OCCUERENCE OF ORGANIC MICRO–POLLUTANTS IN THE AQUATIC ENVIRONMENT IN VIETNAM

DUONG THI HANH

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OCCUERENCE OF ORGANIC MICRO–POLLUTANTS IN THE AQUATIC ENVIRONMENT IN VIETNAM

by

DUONG THI HANH
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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.

Duong Thi Hanh

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SUMMARY

This study makes an attempt to figure out a more detailed picture of anthropogenic chemicals in aquatic environmentthroughout Vietnam by applying comprehensive analytical methods utilizing a comprehensive gas chromatography–mass spectrometry–database that allowsto automaticallyidentify and quantify of 940 organic micro–pollutants (OMPs)in environmental samples (waters and sediments). In addition, an investigation of 16 perfluoroalkyl acids (PFAAs) in environmental waters in Vietnam by applying high performance liquid chromatography tandem mass spectrometry was carried out. Hundreds of OMPs at high concentrations were detected in waters (235) and sediments (185). Moreover, the pollution characteristics, potential pollution sources as well as the potential risk of detected contaminants were clarified.

The list of the studied tasks and results is summarized as below:

Chapter I reviewed the general information of chemicals: use, production volume, essentialto human life and environmental concerns regarding its pollution. The environmental incidents caused by chemicals in the world and Vietnam as well as the exposure to environmental pollution throughout the world were discussed. Pollution situation of chemicals in the aquatic environment (freshwater systems, groundwater and sediment) and the potential sources (untreated sewage and industrial discharges,storm water runoff, accidental spills, landfills, etc.) of contamination entered to aquatic environment were reviewed. Since occurrence of micro–pollutants in the environment has become a worldwide issue of concerns, accordingly multiple chemicals were added to the listed of priority pollutants (emerging pollutants) that should to be controlled and regulations for some toxic chemicals were set. The historical overview of extraction and instrumental measurement for analyzing pollutants and an approach of analytical methods for this study were also discussed.

In chapter II, an introduction of advancedcomprehensive analytical methods for organic micro–pollutants applied in this study was described.Arapid and reliable screening Automated Identification and Quantification System with a GC–MS Database (AIQS–DB) was developed for the quantitative determination of 940 OMPs without the use of standards. In addition,comprehensive analytical methods for OMPs in various environmental samples (water, sediment, soil, and foodstuff) were also developed in order to optimize the full use of AIQS–DB. As a result, two extraction methods (liquid–liquid extraction method and solid–phase extraction method) were successfully applied for water samples, while a combination of an accelerated solvent extractor and a liquid–liquid extraction method was

applied for sediment samples. The combination of these extraction methods and screening analysis allowed to screen very large numbers of organic contaminants simultaneously in a single analysis using aunique extraction procedure, with the accuracy of measurements and the capability of identification and quantification are almost the same as that obtained by the conventional analytical methods. A brief description of extraction methodologies for OMPs in water and sediment applied for AIQS−DB were also introduced.

Chapter III gave an overview of study areas and sampling locations selected for this study. A brief introduction of sampling methods designed for specific targets was described. Four large cities (Hanoi, Hai Phong, Da Nang, and Ho Chi Minh City), which are the most highly industrialized and urbanized in Vietnam, a historical city (Hue) and the second biggest river (Red River) in Vietnam were selected as study areas to achieve the objective. Surface waters were collected in the all study areas between 2011 to August 2014 while groundwaters were collected twice in Hanoi and Ho Chi Minh City in September 2013 and August 2014. Sediment samples were collected once in four major cities (Hanoi, Hai Phong, Da Nang, Ho Chi Minh City) in October 2011. The different sampling methods were designed for different target analysis as well as the different environmental compartments. A detailed instruction of sampling method for OMPs in water and sediment as well as the sampling method for PFAAs in water was described.

Chapter IV showed the occurrence, contamination levels, pollution characteristic, and the potential pollution sources of 940 OMPs in environmental waters in Vietnam. Two hundred thirty five and 74 OMPs were detected in surface and groundwater, respectively. Chemicals originated from domestic sources mainly polluted environmental waters. Some organochlorine pesticides that were banned 20 years ago were still detected in surface waters, and some drinking water sources were polluted by pesticides at critical levels. Endocrine disrupting chemicals (bisphenol A and nonylphenol) were detected in metropolitan surface waters at levels that may pose adverse effect to aquatic organisms. In general, the number of detected chemicals in surface waters was similar to those found in developed nations such as Japan; however, the levels were much higher due to direct sewage inflow. In contrast, 89% of the detected concentrations in groundwaters were low (less than 0.5 μg L^{-1}). A health risk assessment for detected contaminants in groundwater showed that there were no risk to humans. The investigation indicated that most of the aquifers have been impacted by non−point source, while untreated domestic wastewater was the main source of surface waterpollution.

Chapter V presented the results of investigation of 940 OMPs in sediments in four major industrialized and urbanized cities throughout Vietnam by applying a comprehensive analytical method utilizing AIQS–DB. Although 20% of the targets were detected(185 of 940 OMPs), the discussion was mainly focused on the contaminants which were abundance and presented in the environment at high concentrations or posed adverse effect to human and aquatic organism. For instance, the contaminants that were classified as indicator of domestic wastewater pollution (eg. sterols, pharmaceuticals, etc.); or persistence organic pollutants which posed serious adverse effect to human health and aquatic organisms (eg. organochlorine pesticides and polychlorinated biphenyls); or endocrine disrupting chemicals. Occurrence, concentration levels, pollution characteristics of OMPs as well as an investigation of pollution sources of detected OMPs were discussed. The results showed that n–alkanes, phthalates, sterols andpolycyclic aromatic hydrocarbonwere the most frequently detected compounds at high concentrations. Contamination levels of OMPs in metropolitan areas were higher than those in rural and suburban areas due to untreated domestic wastewater discharge. Pyrethroid insecticides were heavily polluted sediments from cities' inner canals and organochlorine pesticides and polychlorinated biphenyls that were banned several decades ago were still detected at low levels. Since some detected contaminants had levels exceeding guideline values, those may pose potential toxicological stress to aquatic organisms. Overall, the study confirmed that sediments were heavily polluted mainly by domestic wastewater.

Chapter VI presented the first nationwide study of perfluoroalkyl acids in environmental waters in Vietnam. The investigation of PFAAs was carried out on 21 river waters and 22 groundwaters in four major cities and water samples from the Red River. Specific solid–phase extraction method accompanied with high performance liquid chromatography–tandem mass spectrometry as a measurement method has been applied to the determination of 16 PFAAs in water samples. Occurrence, concentration levels, and characteristic of PFAAs in surface, ground waters, and in Red River water were described. Briefly, perfluorooctanesulfonic acid (PPFOS), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA) were the most prevalent of 11 detected PFAAs with maximum concentrations in urban river water of 5.3, 18 and 0.93 ng L^{-1}, respectively, and in groundwater of 8.2, 4.5 and 0.45 ng L^{-1}, respectively. PFAAs in the Red River water were relatively low. Concentrations of PFAAs detected in this study were the same level as those in Southeast Asian countries but lower than in developed nations. Pollution sources of PFAAs in Vietnam were evaluated by comparing the pollution profile of PFAAs in surface waters with those in other countries. The results demonstrated that imported products containing PFAAs from China and Japan are one of the major sources of PFAAs in the Vietnamese aquatic environment. Risk evaluation of some PFAAs was performed by comparing the detected concentrations with health–based values and guideline values for the protection of aquatic organisms, which shows that the detected PFAAs do not pose an immediate health risk to humans and aquatic organisms.

