154	3,5-di-tert-Butyl-4-hydroxybenzaldehyde		ND	ND	ND	ND	ND	ND	53	ND	ND	ND
155	*cis*-11,14,17-Eicosatrienoic acid methyl ester		ND	ND	161	ND	740	ND	ND	105	ND	68
156	Elaidic acid methyl ester	Fatty acid	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
157	Methyl palmitate	methy ester	ND	ND	ND	ND	ND	80	ND	ND	19	ND
158	Stearic acid methyl ester		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
159	Tributyl phosphate	Fire retardant	ND	215	236	306	201	256	481	135	ND	181

160	Tris(1,3-dichloro-2-propyl) phosphate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
161	Tris(2-chloroethyl) phosphate		466	163	511	544	458	ND	318	ND	195	ND
162	Tris(2-ethylhexyl) phosphate		ND	ND	ND	ND	ND	ND	ND	77	ND	ND
163	Triphenyl phosphate		37	50	ND	712	134	44	82	18	59	87
164	Bis(2-ethylhexyl) sebacate	Plasticizer	43	ND	ND	ND	ND	ND	ND	ND	ND	ND
165	Bis(2-ethylhexyl) phthalate		192	250	461	764	214	916	525	128	409	238
166	Butyl benzyl phtalate		ND	ND	ND	ND	ND	20	ND	17	11	10
167	Di(2-ethylhexyl)adipate		143	2.4	ND	23	18	17	166	36	ND	15
168	Diethyl phthalate	Plasticizer	ND	20	ND	230	102	23	911	86	214	86
169	Dimethyl phthalate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	Di-n-butyl phthalate		ND	ND	430	373	448	1117	37	290	56	357
171	Di-iso-butyl phthalate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
172	4-nonylphenol	Surfactants	ND	ND	ND	1110	550	ND	619	ND	2514	ND
173	Octanol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
174	Benzyl alcohol		ND	ND	ND	ND	ND	ND	ND	ND	147	ND
175	Butanoic acid, butyl ester	Fragrance	ND	ND	ND	ND	ND	1310	ND	ND	ND	ND
176	Phenylethyl alcohol		ND	ND	ND	ND	ND	ND	ND	ND	4.1	ND
177	Anthraquinone		51	ND	67	97	74	212	48	39	71	88
178	alpha-Terpineol		ND	ND	ND	ND	ND	ND	ND	ND	178	ND
179	3-&4-Methylphenol	Disinfectant	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
180	Phenol		27	ND	ND	0.8	1.6	ND	ND	ND	7.0	ND
181	1,3-Dicyclohexylurea		3449	ND	ND	ND	419	ND	ND	ND	ND	ND
182	2-Cyclohexen-1-one		207	ND	ND	ND	ND	ND	ND	ND	ND	ND
183	Acetamide, N-phenyl-		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
184	Cyclohexanol	Leaching from tire	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
185	Formamide, N-cyclohexyl-		1232	ND	ND	ND	ND	ND	ND	ND	ND	ND
186	Phthalimide		ND	ND	ND	756	ND	ND	ND	ND	ND	ND
187	Ethanol, 2-phenoxy-		ND	ND	ND	ND	ND	ND	73	ND	ND	ND
188	3- & 4-tert-Butylphenol		ND	ND	ND	530	85	ND	ND	ND	12	ND
189	Dicyclopentadiene	Intermediate for resin	ND	ND	ND	ND	38	984	ND	ND	ND	ND
190	Bisphenol A		ND	ND	ND	149	ND	ND	ND	ND	150	10
191	1,2,4-Trichlorobenzene		ND	ND	ND	ND	ND	34	ND	ND	ND	ND
192	Longifolene		407	ND	ND	ND	ND	ND	428	ND	ND	ND
193	Pentamethylbenzene		ND	ND	ND	ND	ND	261	ND	ND	47	ND
194	Phenazine	Industry	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	2,4,6-Trichlorophenol		ND	ND	ND	133	ND	ND	ND	ND	ND	ND
196	Biphenyl		ND	ND	5.2	20	51	555	ND	75	ND	5.5

197	Dibenzofuran		17	ND	71	84	132	659	6.9	136	19	89
198	Isophorone		139	ND	ND	ND	89	ND	ND	74	67	ND
199	2,4-Dichloroaniline		112	ND	ND	ND	ND	ND	ND	ND	ND	ND
200	1,2-Dichlorobenzene		ND	ND	ND	ND	ND	128	ND	ND	ND	ND
201	1,3-Dichloro-2-propanol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
202	4-Cymene		ND	ND	ND	ND	39	ND	ND	44	26	ND
203	*trans*-Decahydronaphthalene		ND	ND	ND	ND	ND	707	ND	ND	ND	ND
204	Trimethyl phosphate		ND	ND	ND	ND	3927	ND	ND	ND	ND	ND
205	PCB#33		ND	ND	ND	ND	ND	ND	0.11	ND	ND	ND
206	Benzanthrone		ND	ND	ND	ND	ND	104	ND	ND	ND	31
207	2-Anisidine		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	2-Chloroaniline		ND	ND	ND	ND	30	ND	ND	ND	ND	ND
209	2-Methylaniline	Intermediate for dyes	ND	ND	ND	82	ND	ND	ND	ND	ND	ND
210	N,N-Dimethylaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
211	N-Ethylaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
212	Diphenylamine		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
213	2,5-Dimethylaniline		ND	ND	ND	43	ND	ND	ND	ND	ND	ND
214	e-Caprolactam		ND	100	ND	ND	ND	ND	ND	100	ND	128
215	2,4-Dimethylphenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
216	2-Naphthol		66	ND	ND	ND	ND	ND	25	ND	ND	ND
217	3,5-Dimethylphenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	161
218	4-Chloronitrobenzene		ND	ND	ND	ND	ND	322	ND	458	ND	32
219	4-Nitroaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
220	Carbazole		ND	ND	ND	ND	ND	34	ND	28	ND	ND
221	N-Methylaniline		ND	ND	ND	65	ND	ND	ND	ND	ND	93
222	Phenothiazine		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
223	Quinoline	Intermediate in organic synthesis	ND	ND	12	ND	330	395	ND	94	39	10
224	2-Nitrophenol		ND	ND	ND	ND	ND	815	ND	45	ND	ND
225	2-Ethyl-1-hexanol		1098	ND	ND	ND	ND	1154	487	ND	ND	ND
226	Aniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
227	Acetophenone		60	ND	ND	ND	23	1426	2.2	ND	ND	ND
	Total concentration		82359	24685	10474	26943	32606	30003	15935	11922	43153	14179
	Sum of sterols		8186	20109	6107	12288	9960	4228	6487	6030	21810	8775
	Sum of PAHs		93	ND	491	556	1629	12858	185	2556	374	1042
	Sum of PPCPs		3049	1312	1081	3753	2719	113	3574	957	6369	1339
	Sum of pesticides		2387	2463	761	1656	522	1151	1028	340	10200	1287
	Sum of domestic chemicals		66747	701	1945	8263	13156	5091	3712	987	4201	1187

	Sum of industrial chemicals		1898	100	88	427	4621	6561	949	1053	198	550

Continued)

No.	Compounds	Group	H5	H6	H7	H8	H9	H10	H11	D1	S1	S2
1	Cholesterol	Cholesterol	2895	1966	3170	2649	5267	1937	5083	1979	5297	4564
2	beta-Sitosterol	Phytosetrol	1358	1207	1874	1018	2692	1136	1323	943	1213	2878
3	Stigmasterol		433	297	862	968	565	503	704	1551	887	262
4	Campesterol		168	213	881	354	1000	160	535	434	538	192
5	Ergosterol		1842	874	ND	544	2614	1163	3599	1981	ND	2702
6	Fucosterol		530	ND	2167	823	3978	828	1297	1053	153	469
7	Stigmastanol		43	ND	80	ND	168	ND	ND	ND	102	69
8	Coprostanol	Zoosterol	1211	447	1004	902	2799	447	126	119	5333	4927
9	Epicoprostanol		253	90	177	146	883	69	68	ND	1567	1394
10	24-Ethyl coprostanol		ND	111	ND	468	1057	ND	ND	ND	1111	975
11	Cholestanol		465	322	656	450	1079	431	428	ND	488	132
12	Coprostanone		188	72	190	149	426	92	95	25	780	1310
	Coprostanol/Cholesterol		0.42	0.23	0.32	0.34	0.53	0.23	0.02	0.06	1.0	1.08
	$5\beta/(5\beta+5\alpha)$		0.72	0.58	0.60	0.67	0.72	0.51	0.23	1.00	0.92	0.97
	Epicoprostanol/Coprostanol		0.21	0.20	0.18	0.16	0.32	0.15	0.54	ND	0.29	0.28
13	1,2-Dimethylnaphthalene	2-Ring PAHs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	1,3-Dimethylnaphthalene		258	ND	50	8.5	ND	147	167	77	ND	ND
15	1,4-&2,3-Dimethylnaphthalene		143	ND	ND	ND	ND	79	62	61	ND	ND
16	2,6-Diisopropylnaphthalene		ND	ND	ND	51	11	ND	ND	100	ND	ND
17	2,6-Dimethylnaphthalene		196	ND	41	5.2	ND	124	54	43	ND	ND
18	2-Methylnaphthalene		305	ND	53	ND	ND	177	89	77	ND	429
19	Diphenylmethane		26	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	Naphthalene		2952	ND	366	ND	ND	539	282	389	ND	ND
21	1-Methylnaphthalene		172	ND	34	ND	ND	85	44	47	6.1	375
22	2-Methylphenanthrene	3-Ring PAHs	ND	ND	ND	14	ND	19	12	12	ND	42
23	2-Phenylnaphthalene		30	ND	ND	ND	ND	ND	ND	ND	ND	ND
24	4,5-Methylene-phenanthrene		ND	ND	ND	30	ND	38	ND	29	ND	ND
25	Acenaphthene		33	ND	12	ND	ND	19	ND	18	ND	108
26	Acenaphthylene		124	ND	26	ND	ND	27	ND	27	ND	92
27	Anthracene		41	ND	12	18	ND	22	20	17	17	47
28	Fluorene		144	5.1	32	35	10	70	47	41	42	271
29	Phenanthrene		267	5.7	85	184	44	212	154	108	83	491

30	3-Methylphenanthrene		19	ND	ND	12	ND	14	11	11	11	33
31	9-Methylphenanthrene		ND	ND	ND	ND	ND	ND	ND	ND	ND	20
32	2,3-Benzofluorene		ND	ND	ND	ND	ND	ND	ND	ND	ND	112
33	Benzo(a)anthracene		ND	ND	ND	ND	ND	ND	ND	ND	ND	147
34	Benzo(c)phenanthrene	4-Ring PAHs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
35	Chrysene & Triphenylene		21	ND	ND	ND	ND	ND	ND	ND	ND	39
36	Fluoranthene		80	11	41	45	26	45	42	41	ND	18
37	Pyrene		46	ND	33	25	14	23	21	22	13	84
38	Benzo(a)pyrene	5-Ring PAHs	28	ND	ND	ND	ND	ND	ND	ND	ND	44
39	Benzo(e)pyrene		85	ND	ND	ND	ND	ND	ND	ND	ND	ND
40	Benzo(j&b)fluoranthene		44	ND	ND	ND	ND	ND	ND	ND	ND	122
41	Benzo(ghi)perylene	6-Ring PAHs	19	ND	ND	ND	ND	ND	ND	ND	ND	ND
42	Indeno(1,2,3-cd)pyrene		18	ND	ND	ND	ND	ND	ND	ND	ND	35
	2-3 rings PAHs/Total PAHs		93	49	91	84	62	96	94	94	92	76
	Anthracene/(Anthracene+Phenathrene)		0.13	ND	0.13	0.09	ND	0.09	0.11	0.13	0.17	0.09
	Flurene/(Flurene+Pyrene)		0.63	1.00	0.55	0.64	0.65	0.66	0.66	0.65	ND	0.18
43	4-tert-Octylphenol		ND	ND	ND	ND	ND	ND	ND	ND	138	ND
44	Caffeine		115	104	316	798	509	260	380	277	138	316
45	Diethyltoluamide		14	ND	15	30	87	ND	83	71	65	79
46	Ibuprofen		ND	ND	ND	ND	612	ND	ND	ND	ND	ND
47	L-Menthol		32	2.5	35	ND	218	26	ND	106	470	357
48	Nicotine		ND	ND	ND	ND	ND	ND	ND	ND	390	ND
57	Cotinine		154	96	235	315	392	122	192	113	911	480
49	Thymol		ND	ND	ND	ND	ND	ND	ND	48	ND	ND
50	Quinoxaline-2-carboxylic acid		44	33	53	88	203	27	196	274	403	250
51	Acetaminophen	PPCPs	202	51	80	18	63	77	35	ND	6402	478
52	Antipyrine		20	21	45	54	293	20	76	182	92	225
53	Atenolol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	Bezafibrate		93	ND	39	112	ND	ND	ND	ND	ND	ND
55	Cimetidine		ND	ND	ND	ND	ND	ND	ND	ND	90	ND
56	Clarithromycin		18	ND	5.6	24	72	ND	5.5	6.5	166	76
58	Lidocaine		87	66	87	121	120	39	109	87	49	216
59	Lincomycin		ND	ND	ND	ND	1791	ND	ND	ND	233	ND
60	Losartan		ND	ND	ND	ND	ND	ND	ND	ND	83	ND
61	Metformin		178	156	225	776	1611	105	807	1777	20015	ND
62	Oleandomycin		ND	ND	ND	ND	ND	ND	ND	ND	ND	71

63	Phenacetin		ND	ND	ND	ND	ND	ND	ND	ND	ND	121
64	Roxithromycin		ND	ND	10	26	257	8.2	13	35	292	220
65	Salinomycin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
66	Sulfamethoxazole		ND	ND	ND	83	ND	ND	ND	143	115	173
67	Acetochlor		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
68	Atrazine		ND	ND	ND	183	190	ND	322	242	ND	171
69	Clomazone		ND	ND	ND	22	ND	ND	ND	ND	ND	ND
70	Prometryn		26	ND	ND	65	534	ND	651	489	ND	ND
71	Simetryn		ND	ND	ND	ND	ND	ND	ND	237	ND	ND
72	1,4-Dichlorobenzene		ND	ND	11	ND	ND	ND	ND	324	65	ND
73	3-Hydroxycarbofuran		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	Acetamiprid		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
75	Bendiocarb		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
76	Bis(2-chloroisopropyl)ether	Pestcide	55	ND	ND	ND	ND	ND	ND	ND	38	3170
77	Dinoseb		ND	ND	ND	ND	ND	ND	ND	ND	ND	8394
78	Fenobucarb		ND	ND	ND	ND	68	ND	ND	ND	ND	ND
79	2,5-Dichlorophenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
80	Hexachlorobenzene		3.5	0.14	1.8	1.8	0.31	2.3	1.7	1.9	0.66	17.2
81	a-HCH		0.6	0.43	0.54	1.3	31.7	0.47	5.6	2.5	1.2	11.6
82	b-HCH		0.8	0.49	0.94	1.7	13.1	0.46	7.3	1.7	ND	2.3
83	d-HCH		0.4	ND	ND	0.82	ND	ND	3.6	ND	5.9	0.68
84	g-HCH		ND	ND	ND	ND	19.7	ND	0.6	ND	ND	1.3
90	*p,p'*-DDT		0.16	ND	0.40	0.50	0.10	ND	0.25	ND	0.16	ND
89	*p,p'*-DDE		1.4	2.0	2.0	1.3	0.24	1.5	ND	ND	0.22	0.11
88	*p,p'*-DDD		0.7	0.75	0.87	0.66	0.21	0.70	0.14	0.12	0.18	0.37
87	*o,p'*-DDT		1.1	1.0	1.2	1.0	0.14	0.76	0.41	0.34	0.34	0.14
86	*o,p'*-DDE		1.4	1.5	1.8	1.2	ND	1.2	ND	ND	ND	ND
85	*o,p'*-DDD		1.0	2.2	1.5	0.75	0.11	1.0	ND	2.1	2.0	2.6
91	Alachlor		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
92	Aldicarb sulfone		ND	ND	30	ND	ND	ND	ND	ND	ND	ND
93	Benzofenap		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
94	Butafenacil		ND	ND	8.4	ND	ND	ND	ND	ND	ND	ND
95	Carbaryl		ND	ND	18	ND	ND	ND	ND	ND	ND	ND
96	Carbofuran		ND	4.4	25	ND	ND	ND	ND	ND	8.6	ND
97	Chloroxuron		ND	8.5	11	ND	15	13	ND	ND	ND	ND
98	Clomeprop		ND	58	85	ND	ND	ND	ND	ND	125	ND
99	Cumyluron	Pestcide	ND	ND	12	ND	ND	ND	ND	ND	ND	ND

100	Cyanazine		ND	ND	ND	ND	ND	ND	ND	ND	ND	77
101	Dimethoate		ND	ND	ND	ND	ND	ND	ND	ND	225	ND
102	Diuron		4.5	ND	23	ND	14	ND	ND	4.5	23	11
103	Dymron		ND	9.0	24	ND	ND	14	ND	ND	ND	ND
104	Fenoxaprop-ethyl		ND	ND	ND	ND	ND	ND	ND	ND	36	ND
105	Fenpyroximate		ND	ND	ND	ND	ND	ND	ND	ND	56	ND
106	Fenthion Oxon Sulfone		ND	ND	6.7	ND	ND	ND	ND	ND	ND	ND
107	Fenthion Oxon Sulfoxide		ND	ND	ND	ND	ND	ND	ND	ND	5.0	ND
108	Fenthion Sulfone		ND	27	32	ND	73	31	ND	ND	36	ND
109	Fenthion Sulfoxide		ND	65	ND	ND	188	ND	ND	ND	ND	ND
110	Flufenacet		ND	16	32	ND	51	12	ND	ND	20	ND
111	Fomesafen		ND	ND	ND	228	ND	ND	ND	ND	ND	ND
112	Furathiocarb		ND	ND	ND	ND	ND	ND	ND	ND	23	ND
113	Linuron		ND	ND	ND	ND	ND	ND	ND	ND	125	ND
114	Mefenacet		ND	ND	ND	ND	ND	ND	ND	ND	966	23
115	Methabenzthiazuron		ND	5.7	25	ND	12	4.2	ND	ND	8.8	ND
116	Naproanilide		ND	27	28	ND	ND	ND	ND	43	31	ND
117	Naptalam		ND	ND	ND	ND	ND	ND	ND	ND	ND	270
118	Oxaziclomefone		ND	ND	23	ND	ND	ND	ND	ND	22	ND
119	Pirimicarb		ND	ND	16	ND	ND	ND	ND	ND	ND	ND
120	Propoxur		ND	ND	ND	ND	ND	ND	ND	ND	22	ND
121	Quizalofop-ethyl		ND	ND	22	ND	ND	ND	ND	ND	ND	ND
122	Siduron		253	145	140	129	353	278	176	137	215	384
123	Simazine		ND	ND	17	ND	ND	ND	ND	ND	ND	ND
124	Tebufenpyrad		ND	ND	ND	ND	ND	ND	ND	ND	ND	4.8
125	Tebuthiuron		ND	4.1	17	ND	7.1	ND	ND	ND	ND	ND
126	Tetrachlorvinphos		ND	15	18	ND	43	ND	ND	ND	ND	ND
127	Isoprothiolane	Pestcide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
128	Myclobutanil		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
129	Pyrimethanil		ND	ND	ND	ND	ND	ND	ND	14	ND	ND
130	Tebuconazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
131	Triadimenol 2		ND	ND	ND	ND	370	ND	ND	ND	ND	ND
132	Tricyclazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
133	4-Chloro-3-methylphenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
134	Azoxystrobin		ND	6.0	12	ND	15	ND	ND	15	9.1	ND
135	Boscalid		ND	ND	30	ND	ND	ND	ND	ND	ND	ND
136	Carbendazim		9.0	5.9	10	16	36	5.1	34	39	65	38