Chapter VII indicated general conclusionsand further studies.

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ABBREVIATIONS

^{13}C2PFDA	Perfluoro-n-[1,2-^{13}C2]- decanoic acid
^{13}C2PFDoA	Perfluoro-n-[1,2,^{13}C2]-dodecanoic acid
^{13}C2PFHxA	Perfluoro-n-[1,2-^{13}C2]-hexanoic acid
^{13}C2–PFUdA	Perfluoro-n-[1,2-^{13}C2]-undecanoic acid
^{13}C4PFBA	Perfluoro-n-[1,2,3,4-^{13}C4]- butanoic acid
^{13}C4PFOA	Perfluoro-n-[1,2,3,4,-^{13}C4]-octanoic acid
^{13}C4PFOS	Sodium perfluoro-1-[1,2,3,4-^{13}C4]- octanesulfonate
^{13}C5PFNA	Perfluoro-n-[1,2,3,4,5-^{13}C5]- nonanoic acid
^{18}O2PFHxS	Sodium perfluoro-1-hexane-[^{18}O2]-sulfonate
AC	Activated carbon
AIQS	Automated identification and quantification system
Ant	Anthracene
APFO	Ammonium perfluorooctanoate
ASE	Accelerated solvent extractor
BaA	Benz(a) anthracene
BOD	Biological oxygen demand
BOD_5	Biochemical oxygen demand after five days
BPA	Bis phenol A
BRIC	Brazil, Russia, India and China
CAS	Chemical abstracts service
CCME	Canadian Council of the Ministers of the Environment
CHL	Chlordance
Chr	Chrysene
COD	Chemical oxygen demand
2,4–D	2,4–Dichlorophenoxyacetic acid
DALY	Disability–Adjusted Life Year
DBP	Di–n–butyl phthalate
DCM	Dichloromethane

DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DEET	N,N−diethyl−m−toluamide (or diethyltoluamide)
DEHP	Bis(2−ethylhexyl)phthalate
DEP	Diethyl phthalate
DF	Detection frequency
δ−HCH	Delta hexachlorocyclohexane.
DMP	Dimethyl phthalate
DN	Da Nang
DO	Dissolved oxygen
DOSTE	Department of Science, Technology and Environment
EC	Emerging contaminant
ECHA	The European Chemicals Agency
EDC	Endocrine disrupting chemical
EI	Electron Ionization
EINECS	European inventory of existing chemical substances
EU	European Union
Flu	Fluoranthene
GC−MS	Gas chromatography−mass spectrometry
GC−MS−MS	Triple quadrupole gas chromatography−mass spectrometry
GMF	Glass microfiber filter
HCB	Hexachlorobenzene
HCM	Ho Chi Minh City
He	Helium
HMW	High molecular weight
HN	Ha Noi
HP	Hai Phong
HU	Hue

ICP–MS	Inductively coupled plasma mass spectrometry
IDL	Instrument detection limit
IGES	Institute for Global Environmental Strategies
IS	Internal standard
ISQG	Interim Sediment Quality Guideline
K_{ow}	Octanol–water partition coefficient
LC–MS–MS	High performance liquid chromatography tandem mass spectrometry
LLE	Liquid–liquid extraction
LMW	Low molecular weight
LOD	Limit of detection
LOQ	Limit (level) of quantification
M3PFHxS	Sodiumperfluoro-1-[1,2,3-^{13}C3]-hexanesulfonate
M4PFHpA	Perfluoro-n-[1,2,3,4-^{13}C4]-heptanoic acid
M5PFHxA	Perfluoro-n-[1,2,3,4,6-^{13}C5]-hexanoic acid
M5PFPeA	Perfluoro-n-[^{13}C5]-pentanoic acid
M6PFDA	Perfluoro-n-[1,2,3,4,5,6-^{13}C6]-decanoic acid
M7PFUdA	Perfluoro-n-[1,2,3,4,5,6,7-^{13}C7]-undecanoic acid
M8PFOA	Perfluoro-n-[^{13}C8]-octanoic aicd
M9PFNA	Perfluoro-n-[^{13}C9]-nonanoic acid
MC	Model compound
MDH	Minnesota Department of Health, USA
MDL	Method detection limit
MOE	Ministry of Environment, Japan
MONRE	Ministry of Natural Resources and Environment
MPhens	Methylphenanthrene
Na_2HPO_4	Disodium phosphate
Na_2SO_4	Sodium sulfate
NaCl	Sodium chloride
NaH_2PO_4	Monosodium phosphate

Nap	Naphthalene
NIST	National Institute of Standards and Technology
NJDEP	New Jersey Department of Environmental Protection
NP	Nonylphenol
OCP	Organochlorine pesticide
OECD	Organization for Economic Cooperation and Development
OMP (or SVOC)	Organic micro–pollutant
OPs	Persistent organic pollutants
OP	4–tert–octylphenol
PAH	Polycyclic aromatic hydrocarbon
PCA	Principal component analysis
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PCS	Performance check standard
PEL	Probable effect level
PET	Polyethylene terephthalate
PFAA	Perfluoroalkyl acid
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptane sulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid

PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonyl fluoride
PFPeA	Perfluoropentanoic acid
PFSA	Perfluoroalkane sulfonic acid
PFTeDA	Perfluorotetradecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFUdA	Perfluoroundecanoic acid
PHC	Phthalate compound
Phen	Phenanthrene
PNEC	Predicted no effect concentration
POSF	Perfluorooctane sulfonyl fluoride
PPCP	Pharmaceutical and personal care products
Pyr	Pyrene
RE	Rotary evaporator
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RSD	Relative standard deviation
SCC	Secondary continuous concentration
SDB–XD	Styrene–divinylbenzene polymer
SIM	Selected ion monitoring
SMC	Secondary maximum concentration
SNUR	Significant new use rule
SPE	Solid–phase extraction
SRM	Standard reference material
SRM	Selected reaction monitoring
STP	Sewage treatment plant
2,4,5–T	2,4,5–Trichlorophenoxyacetic acid
TIM	Total ion current chromatograms
TSCA	Toxic substances control act
UNEP	United Nations Environment Programme

US–EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WHO	World Health Organization
WWTP	Wastewater treatment plant
α–HCH	Alpha hexachlorocyclohexane
β–HCH	Beta hexachlorocyclohexane
γ–HCH	Gamma hexachlorocyclohexane (lindane)
µg	Microgram (10^{-6} gram)
ng	Nanogram (10^{-9} gram)
ng g^{-1} dry–wt	Nanogram per gram dry weight
µg L^{-1}	Microgram per liter
ng L^{-1}	Nanogram per liter
L	Liter
%	Percent

CHAPTER I GENERAL INTRODUCTION

1.1 CHEMICALS AND ENVIRONMENTAL CONCERNS

Chemicals play an important role in human life, economic, development, and prosperity. Chemicals provide valuable benefits to humanity including in agriculture, medicine, industrial manufacturing, energy extraction and generation, and public health and disease vector control. Chemicals also play an important role in achieving developmental and social goals, especially for improving maternal health, reducing child mortality, and ensuring food security, and advances in their production and management have increased their safe application (URL1). It has been reported that 100 million organic and inorganic chemical substances have been synthesized until now (URL2) and subject to regulatory and inventory systems, and eighty thousand man–made chemicals are currently used in vast quantities in today's society (Schaider et al., 2014). In the European Union (EU), there are more than 100200 registered chemicals (URL3), of which 30000–70000 are in daily use (Schwarzenbach et al., 2006).