137	Cyprodinil		ND	22.5	28	ND	45	ND	ND	ND	36	ND
138	Dimethomorph(E)		ND	ND	ND	45	254	ND	51	68	136	40
139	Dimethomorph(Z)		ND	ND	ND	20	112	ND	23	31	62	18
140	Epoxiconazole		ND	23	32	ND	37	11	ND	ND	ND	ND
141	Ethoxyquin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
142	Fenarimol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
143	Ferimzone(E)	Pesticide	ND	ND	28	ND	ND	ND	ND	ND	ND	ND
144	Ferimzone(Z)		ND	ND	16	ND	ND	ND	ND	ND	ND	ND
145	Mepanipyrim		ND	16	28	ND	54	27	ND	ND	18	ND
146	Thiabendazole		ND	ND	27	ND	10	ND	ND	ND	ND	ND
147	Triticonazole		ND	8.0	26	ND	ND	ND	ND	ND	ND	ND
148	2-Methylbenzothiazole		ND	ND	ND	ND	ND	ND	ND	ND	7904	ND
149	2(3H)-Benzothiazolone	Vulcanisation	ND	ND	ND	ND	ND	ND	ND	ND	18185	ND
150	2-(Methylthio)-benzothiazol	accelerator	63	ND	30	38	230	30	145	150	31765	1753
151	Benzothiazole		ND	ND	ND	ND	ND	ND	ND	ND	30867	ND
152	2,6-Di-tert-butyl-4-benzoquinone		ND	ND	ND	ND	ND	ND	ND	111	ND	55
153	4-Methyl-2,6-di-t-butylphenol	Antioxidant	36	ND	ND	ND	ND	ND	ND	25	163	82
154	3,5-di-tert-Butyl-4-hydroxybenzaldehyde		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
155	*cis*-11,14,17-Eicosatrienoic acid methyl ester		115	ND	ND	ND	57	72	81	343	ND	ND
156	Elaidic acid methyl ester	Fatty acid	ND	ND	ND	ND	ND	ND	ND	ND	ND	25
157	Methyl palmitate	methy ester	ND	ND	ND	ND	ND	ND	ND	ND	ND	38
158	Stearic acid methyl ester		ND	ND	ND	ND	ND	ND	ND	ND	ND	28
159	Tributyl phosphate		154	232	ND	ND	ND	ND	344	524	358	2610
160	Tris(1,3-dichloro-2-propyl) phosphate		ND	ND	ND	ND	143	ND	ND	ND	ND	ND
161	Tris(2-chloroethyl) phosphate	Fire retardant	ND	ND	ND	157	377	ND	333	461	440	46
162	Tris(2-ethylhexyl) phosphate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
163	Triphenyl phosphate		76	44	15	68	186	45	16	19	34	28
164	Bis(2-ethylhexyl) sebacate	Plasticizer	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
165	Bis(2-ethylhexyl) phthalate		265	85	127	282	389	248	253	87	395	5454
166	Butyl benzyl phtalate		11	17	ND	ND	ND	ND	ND	ND	ND	ND
167	Di(2-ethylhexyl)adipate		17	52	ND	597	ND	38	5.2	ND	ND	209
168	Diethyl phthalate	Plasticizer	304	112	191	291	379	206	165	509	180	995
169	Dimethyl phthalate		ND	ND	ND	ND	5785	ND	ND	ND	ND	125
170	Di-n-butyl phthalate		206	ND	ND	288	ND	280	417	ND	ND	1143
171	Di-iso-butyl phthalate		ND	ND	ND	ND	8804	ND	ND	ND	ND	ND
172	4-nonylphenol	Surfactants	214	ND	243	66	601	366	419	922	1045	2622
173	Octanol	Fragrance	ND	ND	ND	ND	ND	ND	ND	155	ND	ND

174	Benzyl alcohol		ND	ND	4396	ND	ND	ND	ND	5321	60	15537
175	Butanoic acid, butyl ester		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
176	Phenylethyl alcohol		ND	ND	41	1.4	ND	ND	ND	166	35	53
177	Anthraquinone		46	ND	38	54	52	53	60	65	ND	293
178	alpha-Terpineol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
179	3-&4-Methylphenol	Disinfectant	ND	ND	ND	ND	ND	ND	ND	ND	ND	491
180	Phenol		ND	ND	35	ND	ND	ND	ND	110	ND	928
181	1,3-Dicyclohexylurea		ND	ND	ND	ND	ND	ND	ND	ND	12699	ND
182	2-Cyclohexen-1-one		ND	ND	ND	ND	ND	ND	ND	ND	4722	ND
183	Acetamide, N-phenyl-		ND	ND	ND	ND	ND	ND	ND	ND	258	ND
184	Cyclohexanol	Leaching from tire	ND	ND	ND	ND	ND	ND	ND	ND	9496	ND
185	Formamide, N-cyclohexyl-		ND	ND	ND	ND	ND	ND	ND	ND	22564	2771
186	Phthalimide		ND	ND	ND	ND	ND	ND	ND	ND	19	3467
187	Ethanol, 2-phenoxy-		ND	ND	16	ND	ND	ND	ND	47	ND	ND
188	3- & 4-tert-Butylphenol		14	ND	ND	ND	17	ND	ND	ND	120	ND
189	Dicyclopentadiene	Intermediate for resin	345	ND	40	ND	ND	ND	ND	41	ND	ND
190	Bisphenol A		36	ND	ND	ND	ND	ND	6.2	ND	151	ND
191	1,2,4-Trichlorobenzene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
192	Longifolene		ND	522	126	ND	138	ND	ND	240	ND	109
193	Pentamethylbenzene		ND	ND	ND	ND	ND	ND	ND	56	26	136
194	Phenazine		ND	ND	ND	ND	ND	ND	ND	ND	ND	260
195	2,4,6-Trichlorophenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	144
196	Biphenyl		104	1.4	22	4.7	ND	37	28	27	19	742
197	Dibenzofuran		177	3.1	43	44	4.7	100	61	55	ND	ND
198	Isophorone	Industry	113	37	90	ND	ND	53	37	45	118	ND
199	2,4-Dichloroaniline		ND	ND	ND	ND	ND	ND	ND	ND	670	128
200	1,2-Dichlorobenzene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
201	1,3-Dichloro-2-propanol		ND	ND	ND	ND	ND	ND	ND	ND	ND	577
202	4-Cymene		ND	ND	38	ND	1.0	ND	22	174	ND	ND
203	*trans*-Decahydronaphthalene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
204	Trimethyl phosphate		ND	ND	ND	ND	ND	ND	ND	ND	782	ND
205	PCB#33		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	Benzanthrone		31	ND	ND	ND	ND	ND	ND	ND	ND	45
207	2-Anisidine		ND	ND	ND	ND	ND	ND	ND	ND	ND	1333
208	2-Chloroaniline	Intermediate for dyes	ND	ND	ND	ND	ND	ND	ND	145	35	ND
209	2-Methylaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
210	N,N-Dimethylaniline		338	ND	ND	ND	ND	ND	ND	ND	ND	ND

211	N-Ethylaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	39
212	Diphenylamine		ND	ND	ND	ND	ND	ND	ND	ND	ND	259
213	2,5-Dimethylaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
214	e-Caprolactam		101	ND	ND	ND	ND	147	ND	ND	ND	ND
215	2,4-Dimethylphenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	440
216	2-Naphthol		ND	ND	ND	62	ND	ND	ND	ND	ND	50740
217	3,5-Dimethylphenol		ND	ND	ND	74	ND	ND	ND	ND	340	3410
218	4-Chloronitrobenzene		296	ND	ND	ND	ND	44	48	197	ND	ND
219	4-Nitroaniline		ND	ND	ND	ND	ND	ND	ND	ND	ND	3733
220	Carbazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
221	N-Methylaniline		209	ND	ND	ND	ND	ND	ND	90	ND	ND
222	Phenothiazine	Intermediate in organic synthesis	ND	ND	ND	ND	ND	ND	ND	ND	25	ND
223	Quinoline		103	ND	52	5.5	38	40	39	68	ND	1874
224	2-Nitrophenol		ND	ND	ND	ND	ND	69	ND	168	ND	ND
225	2-Ethyl-1-hexanol		ND	ND	ND	ND	ND	ND	ND	431	929	241
226	Aniline		ND	ND	ND	ND	ND	ND	ND	ND	757	308
227	Acetophenone		ND	ND	60	ND	ND	ND	59	132	7.3	ND
	Total concentration		19124	7728	19473	14094	48611	11320	19974	24861	195251	141355
	Sum of sterols		9386	5599	11062	8473	22528	6766	13258	8086	17468	19873
	Sum of PAHs		5050	22	785	426	105	1640	1005	1119	171	2511
	Sum of PPCPs		956	530	1146	2444	6230	683	1896	3121	30053	3061
	Sum of pesticides		358	473	878	719	2546	404	1277	1653	2389	12637
	Sum of domestic chemicals		1901	542	5172	1842	17020	1336	2245	9054	141462	38755
	Sum of industrial chemicals		1472	563	431	190	182	491	293	1828	3709	64518

Continued)

No.	Compounds	Group	Freq. %	Mean ng/L	Median ng/L	Minimum ng/L	Maximum ng/L
1	Cholesterol	Cholesterol	100	3145	2772	1141	6378
2	beta-Sitosterol	Phytosetrol	100	1516	1210	665	3270
3	Stigmasterol		90	646	624	ND	1551
4	Campesterol		85	379	302	ND	1000
5	Ergosterol		90	1577	1604	ND	4370
6	Fucosterol		80	1040	826	ND	3978
7	Stigmastanol		40	41	ND	ND	189
8	Coprostanol	Zoosterol	95	1510	728	ND	5333
9	Epicoprostanol		80	398	149	ND	1567
10	24-Ethyl coprostanol		35	277	ND	ND	1137
11	Cholestanol		90	519	461	ND	1373
12	Coprostanone		100	278	126	15	1310
	Coprostanol/Cholesterol			0.39	0.32	ND	1.08
	$5\beta/(5\beta+5\alpha)$			0.62	0.66	ND	1.00
	Epicoprostanol/Coprostanol			0.21	0.21	ND	0.54
13	1,2-Dimethylnaphthalene	2-Ring PAHs	5	3	ND	ND	62
14	1,3-Dimethylnaphthalene		55	146	29	ND	1611
15	1,4-&2,3-Dimethylnaphthalene		30	47	ND	ND	463
16	2,6-Diisopropylnaphthalene		20	10	ND	ND	100
17	2,6-Dimethylnaphthalene		50	75	0.79	ND	706
18	2-Methylnaphthalene		45	167	ND	ND	1631
19	Diphenylmethane		5	1.3	ND	ND	26
20	Naphthalene		45	536	ND	ND	5067
21	1-Methylnaphthalene		50	92	3.0	ND	815
22	2-Methylphenanthrene	3-Ring PAHs	60	14	13	ND	54
23	2-Phenylnaphthalene		20	6.1	ND	ND	37
24	4,5-Methylene-phenanthrene		35	17	ND	ND	105
25	Acenaphthene		50	18	6.1	ND	108
26	Acenaphthylene		50	23	6.3	ND	124
27	Anthracene		80	24	19	ND	55
28	Fluorene		95	72	44	ND	288
29	Phenanthrene		95	196	169	ND	672
30	3-Methylphenanthrene		65	12	12	ND	48
31	9-Methylphenanthrene		15	2.9	ND	ND	26
32	2,3-Benzofluorene	4-Ring PAHs	5	5.6	ND	ND	112
33	Benzo(a)anthracene		10	8.3	ND	ND	147
34	Benzo(c)phenanthrene		5	1.0	ND	ND	21
35	Chrysene & Triphenylene		20	7.9	ND	ND	77
36	Fluoranthene		90	49	41	ND	235
37	Pyrene		90	31	23	ND	136
38	Benzo(a)pyrene	5-Ring PAHs	25	9.4	ND	ND	79
39	Benzo(e)pyrene		15	22	ND	ND	328
40	Benzo(j&b)fluoranthene		20	23	ND	ND	227
41	Benzo(ghi)perylene	6-Ring PAHs	15	5.1	ND	ND	65
42	Indeno(1,2,3-cd)pyrene		20	7.0	ND	ND	68
	2-3 rings PAHs/Total PAHs			78	86	ND	96
	Anthracene/(Anthracene+Phenathrene)			0.09	0.12	ND	0.17
	Flurene/(Flurene+Pyrene)			0.57	0.65	ND	1.00
43	4-tert-Octylphenol	PPCPs	15	11	ND	ND	138
44	Caffeine		95	348	279	ND	1434
45	Diethyltoluamide		70	40	40	ND	87
46	Ibuprofen		15	58	ND	ND	612
47	L-Menthol		65	82	27	ND	470
48	Nicotine		10	31	ND	ND	390

57	Cotinine		95	260	194	ND	911
49	Thymol		5	2.4	ND	ND	48
50	Quinoxaline-2-carboxylic acid		90	168	137	ND	642
51	Acetaminophen		70	395	57	ND	6402
52	Antipyrine		100	95	76	13	293
53	Atenolol		5	0.7	ND	ND	15
54	Bezafibrate		20	14	ND	ND	112
55	Cimetidine		5	4.5	ND	ND	90
56	Clarithromycin		75	25	11	ND	166
58	Lidocaine		100	98	96	7.5	218
59	Lincomycin		15	114	ND	ND	1791
60	Losartan		5	4.1	ND	ND	83
61	Metformin		90	1841	613	ND	20015
62	Oleandomycin		5	3.5	ND	ND	71
63	Phenacetin		5	6.0	ND	ND	121
64	Roxithromycin		75	57	19	ND	292
65	Salinomycin		5	22	ND	ND	438
66	Sulfamethoxazole		45	40	ND	ND	173
67	Acetochlor		5	8.3	ND	ND	166
68	Atrazine		50	183	39	ND	1829
69	Clomazone		5	1.1	ND	ND	22
70	Prometryn		55	181	41	ND	651
71	Simetryn		20	23	ND	ND	237
72	1,4-Dichlorobenzene		40	38	ND	ND	324
73	3-Hydroxycarbofuran	Pestcide	10	116	ND	ND	1386
74	Acetamiprid		5	82	ND	ND	1639
75	Bendiocarb		5	5.8	ND	ND	117
76	Bis(2-chloroisopropyl)ether		25	202	ND	ND	3170
77	Dinoseb		5	420	ND	ND	8394
78	Fenobucarb		5	3.4	ND	ND	68
79	2,5-Dichlorophenol		5	69	ND	ND	1382
80	Hexachlorobenzene		100	5.2	2.1	0.14	39
81	a-HCH		90	3.9	1.3	ND	32
82	b-HCH		90	2.6	0.9	ND	13
83	d-HCH		55	1.1	0.4	ND	5.9
84	g-HCH		45	1.3	ND	ND	20
90	*p,p'*-DDT		45	0.17	ND	ND	0.82
89	*p,p'*-DDE		90	0.95	0.77	ND	2.3
88	*p,p'*-DDD		100	0.91	0.69	0.12	5.5
87	*o,p'*-DDT		85	0.76	0.67	ND	2.8
86	*o,p'*-DDE		55	0.73	0.44	ND	2.2
85	*o,p'*-DDD		80	1.1	1.2	ND	2.6
91	Alachlor	Pestcide	5	8.0	ND	ND	160
92	Aldicarb sulfone		5	1.5	ND	ND	30
93	Benzofenap		5	1.3	ND	ND	25
94	Butafenacil		10	1.1	ND	ND	13
95	Carbaryl		5	0.92	ND	ND	18
96	Carbofuran		20	7.4	ND	ND	111
97	Chloroxuron		20	2.4	ND	ND	15
98	Clomeprop		30	21	ND	ND	125
99	Cumyluron		5	0.59	ND	ND	12
100	Cyanazine		5	3.8	ND	ND	77
101	Dimethoate		5	11	ND	ND	225
102	Diuron		45	7.0	ND	ND	49
103	Dymron		25	3.6	ND	ND	24
104	Fenoxaprop-ethyl		10	3.1	ND	ND	36
105	Fenpyroximate		5	2.8	ND	ND	56
106	Fenthion Oxon Sulfone		5	0.34	ND	ND	6.8
107	Fenthion Oxon Sulfoxide		5	0.25	ND	ND	5.1
108	Fenthion Sulfone		50	15.8	3.2	ND	73
109	Fenthion Sulfoxide		20	17.5	ND	ND	188
110	Flufenacet		45	9.3	ND	ND	51

111	Fomesafen	Pestcide	10	41.1	ND	ND	595
112	Furathiocarb		10	2.4	ND	ND	25
113	Linuron		5	6.3	ND	ND	125
114	Mefenacet		20	55.9	ND	ND	966
115	Methabenzthiazuron		25	2.8	ND	ND	25
116	Naproanilide		30	8.7	ND	ND	43
117	Naptalam		5	13.5	ND	ND	270
118	Oxaziclomefone		15	3.7	ND	ND	30
119	Pirimicarb		5	0.82	ND	ND	16
120	Propoxur		5	1.1	ND	ND	22
121	Quizalofop-ethyl		5	1.1	ND	ND	22
122	Siduron		100	209	198	51	428
123	Simazine		10	1.4	ND	ND	17
124	Tebufenpyrad		5	0.24	ND	ND	4.9
125	Tebuthiuron		15	1.4	ND	ND	17
126	Tetrachlorvinphos		15	3.8	ND	ND	43
127	Isoprothiolane	Pesticide	5	1.8	ND	ND	36
128	Myclobutanil		5	113	ND	ND	2252
129	Pyrimethanil		10	21	ND	ND	412
130	Tebuconazole		5	48	ND	ND	961
131	Triadimenol 2		10	25	ND	ND	370
132	Tricyclazole		5	26	ND	ND	515
133	4-Chloro-3-methylphenol		5	23	ND	ND	470
134	Azoxystrobin		35	4.7	ND	ND	32
135	Boscalid		5	1.5	ND	ND	30
136	Carbendazim		90	28	21	ND	99
137	Cyprodinil		25	7.7	ND	ND	45
138	Dimethomorph(E)		35	31	ND	ND	254
139	Dimethomorph(Z)		40	16	ND	ND	112
140	Epoxiconazole		25	5.5	ND	ND	37
141	Ethoxyquin		5	4.2	ND	ND	83
142	Fenarimol		5	61	ND	ND	1224
143	Ferimzone(E)		10	2.6	ND	ND	28
144	Ferimzone(Z)		15	1.9	ND	ND	16
145	Mepanipyrim		30	8.0	ND	ND	54
146	Thiabendazole		10	1.8	ND	ND	27
147	Triticonazole		10	1.7	ND	ND	26
148	2-Methylbenzothiazole	Vulcanisation accelerator	15	534	ND	ND	7904
149	2(3H)-Benzothiazolone		20	3367	ND	ND	41083
150	2-(Methylthio)-benzothiazol		85	2469	112	ND	31765
151	Benzothiazole		20	1880	ND	ND	30867
152	2,6-Di-tert-butyl-4-benzoquinone	Antioxidant	20	15	ND	ND	118
153	4-Methyl-2,6-di-t-butylphenol		30	19	ND	ND	163
154	3,5-di-tert-Butyl-4-hydroxybenzaldehyde		5	2.6	ND	ND	53
155	*cis*-11,14,17-Eicosatrienoic acid methyl ester	Fatty acid methy ester	45	87	ND	ND	740
156	Elaidic acid methyl ester		5	1.2	ND	ND	25
157	Methyl palmitate		15	6.9	ND	ND	80
158	Stearic acid methyl ester		5	1.4	ND	ND	28
159	Tributyl phosphate	Fire retardant	70	312	208	ND	2610
160	Tris(1,3-dichloro-2-propyl) phosphate		5	7.2	ND	ND	143
161	Tris(2-chloroethyl) phosphate		65	224	179	ND	544
162	Tris(2-ethylhexyl) phosphate		5	3.9	ND	ND	77
163	Triphenyl phosphate		95	88	44	ND	712
164	Bis(2-ethylhexyl) sebacate	Plasticizer	5	2.2	ND	ND	43
165	Bis(2-ethylhexyl) phthalate		100	584	259	85	5454
166	Butyl benzyl phtalate		30	4.3	ND	ND	20
167	Di(2-ethylhexyl)adipate		70	67	17	ND	597
168	Diethyl phthalate	Plasticizer	90	250	185	ND	995

169	Dimethyl phthalate		10	296	ND	ND	5785
170	Di-n-butyl phthalate		65	272	243	ND	1143
171	Di-iso-butyl phthalate		5	440	ND	ND	8804
172	4-nonylphenol	Surfactants	65	565	305	ND	2622
173	Octanol	Fragrance	5	7.7	ND	ND	155
174	Benzyl alcohol		25	1273	ND	ND	15537
175	Butanoic acid, butyl ester		5	66	ND	ND	1310
176	Phenylethyl alcohol		30	15	ND	ND	166
177	Anthraquinone		85	70	54	ND	293
178	alpha-Terpineol		5	8.9	ND	ND	178
179	3-&4-Methylphenol	Disinfectant	5	25	ND	ND	491
180	Phenol		35	55	ND	ND	928
181	1,3-Dicyclohexylurea	Leaching from tire	15	828	ND	ND	12699
182	2-Cyclohexen-1-one		10	246	ND	ND	4722
183	Acetamide, N-phenyl-		5	13	ND	ND	258
184	Cyclohexanol		5	475	ND	ND	9496
185	Formamide, N-cyclohexyl-		15	1328	ND	ND	22564
186	Phthalimide		15	212	ND	ND	3467
187	Ethanol, 2-phenoxy-		15	6.8	ND	ND	73
188	3- & 4-tert-Butylphenol	Intermediate for resin	30	39	ND	ND	530
189	Dicyclopentadiene		25	72	ND	ND	984
190	Bisphenol A		30	25	ND	ND	151
191	1,2,4-Trichlorobenzene		5	1.7	ND	ND	34
192	Longifolene	Industry	35	98	ND	ND	522
193	Pentamethylbenzene		25	26	ND	ND	261
194	Phenazine		5	13	ND	ND	260
195	2,4,6-Trichlorophenol		10	14	ND	ND	144
196	Biphenyl		75	85	19	ND	742
197	Dibenzofuran		85	85	49	ND	659
198	Isophorone		55	43	37	ND	139
199	2,4-Dichloroaniline		15	45	ND	ND	670
200	1,2-Dichlorobenzene		5	6.4	ND	ND	128
201	1,3-Dichloro-2-propanol		5	29	ND	ND	577
202	4-Cymene		35	17	ND	ND	174
203	*trans*-Decahydronaphthalene		5	35	ND	ND	707
204	Trimethyl phosphate		10	235	ND	ND	3927
205	PCB#33		5	0.01	ND	ND	0.11
206	Benzanthrone	Intermediate for dyes	20	11	ND	ND	104
207	2-Anisidine		5	67	ND	ND	1333
208	2-Chloroaniline		15	10	ND	ND	145
209	2-Methylaniline		5	4.1	ND	ND	82
210	N,N-Dimethylaniline		5	17	ND	ND	338
211	N-Ethylaniline		5	2.0	ND	ND	39
212	Diphenylamine		5	13	ND	ND	259
213	2,5-Dimethylaniline		5	2.1	ND	ND	43
214	e-Caprolactam	Intermediate in organic synthesis	25	29	ND	ND	147
215	2,4-Dimethylphenol		5	22	ND	ND	440
216	2-Naphthol		20	2545	ND	ND	50740
217	3,5-Dimethylphenol		20	199	ND	ND	3410
218	4-Chloronitrobenzene		35	70	ND	ND	458
219	4-Nitroaniline		5	187	ND	ND	3733
220	Carbazole		10	3.1	ND	ND	34
221	N-Methylaniline		20	23	ND	ND	209
222	Phenothiazine		5	1.3	ND	ND	26
223	Quinoline		70	155	38	ND	1874
224	2-Nitrophenol		20	55	ND	ND	815
225	2-Ethyl-1-hexanol		30	217	ND	ND	1154
226	Aniline		10	53	ND	ND	757
227	Acetophenone		40	88	ND	ND	1426