Chemicals are released to the environment at many steps in their life cycle, from the extraction of raw materials, through production chains, transport, consumption, and final waste disposal. They are spread to everywhere: indoor environments, food and drinking water, air, soils, rivers, lakes and living things. Certain long–lived chemicals such as persistent organic pollutants (POPs) and heavy metals are transported globally; reaching otherwise pristine environments such as rain forests, deep oceans or polar regions, and can quickly pass along the food chain, bioaccumulation to cause toxic effects on humans and wildlife (URL1). Products derived from chemicals often become hazardous wastes in their end–of–life phase, generating pollution risks. Pollution from dumping and uncontrolled open burning is common (UN–Habitat 2010), and is even increasing in some parts of the world. Electronic equipment waste (e–waste) has become one of the major environmental challenges of the 21st century since it contains not only hazardous substances (eg. mercury and lead, and endocrine–disrupting substances, brominated flame-retardants) but also many strategic metals (URL1). Every year, 20 to 50 million tons of electrical and electronic equipment waste are generated world–wide, which could bring serious risks to human health and the environment (Schwarzer, 2005).

Over the last decade chemical production has shifted from the countries of the Organization for Economic Cooperation and Development (OECD) to the BRIC countries (Brazil, Russia, India and China) and other developing countries, accompanied by a doubling of sales and the development of many new types of chemical. In 2004, China accounted for the largest share of BRIC production at 48 per cent, followed by Brazil and India at 20 per cent each, and Russia at 12 per cent (OECD, 2008). Chemical consumption in developing countries is likewise growing much faster than in the developed world and could account for a third of global consumption by 2020 (URL1). The increasing use of chemicals in developing countries while their impacts on the environment and human health remain poorly monitored and little understood. A recent study by the World Health Organization (WHO) (Prüss–Ustün et al., 2011) indicated that 4.9 million deaths and 86 million Disability–Adjusted Life Years (DALYs) were attributable to environmental exposure and management of selected chemicals in 2004. And more than 90 per cent of water and fish samples from the aquatic environment are contaminated by pesticides. Estimates indicate that about 3 percent of exposed agricultural workers suffer from an episode of acute pesticide poisoning every year (Thunduyil et al., 2008). Pollution with POPs is widespread, in particular affecting remote areas such as the Arctic and Antarctic (URL1).Consequently it is confirmed that environmental pollution by chemical substances is one of the most important environmental issues in the 21th century and is a issue to solve for creating sustainable society.

1.2 ENVIRONMENTAL INCIDENTS CAUSED BY CHEMICALS

Various environmental incidents, which relate to the production and application of chemicals, have occurred around the world. For instance, an incident caused by methyl mercury, which was released from Chisso corporation's chemical factory to Minamata Bay, Japan (1932–1968), killed 1784 people, and 2265 had been officially recognized as having Minamata disease (URL4). Yushō disease was a mass poisoning by polychlorinated biphenyls (PCBs) which occurred in northern Kyūshū, Japan in 1968. About 14000 people who had consumed the rice oil contaminated with PCBs and polychlorinated dibenzofurans (PCDFs) were affected in Japan. The same incident was occurred in Taiwan in 1979, which was called Yu–cheng disease. The similar symptoms and effects of the PCBs and PCDFs were observed, especially in children (URL4a). The deadliest chemical disaster in history which occurred in Bhopal, India (1984) due to the releasing of methyl isocyanate at a pesticide plant, resulted in 170000 victims including the death of over 3000 people (URL5). An explosion in an ammonium nitrate and fertilizer factory destroyed the facility and caused widespread damage in the surrounding area, which was occurred in Toulouse, France (2001), resulting in the death of 29 people and 2500 people injured. In view of environmental contamination by chemicals (URL5), Vietnam has been well known as a land of extensive spraying of Agent Orange (a 50/50 mixture of two herbicides: 2,4–D and 2,4,5–T) during the Vietnam War. Over 43 million liters of Agent Orange and 31 million liters of Agent Green, Pink, Purple, Blue, and White were used during 1961–1972 (Young, 2009). Four hundred thousand people were killed or maimed as a result of exposure to herbicides like Agent Orange; half a million children have been born with serious birth defects, while as many as 2 million people are suffering from cancer or other illness caused by Agent Orange (URL6). More recent incident was environmental pollution caused by discharging wastewater from Vedan Company into Thi vai River, Dong Nai province (September 2008), causing the death of fish and seriously effects on agriculture activities and ecosystems.

1.3 HEALTH IMPACTS

Environmental pollution can be simply, if somewhat generally, defined as the presence in the environment of an agent, which is potentially damaging to either the environment or human health. As such, pollutants take many forms, which include not only chemicals, but also organisms and biological materials, as well as energy in its various forms (e.g. noise, radiation, heat) (Briggs, 2003). Exposures to environmental pollution remain a major source of health risk throughout the world, though risks are generally higher in developing countries, where poverty, lack of investment in modern technology and weak environmental legislation combine to cause high pollution levels (Briggs, 2003). The industrial emissions, poor sanitation, inadequate waste management, contaminated water supplies, and exposures to indoor air pollution from biomass fuels in the developing countries mainly affect large numbers of people. Consequently, diverse diseases and deaths caused by pollution have occurred. As reported by WHO (2002), unsafe water, and poor sanitation and hygiene kill an estimated 1.7 million people annually, particularly as a result of diarrheal disease. Globally, 7 million people died–one in eight of total global deaths–as a result of the joint effects of household (household air pollution) and ambient air pollution (ambient air pollution) in 2012 (URL7), almost all in low and middle income countries. Approximately 800000 people annually die due to urban air pollution (generated by vehicles, industries, and energy production). Malaria kills over 1.2 million people annually, mostly African children under the age of five (WHO, 2003) due to poorly designed irrigation and water systems, inadequate housing, poor waste disposal and water storage, deforestation and loss of biodiversity, all may be contributing factors to the most common vector–borne diseases, including malaria, dengue and leishmaniosis. In addition, Fewtrell et al. (2003) reported that lead exposure kills more than 230000 people per year and causes cognitive effects in one third of all children globally; more than 97% of those affected live in the developing world. Climate change impacts – including more extreme weather events, changed patterns of disease and effects on agricultural production – are estimated to cause over 150000 deaths annually (WHO, 2002; McMichael et al., 2003).

1.4 POLLUTION OF AQUATIC ENVIRONMENT AND POTENTIAL SOURCES OF CONTAMINATION

Every day, industries, agriculture, and the general population are using water and releasing various pollutants in wastewaters (Deblonde et al., 2011).More than one–third of the earth’s accessible renewable freshwater is used for agriculture, industrial and domestic purposes, and most of these activities lead to water contamination with numerous synthetic compounds. The increasing contamination of freshwater systems with agriculture practices, industrial discharges and the human being is one of the key environmental problems and become a matter of serious concern today. Rivers due to their role in carrying off the municipal and industrial wastewater and run–off from agricultural land in their vast drainage basins are among the most vulnerable water bodies to pollution (Singh et al., 2005). The municipal and industrial wastewater discharge constitutes the constant polluting source, whereas, the surface run–off is a seasonal phenomenon, largely affected by climate in the basin. Seasonal variations in precipitation, surface run–off, ground water flow and water interception and abstraction have a strong effect on river discharge and subsequently on the concentration of pollutants in river water (Vega et al., 1998).

Sewage pollution in tropical Asian regions due to the direct discharge of domestic waste, leaching from poorly maintained septic tanks and improper management of farm waste are suspected as the major sources of water borne disease (Huttly, 1990). Municipal (domestic) wastewater is the outflow that comes from households, offices, laundries, hospitals, and small industrial plants. Also, rain waters along side with impurities washed away from streets and adjacent areas access municipal wastewater (Kotowska et al., 2012). It has been reported that various organic pollutants, for example phthalates, polycyclic aromatic hydrocarbons (PAHs), phenols, nitrogen–containing pollutants, pharmaceuticals, endocrine–disrupting compounds, volatile organic compounds, sterols, brominated flame retardants, etc. (König et al., 1980; Eganhouse et al., 1988; Grimalt et al., 1990; Seguel et al., 2001; Nakada et al., 2008; Meesters and Schroder, 2002)have been detected in municipal sewages. Pollution sources are various; many of the pollutants originate in everyday products, from which they leach during use or after disposal (Marttinen et al., 2003). Contaminated stormwater constitutes one of the world's main transport mechanisms introducing non–point source pollutants into receiving waters since it is being increasingly contaminated by a variety of biological, chemical and/or physical pollutants stemming from anthropogenic activities commonly practiced in urban areas (Pitt et al., 1995). Storm water runoff contains many kinds of chemicals such as heavy metals, PAHs, PCBs, pesticides, alkyl–phenols (Zgheib et al., 2012), nutrient elements (nitrogen and phosphorus) (Ballo et al., 2009)and perfluorinated surfactants (Murakami et al., 2009).

To date, the occurrence of pollutants has been much better characterized in wastewater and surface water environments compared to groundwater (Lapworth, et al., 2012). Groundwater represents the world's largest and most important sources of potable water andis an important resource for many of the world's larger cities. Urban and industrial development can impose major stresses on this resource‒on quantity by increasing water demand, and on quality through the release of contaminants that can compromise groundwater quality and thereby limit its utility (Howard, 2002). Since vast quantities of freshwater are consumed, correspondingly large quantities of wastewater are produced that may, through various transport pathways, have an impact on the groundwater. Groundwater pollution can be classified as point and non‒point (or diffuse) sources pollution. Point source pollution refers to contamination from discrete locations that can be easily identified with a single discharge source (eg. municipal sewage treatment plant discharges, industrial discharges, accidental spills, and landfills). In contrast, non‒point source pollution is caused by pollution over a broad area and often cannot be easily identified as coming from a single or definite source. Groundwater in urban areas is likely to be impacted by pollutants from sewage, industrial activities as well as diffuse leakages from reticulated sewerage and septic systems (Ellis, 2006). Wastewater may contain pharmaceuticals, household detergents, fragrances, flavorings, and plant and animal steroids. Hospital wastewater forms an important source of contaminants including a wide range of pharmaceuticals, while industrial compounds include solvents, detergents, flame‒retardants and PAHs (Stuart et al., 2014). In rural areas, the main contributor to groundwater pollution are probably fertilizers, agrochemicals and veterinary medicines related to agriculture, and animal waste (Boxall et al., 2004; Vàzquez–Suñé et al., 2010). Municipal solid waste leachate contains a wide range of organic compounds (PAHs, phenols, alkyl phenols, pesticides, phthalates, pharmaceuticals, sulfonates, sulfones and sulfonamids, pyridines, alcohols, ethers and ketones, caffeine, anilines, etc.)

River sediments, as basic components of our environment, provide foodstuffs for living organisms and also serve as a sink and reservoir for a variety of environmental contaminants. It has been recognized that aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration (Milenkovic et al., 2005). A wide variety of organic compounds and metals are discharged into the aquatic environment. Some contaminants flow directly from industrial and municipal waste dischargers, while others come from polluted runoff in urban and agricultural areas. Still other contaminants are carried through the air, landing in lakes and streams far from the factories and other facilities that produced them. The contaminants are adsorbed onto suspended particles and eventually settle to the sediments, where they can exert toxic effects on the benthic community that lives in the sediments and can indirectly affect human health.

United States Environmental Protection Agency (US−EPA) (URL8) has reported that there are five major types of pollutants are found in the sediments: (1) nutrients (including phosphorous and nitrogen compounds such as ammonia. Elevated levels of phosphorous can promote the unwanted growth of algae, and high concentrations of ammonia can be toxic to benthic organisms); (2) bulk organics (a class of hydrocarbons that includes oil and grease); (3) halogenated hydrocarbons or persistent organics (a group of chemicals that are very resistant to decay, eg. dichlorodiphenyltrichloroethane (DDT) and PCBs); (4) PAHs; (5) metals. Point sources (waste discharges from industry; municipal sewage treatment plants, overflows from combined sanitary and storm sewers, stormwater discharges from municipal and industrial facilities) and non−point sources (runoff from hazardous and solid−waste sites; runoff from croplands, livestock pens, mining and manufacturing operations, atmospheric deposition is another source of nonpoint pollution) are the main route of these contaminants in the sediments.

1.5 PIORITY AND EMERGING CHEMICALS

Over the last few decades, the occurrence of micro−pollutants in the aquatic environment has become a worldwide issue of increasing environmental concern. Micro−pollutants, also termed as emerging contaminants (ECs), consist of a vast and expanding array of anthropogenic as well as natural substance, which cover not only newly developed compounds but also compounds newly discovered in the environment−often due to analytical developments and compounds that have only recently been categorized as contaminants (Lapworth et al., 2012; Luo et al., 2014). Since the 1970s of most EU and US national water pollution control programs has been devoted to the conventional Priority Pollutants especially those collectively referred to as ‘‘persistent, bioaccumulative, toxic’’, ‘‘persistent organic pollutants’’ and other ‘‘bioaccumulative chemicals of concern’’. However, there is a much wider range of other important ‘‘unrecognized’’ or ‘‘emerging’’ pollutants that are now widely used in everyday urban activities (Ellis, 2006). These include a wide array of different compounds (as well as metabolites and transformation products): pharmaceutical and personal care products (PPCPs), pesticides, steroid hormones, veterinary products, industrial compounds/by−products, food additives as well as engineered nano−materials (Stuart et al., 2014). Many of these are not new chemicals for they have been present in wastewaters for many decades but are only now being recognized as potentially significant, but largely unregulated, water pollutants (Ellis, 2006). ECs are being more widely detected and commonly present in waters at trace concentrations, ranging from a few ng L^{-1} to several μg L^{-1}, which may produce potentially harmful effects on ecosystems and human health (Luo et al., 2014; Stuart et al., 2012).