Table S5 Monitoring results in surface waters from Jinan (ng/L)

No	Compound	Group	JN1	JN2	JN3	JN4	JN5	JN6	JN7	JN8	JN9	JN10	JN11	JN12	JN13	JN14
1	2,6-Di-tert-butyl-4-benzoquinone		92.6	176	152	ND	255	203	194	104	148	ND	116	104	ND	129
2	2-tert-Butyl-4-methoxyphenol		ND	110	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	3,5-di-tert-Butyl-4-hydroxybenzaldehyde		ND	ND	ND	107	ND	ND	ND	22.9	ND	ND	ND	ND	ND	ND
4	Octanol		ND	ND	364	323	ND	ND	ND	ND	ND	187	266	ND	ND	ND
5	2-Methyl-2,4-pentandiol		ND	ND	ND	ND	ND	ND	ND	ND	123	ND	ND	ND	ND	ND
6	Benzyl alcohol		ND	ND	781	1110	ND	ND	1054	1190	ND	ND	1040.4	ND	ND	1228
7	Phenol		ND	22.1	ND	27.5	109	55.3	ND	ND	ND	23.2	65.4	ND	ND	43.6
8	Methyl dodecanoate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	33.4
9	Stearic acid methyl ester		ND	ND	ND	23.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	Tributyl phosphate		ND	129	211	250	105	ND	ND	ND	131	ND	ND	ND	ND	ND
11	Tris(2-chloroethyl) phosphate		217	168	283	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	Diphenyl ether	Domestical chemicals	ND	ND	ND	ND	ND	1434	ND	ND	4145	ND	ND	ND	ND	ND
13	Phenylethyl alcohol		ND	ND	ND	ND	62.6	ND	144	ND	ND	ND	ND	ND	ND	ND
14	Anthraquinone		74.0	79.7	65.2	106	ND	106	ND	ND	128	ND	ND	58.8	ND	ND
15	alpha-Terpineol		ND	ND	ND	245	1653	246	1158	ND	814	ND	ND	ND	98.4	ND
16	Bisphenol A		ND	75.5	96.0	ND	134	117	139	54.0	ND	ND	ND	ND	ND	ND
17	2(3H)-Benzothiazolone		ND	ND	ND	ND	ND	ND	ND	112	ND	ND	ND	ND	ND	ND
18	2-(Methylthio)-benzothiazol		ND	ND	ND	65.4	126	200	94.9	54.6	68.7	ND	ND	ND	ND	ND
19	Benzothiazole		80.8	66.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	4-tert-Octylphenol		ND	29.6	24.5	ND	23.5	43.0	ND	ND	53.5	ND	39.0	26.8	ND	26.8
21	Bis(2-ethylhexyl) sebacate		ND	89.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	35.1	ND	ND
22	Bis(2-ethylhexyl)phthalate		ND	ND	ND	2564	1436	1161	2329	ND	635	846	ND	ND	ND	ND
23	Butyl benzyl phtalate		ND	ND	ND	ND	ND	ND	37	ND	ND	9763	ND	ND	ND	ND
24	Dimethyl phthalate		ND	ND	ND	162	287	ND	198	ND	1668	ND	ND	ND	422	ND
25	Di-n-butyl phthalate		ND	ND	ND	ND	422	ND	684	ND	ND	ND	ND	ND	ND	ND
26	Caffeine		73.8	61.2	38.5	691	6094	4254	2331	1004	5556	ND	ND	ND	1272	ND
27	Diethyltoluamide		ND	ND	ND	ND	56.5	44.0	35.4	ND	24.3	ND	ND	ND	ND	ND
28	Ibuprofen		ND	ND	ND	ND	697	ND	ND	ND	ND	ND	ND	ND	ND	ND
29	L-Menthol	PPCPs	ND	ND	ND	246	1882	383	1499	71.3	627	ND	ND	ND	204	ND
30	Nicotine		ND	ND	ND	ND	998	ND	ND	ND	671	ND	ND	ND	ND	ND
31	Triclosan		ND	ND	ND	ND	ND	63.1	ND	ND	ND	ND	ND	ND	ND	ND
32	Squalane		ND	ND	ND	196	282	315	ND	110	281	345	ND	ND	ND	ND
33	Phenacetin		ND	ND	ND	ND	123	ND	351	ND	120	ND	ND	ND	ND	ND

34	Lidocaine		ND	ND	ND	ND	ND	28.8	ND	ND	ND	ND	ND	ND	ND	ND
35	Azithromycin		ND	ND	ND	ND	ND	291	ND	ND	ND	ND	ND	ND	ND	ND
36	Roxithromycin		ND	ND	ND	168	630	880	196	ND	127	ND	ND	ND	ND	ND
37	Erythromycin		ND	ND	ND	24.7	ND	90.6	15.4	ND	18.7	ND	ND	ND	ND	ND
38	Clarithromycin		ND	ND	ND	18.5	112.6	158.6	56.0	ND	61.2	ND	ND	ND	ND	ND
39	Lincomycin		ND	ND	ND	109	719	762	195	ND	148	ND	ND	ND	ND	ND
40	Sulpiride		ND	ND	ND	148	196	821	547	63.5	83.4	ND	ND	ND	ND	ND
41	Sulfamethoxazole		1854	1312	2485	1893	1117	5033	2012	1004	808	ND	260	ND	ND	ND
42	Flumequine		ND	ND	ND	ND	ND	110.7	ND	ND	ND	ND	ND	ND	ND	ND
43	Metformin		ND	ND	86.8	4963	9441	33814	24253	4297	10884	760	ND	ND	ND	ND
44	Cotinine		437	511	773	1702	13732	7339	11851	696	3345	1852	ND	ND	ND	ND
45	Sulfapyridine		ND	ND	ND	116	278	298	288	ND	55.7	ND	ND	ND	ND	ND
46	Trimethoprim		ND	ND	ND	16.5	70.6	74.6	43.3	ND	19.2	ND	ND	ND	ND	ND
47	Acetaminophen		ND	ND	ND	3506	ND	ND	ND	ND	6812	3132	ND	ND	ND	ND
48	Antipyrine		537	600	917	188	ND	505	158	123	113	ND	ND	ND	ND	ND
49	Hexamethylenetetramine		ND	ND	ND	ND	2787	ND	5529	9158	2241	ND	ND	ND	ND	ND
50	Dicyclohexylamine		ND	ND	ND	ND	466	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	Biphenyl		ND	ND	ND	ND	ND	121	ND	ND	536	ND	ND	ND	ND	ND
52	Longifolene		ND	ND	ND	ND	227	397	ND	ND	ND	ND	ND	ND	ND	ND
53	1,2-Dichlorobenzene		ND	ND	ND	ND	187	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	Isophorone		156.3	ND	ND	67.1	145	119	ND	ND	ND	ND	ND	ND	92.8	ND
55	PCB_#1		0.31	ND	0.36	ND	0.28	0.58	ND	ND	ND	0.2	ND	ND	0.32	ND
56	PCB_#28		ND	ND	ND	0.51	0.27	0.27	0.20	ND	ND	ND	ND	ND	ND	ND
57	PCB_#4&10	Industry	ND	ND	ND	ND	ND	ND	0.24	ND	ND	ND	ND	ND	ND	ND
58	PCB_#60		0.8	ND	0.40	2.46	11.2	8.84	23.0	ND	6.85	ND	ND	ND	ND	ND
59	2-Butoxyethanol		ND	ND	ND	ND	886	ND	ND	ND	ND	ND	ND	ND	ND	ND
60	4-Cymene		ND	ND	ND	ND	682	ND	ND	ND	ND	ND	ND	105	ND	ND
61	3,4-Dichloroaniline		ND	ND	ND	ND	ND	ND	163.5	ND	ND	ND	ND	ND	ND	ND
62	e-Caprolactam		991	ND	ND	ND	1482	ND	ND	ND	810	ND	ND	ND	ND	ND
63	3- & 4-tert-Butylphenol		ND	ND	ND	ND	79.7	65.0	ND	ND	423	ND	ND	ND	ND	ND
64	2-Naphthol		ND	23.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
65	2-tert-Butylphenol		ND	ND	ND	ND	ND	ND	ND	ND	262	ND	ND	ND	ND	ND
66	Quinoline		109	111	94.6	ND	ND	ND	ND	85.7	ND	ND	ND	ND	ND	ND
67	1,3-Dimethylnaphthalene		ND	ND	ND	ND	68.7	ND	61.4	ND	292	ND	ND	ND	ND	ND
68	1-Methylnaphthalene	PAH	ND	ND	ND	ND	27.0	ND	ND	ND	56.1	ND	ND	ND	ND	ND
69	2,6-Diisopropylnaphthalene		ND	ND	ND	ND	67.4	ND	84.1	ND	ND	ND	ND	ND	ND	ND
70	2-Methylnaphthalene		ND	ND	ND	ND	ND	ND	ND	ND	79.1	ND	ND	ND	ND	ND