There has been a wealth studies on the occurrence and/or gate of ECs in surface water (Ellis, 2006; Kim et al., 2009; Chen et al., 2008; Focazio et al., 2008; Kolpin et al., 2002; Ying et al., 2003; Kuch and Ballschmiter, 2001; Jin et al., 2004; Kawahata et al., 2004; Kang and Kondo, 2006; Hung and Thiemann, 2002; Hideshige et al., 2002; Leeming et al., 1996); wastewaters (Nakada et al., 2008; Meesters and Schroder, 2002; Sánchez et al., 2009; Writer et al., 1995; Hatcher and McGillivary, 1979; Seguel et al., 2001; Grimalt et al., 1990); sediments (Venkatesan and Kaplan, 1990; Khim et al., 2001; He et al., 2007; Hoai et al., 2010; Kuivila et al., 2012; Boonyatumanond et al., 2006; Guo et al., 2007; Kadokami et al., 2013). There have also been many comprehensive review articles on fate studies as well ecotoxicological effects (Campbell et al., 2006; Combalbert and Hernandez–Raquet, 2010; Heberer, 2002; Santos et al., 2010; Richardson, 2007).In addition, a preliminary risk assessment database for common pharmaceuticals and their risk to the environment has been reported (Cooper et al., 2008).

The occurrence of micro–pollutants 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 (Fent et al., 2006; Pruden et al., 2006). To date, discharge guidelines and standards do not exist for most micro–pollutants. Some countries or regions have adopted regulations for a small number of micro–pollutants. For example, environmental quality standards for a minority of micro–pollutants (e.g. nonylphenol, bisphenol A, bis(2–ethylhexyl) phthalate, 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 micro–pollutants, such as PPCPs and steroid hormones, are not included in the list of regulated substances yet. To set regulatory limits for micro–pollutants, 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 micro–pollutants, but also their synergistic, additive, and antagonistic effects (Luo et al., 2014).

1.6 ANALYTICAL METHODS FOR POLLUTANTS

Although a large number and quantities of chemicals have been produced and released into the environment worldwide and the number is increasing, the number of environmentally monitored chemicals is limited and is not enough to assess ecological and human health risks posed by chemicals in general. It is thus of fundamental importance to study and control the presence of as many chemical substances as possible in various environmental compartments, which is essential for causation validation in dose–effect analysis.

Historically, when assessing large number of heavy metals in environmental samples, methods using inductively coupled plasma mass spectrometry (ICP–MS) have become useful tools in environmental monitoring because ICP–MS can measure almost all of the most harmful metals simultaneously. When assessing organic substance in environmental samples, some methodologies have been found in the literatures. These methods were mainly based on the use of gas or liquid chromatography coupled with different detectors (fluorescence, diode array, mass spectrometry) as analytical techniques. And various extraction techniques were used before instrumental analysis: liquid–liquid extraction (LLE) and solid–phase extraction (SPE) for water samples and soxhlet (Wang et al., 2010), microwave extraction (Shen and Lee, 2003), ultrasonic assisted extraction (García–Varcárcel and Tadeo, 2009; Tadeo et al., 2010), pressurized liquid extraction (García–Rodríguez et al., 2009; Zhang et al., 2011), and super–critical fluid extraction (Hawthorne et al.,1994) for solid samples. The principal problem of all these methodologies is due to the complexity of the matrix, very dirty extracts are sometimes obtained, requiring clean–up procedures and the extraction process becomes more tedious. Moreover, when a pre–concentration step is also carried out in order to obtain better limits of detection, the difficulty of analysis increases because the matrix is also concentrated (Camino–Sánchez et al., 2011).

Nowadays, it is very important to have analytical methods that can perform a rapid, sensitive, and selective determination of a broad range of compounds in complex environmental matrices and are more efficient and less expensive than individual methods. Multi–residue analytical methodologies are becoming the required tools, as they provide greater knowledge about the contamination and they reduce the overall analysis time, field sampling and cost, however, most of them are focused on target analysis methods, focusing on several compounds or families simultaneously (Gómez et al., 2009; Camino–Sánchez et al., 2011). There is therefore a need for methods offering rapid and reliable screening of a large number of compounds. Consequently, we developed an Automated Identification and Quantification System with a gas chromatography–mass spectroscopy (GC–MS) database (AIQS–DB) (Kadokami et al., 2004, 2005) that can determine the concentrations of 940 semi–volatile organic contaminants without the use of standards, and comprehensive analytical methods for various environmental substrates by making full use of the AIQS–DB (Jinya et al., 2013; Kadokami et al., 2009, 2012). Analyses are performed by selected ion monitoring (SIM) and scan mode simultaneously so that target compounds can be quantified with high sensitivity using the SIM results. The scan data were analyzed using AIQS together with a GC–MS database that contained GC retention times, calibration curves, and mass spectra of nearly 1000 organic contaminants. Contaminants found by AIQS–DB can be added to the list of target compounds to be quantified in detailed analyses. Most importantly, the method can be used to screen for very large numbers of organic contaminants simultaneously in a single analysis using only one extraction procedure, and the accuracy and precision of measurements are almost the same as that obtained by the conventional internal standard methods (except for polar substances) (Kadokami et al., 2012). This method has been fully optimized for the analysis of semi–volatile organic compounds in environmental samples; however do not include the analysis of polar or semi–polar substances. In addition, the chromatographic signals of samples with complex matrices such as sediment samples are neither clear nor easy for processing, which requires a time for data processing.

1.7 RESEACH MOTIVATIONS

Vietnam has experienced rapid development accompanied with extensive changes in its social and economic structure. The rapid development of industry and high population growth in conjunction with lack of proper wastewater treatment facilities have led to increase of quantities of toxic chemicals discharged from industrial, medical, and domestic activities to rivers (Duong et al., 2008). For instance, Hoai et al. (2010) reported that 95% of the capital’s wastewater effluents are discharged into its inner rivers without treatment, which has turned city’s rivers into open sewers receiving mainly domestic wastewater discharged. Domestic chemicals, such as PPCPs and sterols have become a matter of concern in Vietnam because its population is growing rapidly without establishing proper wastewater management systems (Takada et al., 2002). Investigations on pollution by chemicals in Vietnam have been carried out in different environmental compartments (water, soil, sediment, food and biota), although the number of chemicals studied is limited, mainly focusing on specific chemical classes such as metals (Ho et al., 2010; Thuy et al., 2000), PCBs, organochlorine pesticides (OCPs), PAHs, dioxins or their related compounds (Iwata et al., 1994; Schecter et al., 1989, 2001; Kishida et al., 2001; Nhan et al.,2001; Hung & Thiemann, 2002; Toan et al., 2007; To et al., 2007). Research has shown that many legacy persistent OCPs (that was banned over 20 years ago) and PCBs enter the environment, disperse, persist to a greater extent and they have been found ubiquitously in waters, soil, biota (in urban, industrialized, and remote areas), and even in human breast milk (Minh et al., 2004). The existence of legacy pollutants in sediments in Vietnam is still of concern because of their persistence, accumulation in sediments, high bioaccumulation potential and harmful biological effects (Iwata et al., 1994). In addition, the contamination levels of these contaminants among the highest ranks for the developing countries and developed nations raise serious concern over the possible toxic impacts on human health.

The occurrence of perfluoroalkyl acids (PFAAs, sulfinic, phosphonic, and phosphinic acids), which are highly persistent substances and have been used in a wide variety of industrial and consumer applications, in various environmental media has been vigorously investigated in the world. Long−chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors have attracted attention as global contaminants due to their highly persistent and bioaccumulative property, and ubiquitous detection in the abiotic environment, biota, food items, and human. PFOS and PFOA were the first PFAAs recognized as global pollutants (Giesy and Kannan, 2001). Additionally, chronic exposure to PFOA and PFOS in experimental animals, and PFOA has been described as a likely human carcinogen by US−EPA Science Advisory Board (URL9), have raised serious concerns about the occurrence and impacts of these pollutants to aquatic environment in Vietnam. However, there is only limited information on the number and levels of PFAAs as it is in the Vietnamese environment. To the best of our knowledge, there are only four reports of PFAAs in environmental waters in Vietnam (Lien et al., 2006a, 2006b; Isobe et al., 2012; Kim et al., 2013) which were focused on limited study areas, but no extensive study throughout Vietnam. In addition, there is no study on PFAAs in groundwater, even though it is well known that groundwater is easily polluted with PFAAs due to their high water solubility.

The serious pollution of pollutants in surface water may lead to pollute sediment beds, especially for the non−polar and persistent chemical substances that have tendency to accumulate and absorb in sediments. It may also affect aquifers via leaks in sewage canals, surface runoff or underground septic tanks, especially rural population of Vietnam is using groundwater pumped from individual private (family based) tube wells as sources for drinking water. Although a large number of chemicals are expected to contaminate the environment, the contamination by wide spectrum of organic pollutants in aquatic environment, particularly in a wide−scale of study areas, has not been examined in Vietnam yet. Therefore, in order to grasp a more complete picture of anthropogenic chemicals in the aquatic environment in Vietnam, a comprehensive survey on 940 organic micro−pollutants in environmental waters and sediments along with the investigation of 16 PFAAs (comprising 11 PFCAs and 5 PFSAs) in environmental waters throughout Vietnam was carried out. To analyze a great deal (940) of organic contaminants in waters and sediments, the combination of targeted analytical methods: (1) a triple quadrupole GC–MS–MS spectrometer instrument (Thermo−TSQ Quantum XLS Triple Quadrupole GC−MS−MS) with Selected Reaction Monitoring (SRM) and (2) a GC–MS instrument (GC–MS QP–2100 Plus, Shimadzu, Kyoto, Japan) with SIM mode, and a screening analysis using an automated identification and quantification system with a GC–MS database were used. Targeted analytical methods have applied for sterols and contaminants (PAHs, PCBs, OCPs), which normally present at trace levels in environmental samples. The target PFAAs (16 compounds) were measured by high performance liquid chromatography tandem mass spectrometry in selected reaction monitoring mode (LC–MS–MS–SRM, Agilent 6460 Trip Quadrupole LC–MS, Agilent Technologies, California, USA) and quantified by internal standard method.

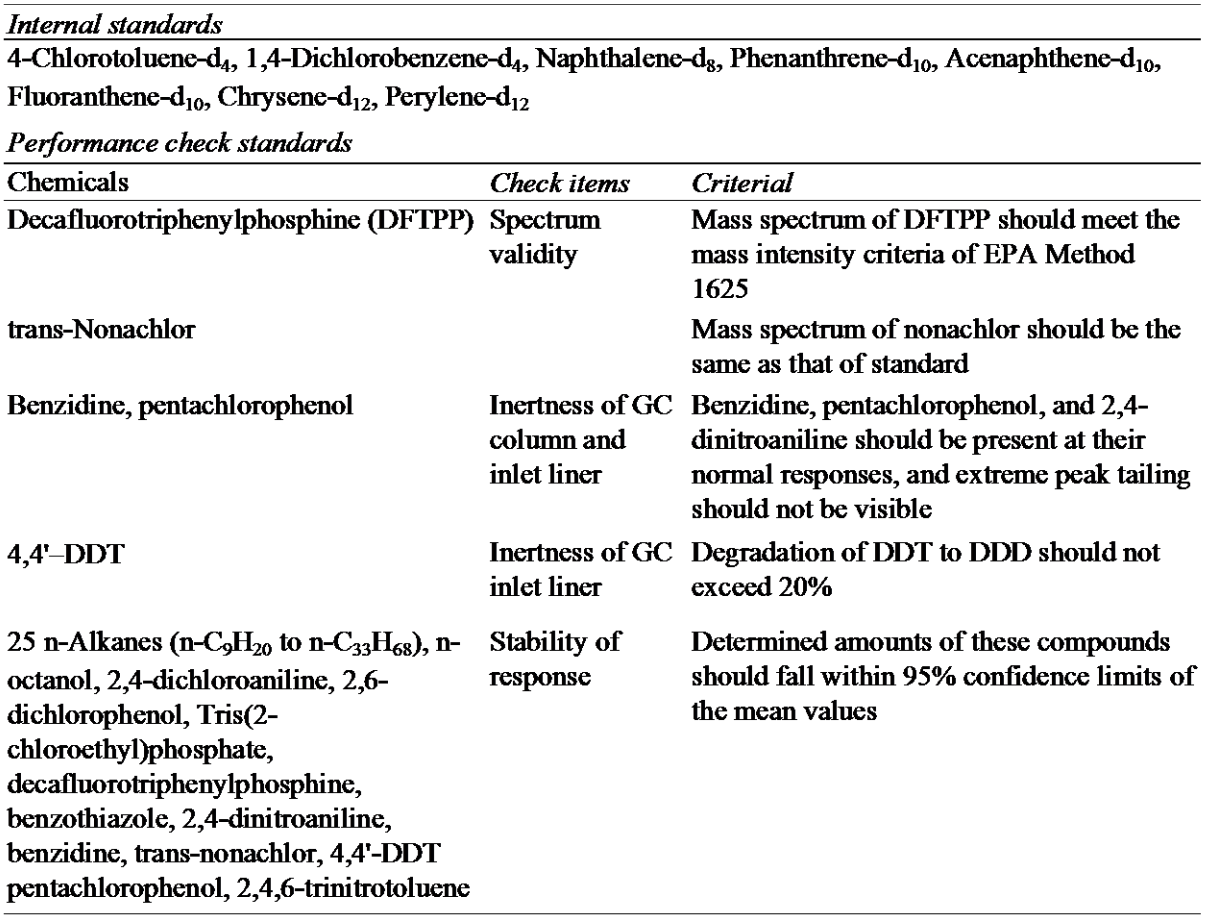
CHAPTER II COMPREHENSIVE ANALYTICAL METHODS FOR ORGANIC MICRO–POLLUTANTS

2.1 INTRODUCTION OF AUTOMATED IDENTIFICATION AND QUANTIFICATION SYSTEM USING GC–MS DATABASE (AIQS–DB)

A novel gas chromatography–mass spectroscopy database for automated identification and quantification of micro pollutants in environmental and food samples was developed by Kadokami in co–operation with Shimadzu Company on 2005. According to Kadokami et al. (2005), the database system consists of the database, which was created with Microsoft Access, and two interface software programs: Software A (trade name: Compound Composer – database registration phase) transfers retention times, mass spectra, and calibration curves in the calibration files of the GC–MS instrument to the database; Software B (trade name: Compound Composer – method creation phase) creates calibration files for the GC–MS instrument from the database. After the GC–MS conditions were set, target tuning to meet the criteria for EPA Method 625 was performed. Then the performance check standards (PCSs) solution was measured, the retention times of n–alkanes were confirmed, and GC–MS performance was determined by evaluating the analytical results in terms of the criteria in Table 2.1. If all the criteria were met, standard solutions of a chemical were measured for preparation of a calibration curve. Then, a calibration file for the chemical, which consisted of mass spectrum, retention time, quantification ion, calibration curve, and so forth, was created according to the conventional method. Finally, the calibration file data and the retention times of two n–alkanes between which the retention time of the chemical fell were registered in the database with Software A.