71	2-Methylphenanthrene		ND	ND	ND	ND	ND	ND	ND	ND	33.7	ND	ND	ND	ND	ND
72	3-Methylphenanthrene		ND	ND	ND	ND	ND	ND	ND	ND	28.9	ND	ND	ND	ND	ND
73	Acenaphthylene		30.3	ND	ND	ND	22.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	Fluoranthene		ND	ND	ND	26.0	22.9	ND	25.4	29.4	24.8	ND	ND	ND	ND	ND
75	Pyrene		ND	ND	ND	ND	ND	ND	ND	ND	23.1	ND	ND	ND	ND	ND
76	Etobenzanid		229	ND	ND	464	748	4431	1298	ND	ND	ND	ND	ND	ND	ND
77	Atrazine		22.5	16.5	19.2	21.5	ND	31.1	ND	12.0	16.0	ND	13.1	13.3	ND	ND
78	Dimethoate		ND	ND	ND	ND	ND	9.7	9.7	ND	ND	ND	ND	ND	ND	ND
79	Hexachlorobenzene		0.7	1.1	2.9	ND	ND	1.1	0.3	ND	2.1	ND	ND	ND	ND	ND
80	Propamocarb		ND	ND	58.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
81	Carbendazim		ND	204	9.0	16.0	27.6	19.8	22.8	ND	49.2	ND	ND	9.4	56.2	ND
82	Oxabetrinil		ND	237	ND	103	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
83	Simetryn		ND	ND	31.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
84	a-HCH		ND	1.07	ND	ND	ND	ND	ND	ND	1.79	ND	ND	ND	ND	1.3
85	b-HCH	Pestcides	1.03	ND	1.45	ND	1.25	1.68	ND	ND	1.25	ND	ND	ND	ND	ND
86	DDVP		ND	ND	ND	ND	ND	ND	75.7	ND	ND	ND	ND	ND	ND	ND
87	Dieldrin		ND	ND	ND	ND	2.40	ND	ND	ND	2.47	ND	ND	ND	ND	ND
88	Endrin		ND	ND	2.01	ND	2.85	ND	2.3	ND	3.00	ND	2.9	ND	ND	ND
89	g-HCH		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.8
90	*o,p'*-DDD		ND	ND	ND	ND	ND	ND	ND	ND	1.04	ND	ND	ND	ND	ND
91	*p,p'*-DDD		ND	ND	0.28	ND	ND	0.24	0.2	ND	2.29	ND	ND	ND	0.4	ND
92	*p,p'*-DDE		ND	ND	ND	ND	1.16	0.43	0.8	ND	1.37	ND	ND	ND	0.4	ND
93	*p,p'*-DDT		ND	ND	0.35	ND	0.52	0.99	0.5	ND	1.79	ND	ND	ND	0.3	ND
94	Siduron		132.7	ND	ND	96.8	111	183	115	ND	154	ND	61.2	96.9	ND	ND
95	Carbofuran		ND	ND	ND	57.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
96	Cholesterol		ND	ND	1030	4931	40871	16531	29201	2421	18612	702	ND	ND	4845	572
97	beta-Sitosterol		233	275	863	1372	12587	8572	10466	1408	8745	290	ND	ND	2102	361
98	Ergosterol		ND	ND	ND	ND	ND	401	2255	ND	512	ND	ND	ND	ND	ND
99	Fucosterol		ND	ND	ND	ND	ND	3767	1596	ND	1099	ND	ND	ND	370	ND
100	Stigmastanol		ND	ND	ND	ND	ND	1618	ND	ND	ND	ND	ND	ND	ND	ND
101	Stigmasterol	sterols	ND	ND	ND	438	4366	1406	3355	ND	1290	ND	ND	ND	317	ND
102	Campesterol		ND	ND	ND	334	4532	1383	1777	236	2204	ND	ND	ND	303	ND
103	24-Ethyl coprostanol		ND	ND	ND	ND	2814	1258	3387	ND	1371	ND	ND	ND	ND	ND
104	Cholestanol		ND	ND	ND	4734	26324	11063	27195	2528	13680	ND	ND	ND	2861	ND
105	Coprostanol		ND	ND	95.6	1847	29604	7576	19646	899	13160	ND	ND	ND	1283	ND
106	Coprostanone		ND	ND	ND	184	1925	619	2027	119.1	763	ND	ND	ND	106	ND
107	Epicoprostanol		ND	ND	ND	512	11044	2345	5968	247.1	4333	ND	ND	ND	354	ND

Sum of Domestical chemicals	464	946	1977	4984	4613	3566	6033	1537	7915	10819	1527	225	520	1460
Sum of PPCPs	2902	2484	4300	13984	36427	55264	43832	7368	29754	6089	260	ND	1477	ND
Sum of Industry	1257	135	95.4	70.1	6953	711	5716	9243	4278	0	ND	105	93.1	ND
Sum of PAH	30.3	ND	ND	26.0	208	ND	171	29.4	538	ND	ND	ND	ND	ND
Sum of Pestcides	386	459	125	760	895	4678	1525	12.0	236	ND	77.2	120	57.4	2.16
Sum of sterols	233	275	1989	14352	134068	56540	106873	7859	65769	991	ND	ND	12540	933

Continued)

No	Compound	ND	Frenquency	Mean ng/L	Median ng/L	Minimum ng/L	Maximum ng/L
1	2,6-Di-tert-butyl-4-benzoquinone	Domestical chemicals	79	120	123	n.d.	255
2	2-tert-Butyl-4-methoxyphenol		7	7.84	ND	ND	110
3	3,5-di-tert-Butyl-4-hydroxybenzal dehyde		14	9.26	ND	ND	107
4	Octanol		29	81.4	ND	ND	364
5	2-Methyl-2,4-pentandiol		7	8.79	ND	ND	123
6	Benzyl alcohol		43	457	ND	ND	1230
7	Phenol		50	24.7	11.0	ND	109
8	Methyl dodecanoate		7	2.39	ND	ND	33.4
9	Stearic acid methyl ester		7	1.65	ND	ND	23.1
10	Tributyl phosphate		36	59.1	ND	ND	250
11	Tris(2-chloroethyl) phosphate		21	47.7	ND	ND	283
12	Diphenyl ether		14	398	ND	ND	4140
13	Phenylethyl alcohol		14	14.8	ND	ND	144
14	Anthraquinone		50	44.1	29.4	ND	128
15	alpha-Terpineol		43	301	ND	ND	1700
16	Bisphenol A		43	44.0	ND	ND	139
17	2(3H)-Benzothiazolone		7	8.03	ND	ND	112
18	2-(Methylthio)-benzothiazol		43	43.5	ND	ND	200
19	Benzothiazole		14	10.5	ND	ND	80.8
20	4-tert-Octylphenol		57	19.1	24.0	ND	53.5
21	Bis(2-ethylhexyl) sebacate		14	8.93	ND	ND	89.9
22	Bis(2-ethylhexyl)phthalate		43	641	ND	ND	2600
23	Butyl benzyl phtalate		14	700	ND	ND	9760
24	Dimethyl phthalate		36	195	ND	ND	1670
25	Di-n-butyl phthalate		14	79.0	ND	ND	684
26	Caffeine	PPCPs	71	1530	383	n.d.	6090
27	Diethyltoluamide		29	11.4	ND	ND	56.5
28	Ibuprofen		7	49.8	ND	ND	697
29	L-Menthol		50	351	35.7	ND	1880
30	Nicotine		14	119	ND	ND	998
31	Triclosan		7	4.50	ND	ND	63.1
32	Squalane		43	109	ND	ND	345
33	Phenacetin		21	42.5	ND	ND	352
34	Lidocaine		7	2.06	ND	ND	28.8
35	Azithromycin		7	20.8	ND	ND	291
36	Roxithromycin		36	143	ND	ND	880
37	Erythromycin		29	10.7	ND	ND	90.6
38	Clarithromycin		36	29.1	ND	ND	159
39	Lincomycin		36	138	ND	ND	762
40	Sulpiride		43	133	ND	ND	821
41	Sulfamethoxazole		71	1270	1070	n.d.	5000
42	Flumequine		7	7.91	ND	ND	111
43	Metformin		57	6320	423	ND	33800
44	Cotinine		71	3020	734	n.d.	13700
45	Sulfapyridine		36	73.9	ND	ND	298
46	Trimethoprim		36	16.0	ND	ND	74.6
47	Acetaminophen		21	961	ND	ND	6810
48	Antipyrine		57	224	118	ND	917
49	Hexamethylenetetramine	Industry	29	1410	ND	ND	9160
50	Dicyclohexylamine		7	33.3	ND	ND	466
51	Biphenyl		14	46.9	ND	ND	536
52	Longifolene		14	44.6	ND	ND	397
53	1,2-Dichlorobenzene		7	13.4	ND	ND	187
54	Isophorone		36	41.4	ND	ND	156
55	PCB_#1		43	0.15	ND	ND	0.58
56	PCB_#28		29	0.09	ND	ND	0.51

57	PCB_#4&10		7	0.02	ND	ND	0.24
58	PCB_#60		50	3.83	0.20	ND	23.0
59	2-Butoxyethanol		7	63.3	ND	ND	886
60	4-Cymene		14	56.2	ND	ND	682
61	3,4-Dichloroaniline		7	11.7	ND	ND	164
62	e-Caprolactam		21	235	ND	ND	1480.00
63	3- & 4-tert-Butylphenol		21	40.6	ND	ND	423
64	2-Naphthol		7	1.67	ND	ND	23.4
65	2-tert-Butylphenol		7	18.7	ND	ND	262
66	Quinoline		29	28.6	ND	ND	111
67	1,3-Dimethylnaphthalene	PAH	21	30.2	ND	ND	292
68	1-Methylnaphthalene		14	5.94	ND	ND	56.1
69	2,6-Diisopropylnaphthalene		14	10.8	ND	ND	84.1
70	2-Methylnaphthalene		7	5.65	ND	ND	79.1
71	2-Methylphenanthrene		7	2.40	ND	ND	33.7
72	3-Methylphenanthrene		7	2.06	ND	ND	28.9
73	Acenaphthylene		14	3.76	ND	ND	30.3
74	Fluoranthene		36	9.18	ND	ND	29.4
75	Pyrene		7	1.65	ND	ND	23.1
76	Etobenzanid	Pestcides	36	512	ND	ND	4430
77	Atrazine		64	11.8	13.2	n.d.	31.1
78	Dimethoate		14	1.38	ND	ND	9.66
79	Hexachlorobenzene		43	0.59	ND	ND	2.95
80	Propamocarb		7	4.15	ND	ND	58.1
81	Carbendazim		64	29.5	12.7	n.d.	204
82	Oxabetrinil		14	24.3	ND	ND	237
83	Simetryn		7	2.23	ND	ND	31.2
84	a-HCH		21	0.30	ND	ND	1.79
85	b-HCH		36	0.48	ND	ND	1.68
86	DDVP		7	5.41	ND	ND	75.7
87	Dieldrin		14	0.35	ND	ND	2.47
88	Endrin		36	0.93	ND	ND	3.00
89	g-HCH		7	0.06	ND	ND	0.83
90	*o,p'*-DDD		7	0.07	ND	ND	1.04
91	*p,p'*-DDD		36	0.25	ND	ND	2.29
92	*p,p'*-DDE		36	0.30	ND	ND	1.37
93	*p,p'*-DDT		43	0.32	ND	ND	1.79
94	Siduron		57	67.8	79.0	ND	183
95	Carbofuran		7	4.13	ND	ND	57.9
96	Cholesterol	sterols	71	8550	1730	n.d.	40900
97	beta-Sitosterol		86	3380	1120	n.d.	12600
98	Ergosterol		21	226	ND	ND	2260
99	Fucosterol		29	488	ND	ND	3770
100	Stigmastanol		7	116	ND	ND	1620.00
101	Stigmasterol		43	798	ND	ND	4370
102	Campesterol		50	769	118	ND	4530
103	24-Ethyl coprostanol		29	631	ND	ND	3390
104	Cholestanol		50	6310	1270.00	ND	27200
105	Coprostanol		57	5290	497	ND	29600
106	Coprostanone		50	410	52.8	ND	2030
107	Epicoprostanol		50	1770	124	ND	11000