Currently, 940 OMPs representing a wide variety of use and origins are registered in the database (Table S2.1 in the Supplementary data). In GC–MS analysis, retention times, mass spectra and calibration curves of target chemicals are essential for both identification and quantification, and these data are registered in calibration files. However, because retention times and calibration curves are often affected by GC–MS conditions, therefore, standards for targets compounds should be measured to confirm retention times and calibration curves before sample analysis. GC–MS conditions used to analyze samples were maintained to be the same as those used to construct the database. To obtain correct analytical results, a PCS solution was used to predict retention times, tune the target mass, and evaluate the performance of the GC–MS system. As long as the analytical results for the PCS solution met the criteria, GC–MS performance was considered nearly the same as that used to construct the database, and therefore we expected the database system to provide reliable results.

Table 2. 1 Internal standards and performance check standards for GC–MS



Internal standards

4-Chlorotoluene-d_4, 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Phenanthrene-d_{10}, Acenaphthene-d_{10}, Fluoranthene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}

Performance check standards

Chemicals	*Check items*	*Criterial*
Decafluorotriphenylphosphine (DFTPP)	Spectrum validity	Mass spectrum of DFTPP should meet the mass intensity criteria of EPA Method 1625
trans-Nonachlor		Mass spectrum of nonachlor should be the same as that of standard
Benzidine, pentachlorophenol	Inertness of GC column and inlet liner	Benzidine, pentachlorophenol, and 2,4-dinitroaniline should be present at their normal responses, and extreme peak tailing should not be visible
4,4'–DDT	Inertness of GC inlet liner	Degradation of DDT to DDD should not exceed 20%
25 n-Alkanes (n-C_9H_{20} to n-$C_{33}H_{68}$), n-octanol, 2,4-dichloroaniline, 2,6-dichlorophenol, Tris(2-chloroethyl)phosphate, decafluorotriphenylphosphine, benzothiazole, 2,4-dinitroaniline, benzidine, trans-nonachlor, 4,4'-DDT pentachlorophenol, 2,4,6-trinitrotoluene	Stability of response	Determined amounts of these compounds should fall within 95% confidence limits of the mean values

The GC retention times of registered chemicals in actual samples were predicted from the retention times of n– alkanes measured before sample analysis. As long as the difference between predicted and actual retention times were less than 3 seconds, the method can be used to accurately predict retention times and designated GC conditions are applicable. However, when the column length was changed, the accuracy of the predicted retention times was still good as long as the same linear velocity, 40 cm/s, was used. But, we occasionally observed unexpected variations due to differences in the film thickness of the stationary phase and/or the internal diameter, even with a new column. These variations can be fixed by increasing the column head pressure from the initial pressure to 0.669 psi per one second delay of perylene–d_{12} to obtain correct predicted retention times.

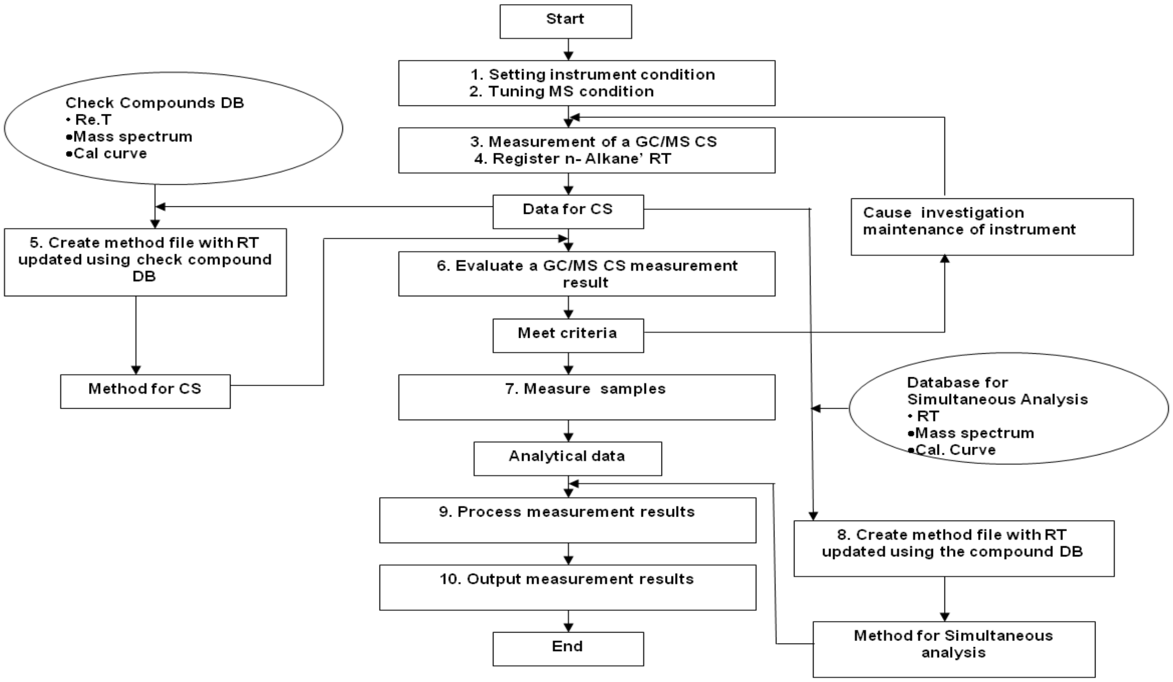


Fig. 2. 1 Measurement flow chart of chemicals using the AIQS database on GC–MS instrument

This database system was applied to various samples such as environmental waters, sediments, soils and foodstuffs (Kadokami et al., 2005). If chemicals registered in the database were presented in the samples, the chemicals could be accurately automated identified and quantified without the use of standards, and the identification method was as reliable as conventional methods. A particular advantage of the database system is that analysts get a comprehensive picture of chemical pollution in samples, which is difficult to achieve by using conventional methods. In addition, since the amounts and types of chemicals being produced have been rapidly increasing, this database system allowed to add new substances to the database therefore most of toxic chemicals to which GC–MS is applicable can be measured using the database in the future. These advantages of the database system arise from the fact that it can be used to measure a large number of chemicals simultaneously within 1 hour and micro–pollutants in samples can be analyzed efficiently and inexpensively (Kadokami et al., 2005). Fig. 2.1 shows a flowchart of an analysis for harmful chemical compounds using the database for simultaneous analysis.