Table S6 Monitoring results in groundwater from Beijing and Tianjin

No	Compound	Group	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14
1	2,6-Di-tert-butyl-4-benzoquinone	Domestic chemicals	13.6	13.2	ND	ND	17.4	13	ND	13.9	ND	10.7	10.2	20.5	16.1	ND
2	2-tert-Butyl-4-methoxyphenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	21.5
3	Phenol		ND	ND	35.1	ND	28.7	ND	ND	ND	ND	ND	ND	ND	ND	33.4
4	*cis*-5,8,11,14,17-Eicosapentaenoic acid, methyl ester		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	Tris(2-chloroethyl) phosphate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	Benzyl alcohol		593	339	290	615	257	281	152	361	ND	523	165	677	570	824
7	Anthraquinone		ND	18.5	ND	ND	ND	ND	ND	15.7	ND	ND	26.3	ND	ND	ND
8	Octanol		15.3	ND	ND	ND	ND	ND	ND	ND	ND	18.7	18.9	ND	ND	ND
9	Phenylethyl alcohol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	12.6
10	4-Cymene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	Benzothiazole		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	26.1	ND
12	2(3H)-Benzothiazolone		ND	ND	11.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	Dibenzothiophene		ND	ND	ND	ND	ND	ND	ND	13.1	ND	ND	ND	ND	ND	ND
14	Dimethyl phthalate		73.3	ND	63.5	51.7	73.6	74.9	81.0	83.0	ND	60.0	105	86.9	142	ND
15	Di-n-butyl phthalate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	741	ND	ND	ND
16	Bis(2-ethylhexyl)phthalate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
17	Diethyl phthalate		29.8	ND	ND	ND	ND	19.0	ND	70.4	ND	20.8	22.8	ND	35.1	ND
18	Bis(2-ethylhexyl) sebacate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	33.3
19	2-Butoxyethanol	Industry	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	282
20	Dibenzofuran		ND	ND	16.9	ND	ND	ND	ND	14.8	ND	48.7	ND	ND	ND	ND
21	Isophorone		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
22	Longifolene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.0	ND	ND
23	PCB_#60		ND	ND	ND	ND	ND	ND	ND	ND	ND	0.15	0.15	ND	ND	ND
24	Pentamethylbenzene		83.3	2829	69.2	107	47.8	50.6	32.5	51.3	50.1	51.8	ND	ND	ND	51.7
25	2-Ethyl-1-hexanol		106	152	72.1	182	149	151	39.1	103	153	105	28.4	778	168	389
26	Nitrobenzene		55.7	12.2	39.8	42.9	36.0	49.2	ND	64.8	20.6	41.2	ND	74.1	99.6	ND
27	3,5-Dimethylphenol		84.7	37.2	ND	78.5	ND	ND	ND	51.4	ND	39.0	ND	66.4	58.7	38.2
28	Carbazole		ND	ND	31.6	ND	11.9	ND	22.6	ND	ND	57.9	32.8	ND	ND	18.0
29	Quinoline		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
30	2-Nitrophenol		ND	ND	16.6	ND	ND	ND	ND	32.0	ND	ND	ND	ND	ND	ND
31	3,5-di-tert-Butyl-4-hydroxybenzaldehyde		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
32	Diphenylmethane		ND	9524	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
33	1,4-&2,3-Dimethylnaphthalene	PAH	ND	12656	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

34	1,2-Dimethylnaphthalene		ND	6449	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
35	2-Methylnaphthalene		31.9	7467	30.8	11.3	23.2	ND	22.0	29.6	14.0	33.0	ND	22.3	11.8	ND
36	1,3-Dimethylnaphthalene		10.7	ND	12.8	ND	ND	ND	12.0	13.2	ND	14.2	ND	ND	ND	ND
37	1-Methylnaphthalene		11.2	5850	14.0	ND	10.2	ND	12.1	13.2	ND	15.1	ND	ND	ND	ND
38	Naphthalene		16.9	2425	28.2	12.7	29.8	16.4	ND	32.8	12.2	88.2	ND	41.2	17.4	ND
39	2,6-Dimethylnaphthalene		27.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
40	Acenaphthene		ND	ND	ND	ND	ND	ND	ND	ND	ND	10.7	ND	ND	ND	ND
41	Phenanthrene		ND	ND	31.3	ND	ND	ND	ND	34.5	ND	ND	35.5	ND	ND	ND
42	Fluorene		ND	ND	18.2	ND	ND	ND	ND	ND	ND	48.8	ND	ND	ND	ND
43	Anthracene		ND	ND	ND	ND	ND	ND	ND	ND	ND	23.3	ND	ND	ND	ND
44	Fluoranthene		11	ND	ND	ND	ND	ND	ND	ND	ND	ND	13.7	ND	ND	ND
45	4,5-Methylene-phenanthrene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
46	Pyrimethanil		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
47	1,4-Dichlorobenzene		ND	ND	89.8	ND	157	ND	ND	60.7	28.5	ND	ND	93.4	34.6	ND
48	Oxadixyl		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	Diflubenzuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
50	Iprodione		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	Atrazine		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	2-Phenylphenol (OPP)		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
53	carbendazim		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1607	ND	ND	ND
54	prochloraz		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	Dimethomorph(E)		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
56	Dimethomorph(z)	Pestcide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
57	fenhexamid		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	diuron		ND	373	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
59	linuron		ND	38.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
60	isouron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
61	Hexachlorobenzene		ND	ND	ND	ND	ND	ND	ND	0.17	ND	ND	0.12	ND	ND	ND
62	a-HCH		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
63	*p,p'*-DDE		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
64	*o,p'*-DDD		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.34	ND	0.18
65	*p,p'*-DDD		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
66	*o,p'*-DDT		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
67	Acetophenone		64.9	86.4	95.6	ND	83.4	79.9	ND	105.2	71.9	88.4	20.6	81.1	56.2	53.9
68	Ethanol, 2-phenoxy-	PPCPs	36.4	28.7	30.2	68.6	62.1	107	129.0	158.9	ND	163	30.8	149	235	173
69	metformin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	oleandomycin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15.1	ND	ND

71	Squalane		60.7	24.2	40.1	ND	ND	ND	ND	ND	ND	101	ND	ND	ND	ND
72	L-Menthol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
73	1,1,1-Trichloro-2-methyl-2-propanol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	Cholesterol	Sterol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
75	beta-Sitosterol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
76	Ergosterol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
77	Stigmasterol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
78	Campesterol		ND	ND	ND	ND	ND	ND	ND	24	ND	ND	ND	ND	ND	ND
	Sum of domestic chemicals		725	370	401	667	376	388	233	557	ND	633.5	1089	784	790	925
	Sum of industrial compounds		330	12554	246	411	245	251	94.125	317	224	343	61.3	938	327	779
	Sum of PAH		109	34847	135	24.0	63.2	16.4	46.0	123	26.2	233	49.1	63.5	29.2	ND
	Sum of pesticide		ND	411	89.8	ND	157	ND	ND	60.9	28.5	ND	1608	93.7	34.6	0.18
	Sum of PPCPs		162	139	166	68.6	145	187	129	264	71.9	352	51.4	245	291	227
	Sum of sterol		ND	ND	ND	ND	ND	ND	ND	24	ND	ND	ND	ND	ND	ND

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No	Compound	Group	G15	G16	G17	G18	G19	G20	G21	G22	G23	G24	G25	G26	G27
1	2,6-Di-tert-butyl-4-benzoquinone	Domestic chemicals	22.0	10.1	12.1	ND	13.9	ND	51.1	13.5	ND	12.6	15.8	10.4	ND
2	2-tert-Butyl-4-methoxyphenol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	Phenol		ND	ND	ND	ND	ND	ND	170	ND	25.2	ND	ND	ND	ND
4	*cis*-5,8,11,14,17-Eicosapentaenoic acid, methyl ester		ND	396	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	Tris(2-chloroethyl) phosphate		32.5	ND	30.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	Benzyl alcohol		582	379	651	739	712	624	775	671	1116	583	49.8	426	1155
7	Anthraquinone		219	ND	ND	ND	ND	ND	51.0	ND	ND	ND	ND	ND	ND
8	Octanol		ND	ND	ND	ND	ND	ND	28.4	ND	55.9	ND	ND	27.7	ND
9	Phenylethyl alcohol		ND	ND	56.2	ND	ND	ND	11.2	ND	ND	ND	ND	ND	ND
10	4-Cymene		ND	ND	ND	ND	ND	ND	68.1	ND	ND	ND	ND	ND	ND
11	Benzothiazole		ND	ND	ND	ND	ND	ND	229	27.8	ND	ND	ND	28.5	ND
12	2(3H)-Benzothiazolone		ND	ND	ND	ND	ND	ND	28.9	ND	ND	22.3	ND	18.6	ND

13	Dibenzothiophene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	Dimethyl phthalate		ND	58.1	60.4	ND	72.6	ND	1230	68.9	ND	43.7	68.7	85.3	41.1
15	Di-n-butyl phthalate		506	587	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	Bis(2-ethylhexyl)phthalate		ND	ND	ND	ND	ND	ND	ND	385	ND	ND	ND	ND	ND
17	Diethyl phthalate		ND	20.9	ND	ND	ND	16.0	ND	33.9	ND	ND	ND	ND	71.5
18	Bis(2-ethylhexyl) sebacate		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	32.7
19	2-Butoxyethanol		ND	ND	ND	ND	ND	152	ND	222	191	ND	ND	ND	ND
20	Dibenzofuran		ND	ND	ND	ND	ND	ND	51.8	ND	ND	ND	ND	10.9	ND
21	Isophorone		13.3	ND	10.0	ND	ND	ND	39.4	ND	ND	ND	ND	ND	ND
22	Longifolene		ND	ND	ND	ND	ND	ND	12.9	ND	ND	ND	ND	ND	ND
23	PCB_#60		ND	ND	ND	ND	ND	ND	0.21	ND	ND	ND	ND	ND	ND
24	Pentamethylbenzene		5050	59.9	81.6	ND	ND	24.5	95.6	94.1	ND	51.8	27.5	38.3	16.7
25	2-Ethyl-1-hexanol		356	96.91	323	152	144	101	390	676	997	230	ND	208	62.2
26	Nitrobenzene		44.0	34.9	51.7	21.4	57.5	ND	548	49.7	85.0	21.8	ND	33.6	ND
27	3,5-Dimethylphenol		ND	46.1	56.4	51.0	58.9	ND	131	60.0	ND	50.6	41.3	32.5	73.7
28	Carbazole	Industry	ND	ND	ND	13.8	ND	ND	59.5	ND	ND	ND	ND	31.1	ND
29	Quinoline		ND	ND	23.5	ND	ND	ND	127	12.5	ND	ND	ND	14.1	11.4
30	2-Nitrophenol		ND	ND	ND	ND	ND	ND	73.8	ND	ND	ND	ND	ND	ND
31	3,5-di-tert-Butyl-4-hydroxybenzaldehyde		ND	ND	ND	ND	ND	ND	13.0	ND	ND	ND	ND	ND	ND
32	Diphenylmethane		1389	ND	ND	16.7	ND	ND	29.5	ND	6187	ND	ND	ND	ND
33	1,4-&2,3-Dimethylnaphthalene		5986	ND	ND	ND	ND	ND	141	ND	29679	ND	ND	ND	ND
34	1,2-Dimethylnaphthalene		3234	ND	ND	13.0	ND	ND	68.4	ND	14018	ND	ND	ND	ND
35	2-Methylnaphthalene	PAH	5409	13.6	15.2	50.2	14.3	ND	641	ND	9574	ND	ND	24.7	ND
36	1,3-Dimethylnaphthalene		19005	ND	ND	23.5	ND	ND	316	ND	ND	ND	ND	11.8	ND
37	1-Methylnaphthalene		4705	ND	ND	20.7	ND	ND	263	ND	6198	ND	ND	11.5	ND

38	Naphthalene		3359	16.9	22.7	37.5	20.2	ND	510	ND	5895	ND	ND	43.2	ND
39	2,6-Dimethylnaphthalene		10035	ND	ND	42.3	ND	ND	318	ND	ND	ND	ND	ND	ND
40	Acenaphthene		ND	ND	ND	ND	ND	ND	19.7	ND	607	ND	ND	ND	ND
41	Phenanthrene		92.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
42	Fluorene		ND	ND	ND	ND	ND	ND	58.3	ND	ND	ND	ND	ND	ND
43	Anthracene		32.5	ND	ND	ND	ND	ND	15.6	ND	ND	ND	ND	ND	ND
44	Fluoranthene		ND	ND	ND	ND	ND	ND	40.7	ND	ND	ND	ND	ND	ND
45	4,5-Methylene-phenanthrene		ND	ND	ND	ND	ND	ND	27.6	ND	ND	ND	ND	ND	ND
46	Pyrimethanil		ND	91.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
47	1,4-Dichlorobenzene		111	ND	19.6	ND	ND	ND	3811	ND	67.4	ND	ND	60.1	ND
48	Oxadixyl		ND	804.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	Diflubenzuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	148.2	ND	ND	ND
50	Iprodione		ND	60.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	Atrazine		ND	ND	55.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	2-Phenylphenol (OPP)		ND	ND	ND	ND	ND	ND	19.3	ND	ND	ND	ND	ND	ND
53	carbendazim		ND	62.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	prochloraz	Pestcide	ND	81.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	Dimethomorph(E)		ND	1472	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
56	Dimethomorph(z)		ND	746	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
57	fenhexamid		ND	66.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	diuron		ND	ND	ND	ND	5.20	ND	ND	ND	ND	ND	ND	ND	ND
59	linuron		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
60	isouron		ND	ND	ND	ND	ND	ND	33.2	ND	ND	ND	ND	ND	ND
61	Hexachlorobenzene		0.18	ND	ND	ND	ND	ND	0.51	ND	ND	ND	ND	ND	ND
62	a-HCH		0.43	ND	ND	ND	ND	ND	ND	0.53	ND	ND	ND	ND	ND
63	*p,p'*-DDE		ND	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

64	*o,p'*-DDD		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.23
65	*p,p'*-DDD		ND	ND	0.28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
66	*o,p'*-DDT		ND	ND	0.19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
67	Acetophenone		204	76.0	88.9	71.7	61.6	26.2	198	90.2	146	72.5	ND	73.9	16.0
68	Ethanol, 2-phenoxy-		127	81.8	122	290	543	228	679	1328	ND	333	158	96.3	507
69	metformin		38	ND	45.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	oleandomycin	PPCPs	ND	ND	ND	ND	ND	ND	ND	39.9	ND	ND	11.9	ND	19.1
71	Squalane		ND	ND	ND	23.0	ND	ND	ND	142	ND	ND	ND	21.8	ND
72	L-Menthol		ND	ND	ND	ND	ND	ND	153	53.0	ND	ND	ND	ND	ND
73	1,1,1-Trichloro-2-methyl-2-propanol		54.3	ND	61.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	Cholesterol		459	ND	ND	297	ND	ND	522	218	131	ND	ND	247	117
75	beta-Sitosterol		204	ND	ND	ND	ND	ND	ND	ND	66.2	ND	ND	ND	55.1
76	Ergosterol	Sterol	ND	ND	ND	ND	ND	ND	ND	117	ND	ND	ND	ND	ND
77	Stigmasterol		32.6	ND	ND	ND	ND	ND	ND	ND	28.0	ND	ND	ND	ND
78	Campesterol		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Sum of domestic chemicals		1361	1450	809	739	799	640	2644	1200	1197	662	134	597	1301
	Sum of industrial compounds		6852	238	546	255	261	278	1571	1114	7460	355	68.8	369	164
	Sum of PAH		51858	30.4	37.9	187	34.4	ND	2420	ND	65971	ND	ND	91.1	ND
	Sum of pesticide		111	3385	75.3	ND	5.20	ND	3864	0.53	67.4	148	ND	60.1	0.23
	Sum of PPCPs		423	158	318	384	605	254	1030	1653	146	406	170	192	542
	Sum of sterol		696	ND	ND	297	ND	ND	522	335	225	ND	ND	247	172

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No	Compound	Group	Frenquency	Mean ng/L	Median ng/L	Minimum ng/L	Maximum ng/L
1	2,6-Di-tert-butyl-4-benzoquinone	Domestic chemicals	67	10.7	12.1	ND	51.1
2	2-tert-Butyl-4-methoxyphenol		4	0.80	ND	ND	21.5
3	Phenol		19	10.8	ND	ND	170
4	*cis*-5,8,11,14,17-Eicosapentaenoic acid, methyl ester		4	14.7	ND	ND	396
5	Tris(2-chloroethyl) phosphate		7	2.32	ND	ND	32.5
6	Benzyl alcohol		96	523	582	ND	1155
7	Anthraquinone		19	12.2	ND	ND	219
8	Octanol		22	6.10	ND	ND	55.9
9	Phenylethyl alcohol		11	2.96	ND	ND	56.2
10	4-Cymene		4	2.52	ND	ND	68.1
11	Benzothiazole		15	11.5	ND	ND	229
12	2(3H)-Benzothiazolone		15	3.03	ND	ND	28.9
13	Dibenzothiophene		4	0.48	ND	ND	13.1
14	Dimethyl phthalate		74	97.2	63.5	ND	1230
15	Di-n-butyl phthalate		11	67.9	ND	ND	741
16	Bis(2-ethylhexyl)phthalate		4	14.2	ND	ND	385
17	Diethyl phthalate		37	12.6	ND	ND	71.5
18	Bis(2-ethylhexyl) sebacate		7	2.44	ND	ND	33.3
19	2-Butoxyethanol	Industry	15	31.4	ND	ND	282
20	Dibenzofuran		19	5.30	ND	ND	51.8
21	Isophorone		11	2.3	ND	ND	39.4
22	Longifolene		7	1.22	ND	ND	20.0
23	PCB_#60		11	0.02	ND	ND	0.21
24	Pentamethylbenzene		78	332	50.6	ND	5050
25	2-Ethyl-1-hexanol		96	234	151	ND	997
26	Nitrobenzene		78	55.0	39.7	ND	548
27	3,5-Dimethylphenol		67	39.1	41.3	ND	131
28	Carbazole		33	10.3	ND	ND	59.5
29	Quinoline		19	6.98	ND	ND	127
30	2-Nitrophenol		11	4.53	ND	ND	73.8
31	3,5-di-tert-Butyl-4-hydroxybenzaldehy de		4	0.48	ND	ND	13.0
32	Diphenylmethane		19	635	ND	ND	9524
33	1,4-&2,3-Dimethylnaphthalene	PAH	15	1795	ND	ND	29679
34	1,2-Dimethylnaphthalene		19	881	ND	ND	14018
35	2-Methylnaphthalene		70	868	15.1700	ND	9574
36	1,3-Dimethylnaphthalene		33	719	ND	ND	19005
37	1-Methylnaphthalene		44	634	ND	ND	6198
38	Naphthalene		70	468	17.4200	ND	5895
39	2,6-Dimethylnaphthalene		15	386	ND	ND	10035
40	Acenaphthene		11	23.6	ND	ND	607
41	Phenanthrene		15	7.16	ND	ND	92.2
42	Fluorene		11	4.64	ND	ND	58.3
43	Anthracene		11	2.64	ND	ND	32.5
44	Fluoranthene		11	2.42	ND	ND	40.7
45	4,5-Methylene-phenanthrene		4	1.02	ND	ND	27.6
46	Pyrimethanil	Pestcide	4	3.40	ND	ND	91.8
47	1,4-Dichlorobenzene		41	168	ND	ND	3811
48	Oxadixyl		4	29.8	ND	ND	805
49	Diflubenzuron		4	5.49	ND	ND	148
50	Iprodione		4	2.25	ND	ND	60.8
51	Atrazine		7	3.7	ND	ND	56.5
52	2-Phenylphenol (OPP)		4	0.71	ND	ND	19.3
53	carbendazim		7	61.8	ND	ND	1607
54	prochloraz		4	3.00	ND	ND	81.0
55	Dimethomorph(E)		4	54.5	ND	ND	1472

56	Dimethomorph(z)		4	27.6	ND	ND	746
57	fenhexamid		4	2.46	ND	ND	66.5
58	diuron		7	14.0	ND	ND	373
59	linuron		4	1.41	ND	ND	38.1
60	isouron		4	1.23	ND	ND	33.2
61	Hexachlorobenzene		15	0.0	ND	ND	0.51
62	a-HCH		7	0.04	ND	ND	0.53
63	*p,p'*-DDE		4	0.0	ND	ND	0.10
64	*o,p'*-DDD		11	0.0	ND	ND	0.34
65	*p,p'*-DDD		4	0.0	ND	ND	0.28
66	*o,p'*-DDT		4	0.0	ND	ND	0.19
67	Acetophenone	PPCPs	89	74.5	73.8	ND	204
68	Ethanol, 2-phenoxy-		93	217	129	ND	1328
69	metformin		7	3.09	ND	ND	45.4
70	oleandomycin		15	3.19	ND	ND	39.9
71	Squalane		26	15.3	ND	ND	142
72	L-Menthol		7	7.64	ND	ND	153
73	1,1,1-Trichloro-2-methyl-2-propanol		7	4.28	ND	ND	61.2
74	Cholesterol	Sterol	26	73.8	ND	ND	522
75	beta-Sitosterol		11	12.1	ND	ND	204
76	Ergosterol		4	4.32	ND	ND	117
77	Stigmasterol		7	2.25	ND	ND	32.6
78	Campesterol		4	0.89	ND	ND	24.0