2.2 REAGENTS AND MATERIALS

All of solvents used (acetone, dichloromethane, methanol and n–hexane) were of pesticide residue purchased from Kanto Chemical Co. (Tokyo, Japan). Reagents used for surrogate compounds and internal standards (IS) were purchased from Kanto Chemical Co., Wako Pure Chemical Industries (Osaka, Japan), Wellington Laboratories (Ontario, Canada), Sigma–Aldrich Japan K.K. (Tokyo, Japan) and Restek (Bellefonte, PA, USA) and were used in a 10 μg mL^{-1} acetone solution (surrogate) or in a 10 μg mL^{-1} hexane solution (IS). Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), disodium phosphate (Na_2HPO_4) and monosodium phosphate (NaH_2PO_4), at grade of 99% were supplied by Kanto Chemical Co., were used to prepare a buffer solution of 1 mol L^{-1} NaH_2PO_4–Na_2HPO_4 (pH 7.0). Empore SDB–XD SPE disks (styrene−divinylbenzene polymer, 47 mm, XD) and Empore Activated Carbon SPE disks (47 mm, AC) were purchased from 3M Co. (St. Paul, MN). Whatman GMF–150 circles(glass microfiber filter, 47 mm) were purchased from GE Healthcare UK LTD. (Buckinghamshire, UK). Activated copper (reduced copper, granular, super grade; Kishida Chemical, Tokyo, Japan), silica−gel cartridge (Sep–Pak VAC 2 g/12 mL; Waters Associates, Milford, MA, USA) and activated carbon column (ENVI−carb; Supelco, Bellefonte, PA, USA) were used in sediment analysis. Chem tube−hydromatrix (Varian, Palo Alto, CA, USA), was used to remove moisture from the sediments before extraction step. Purified water generated by a Milli−Q system (Milli−Q Biocel, Millipore, USA) was passed through Empore SDB−XD and activated carbon SPE disk/ or was washed with dichloromethane twice before used.

2.3 ANALYTIAL METHOD OF ORGANIC MICRO−POLLUTANTS IN ENVIRONMENTAL WATERS

2.3.1 Solid−phase extraction method (SPE−disk type)

2.3.1.1 Extraction method

Nine hundred and forty OMPs (Table S2.1) in the environmental waters were analyzed by the method of Jinya et al. (2013). Briefly, after addition of surrogates (1 μg) to 1–L of a water sample, pH of the sample was adjusted to 7.0 with a phosphate buffer. The sample was loaded on to disks (a flow rate less than 100 mL min^{-1}) in the sequence of (1) a glass microfiber filter GMF 150, (2) XD and (3) AC. These disks were previously pre−conditioned by passing 10 mL of dichloromethane (DCM), 10 mL of acetone, 10 mL of methanol and 20 mL water before use. Note that there are no bubbles exist between the disks during pre−conditioned steps and the disks were prevented from drying at all times during sample loading. The water remained in the disks was completely removed by using vacuum pump for 30 min. The target analytes on the GMF150 and 3M Empore XD were then together eluted with 5 mL of acetone (twice), followed by 5 mL of DCM. The targets on the AC were eluted with 5 mL of acetone (twice). The eulates were combined and concentrated into 1 mL under a gentle nitrogen stream, and then 10 mL of hexane was added to the concentrate. The water remained in the solution was removed by adding Na_2SO_4 (pre–heated at 700 °C in 6 hrs). The final solution was adjusted to 1 mL under a gentle nitrogen stream and was spiked with 100 μL of a IS solution (10 μg mL^{-1}) prior to instrumental analysis (GC–MS/ total ion current chromatograms (TIM)). Measurement conditions of GC–MS–TIM (Scan) were shown in Table 2.2. Total ion current chromatograms obtained by a GC–MS–Scan were treated with an identification and quantification system with a GC–MS database (AIQS–DB) (Kadokami et al., 2005), that can determine the concentrations of the 940 OMPs. The method detection limits (MDL) of the compounds measured by TIM were 5 to 500 ng L^{-1}.

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	2 min at 40°C, 8°C/min to 310°C, 5 min at 310°C
Injector	250°C
Transfer line	300°C
Ion source	200°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

2.3.1.2 Quality control

Verification of analytical method was carried out by spiking of 202 model compounds (MCs), representatives of OMPs that can be measured in the GC−MS condition of AIQS−DB, into purified water and environmental samples (Jinya et al., 2013). For purified water spike test, 1L of purified water spiked with the MCs at 0.1 μg L^{-1} was extracted. As a result, good recoveries were obtained: over 50% for 191 of the 202 MCs with an average recovery of

96% (50 – 118%) and less than 50% for eleven MCs. The MDLs of the SPE method were, on average, 0.034 μg L^{-1} (ranging from 0.011 to 0.078 μg L^{-1}) for the 191 MCs. These MDLs were deemed acceptable for the purpose of environmental water screening. For environmental sample spike test, three environmental samples (seawater, river water and a sewage treatment plant (STP) effluent, 1 L of each) were spiked with the MCs (0.1 μg L^{-1}) and extracted. Recoveries of over 50% from all three water samples for 186 MCs with an average recovery of 94% (50 – 111%) were obtained. Sixteen MCs had recoveries of less than 50% for at least one sample in this experiment. Overall, the SPE disk method can extract almost all of the OMPs from environmental samples, with the exception of aromatic compounds with logarithm of the octanol–water partition coefficient (log K_{ow}) of less than 1.

2.3.2 Liquid–liquid extraction method (LLE)

2.3.2.1 Extraction method

A water sample was warmed to room temperature before extraction. Thirty gram of sodium chloride (pre–heated at 700°C for 6 hrs) was added into a separatory funnel containing 1L of a water sample. The pH of the sample was adjusted at 7.0 with a phosphate buffer prior adding surrogate (1 μg) to the sample. The sample was extracted twice with 100 mL and 50 mL of DCM for 10 min each. Extracts were combined and dehydrated by passing through an anhydrous sodium sulfate column (10 mL) (Na_2SO_4 was pre–heated at 700°C for 6 hrs), then concentrated with a rotary evaporator (RE) to about 5 mL. And then 20 mL of hexane was added to the concentrate and the mixture was re–concentrated to 5 mL; the same procedure was repeated twice. Final concentrate was further concentrated to exact 1 mL under a gentle nitrogen stream, and then an internal standard solution (1μg each), which was designated for the use of measurement using the AIQS–DB, was added into the final concentrate and then was measured by automated identification and quantification system with a gas chromatography mass spectrometry database using a GC–MS (TIM). Measurement conditions of GC–MS–TIM were shown in Table 2.2. The MDL of the compounds measured by TIM were 5 to 500 ng L^{-1}.

2.3.2.2 Quality control

Quality controls were performed by analysis of 98 MCs, which were chosen from 882 compounds based on the physico–chemical properties, e.g. varied structure, functional groups, log K_{ow} and water solubility, spiking to purified and river waters (Kadokami et al., 2009). One liter of purified water and river water were spiked with the MCs at 1 μg L^{-1} and then treated in the same manner as in pretreatment of samples. Kadokami et al. (2009) had reported that, most compounds having log K_{ow}>1 were recovered at over 70% but hydrophilic compounds (log $K_{ow}<1$) could not be recovered sufficiently. Results of recovery test for river water samples were almost the same as those of purified waters. These results demonstrated that the LLE method with DCM was applicable to extract most of the OMPs in environmental water samples.

2.4 ANALYTICAL METHOD OF ORGANIC MICRO−POLLUTANTS IN SEDIMENT

2.4.1 Extraction method

Organic micro−pollutants (Table S2.1) in the sediments were analyzed by the method of Kadokami et al. (2012). Ten gram of wet sample was mixed with 7 g of hydromatrix and spiked with surrogates before extraction with DCM/acetone (1:1) for 30 min using an accelerated solvent extractor (ASE 350; Japan Dionex, Osaka, Japan). Thereafter, the extract was concentrated to 10 mL using a RE, and then the concentrate was added to 200 mL of a 5% sodium chloride solution. The solution was extracted with 30 mL of DCM twice. After dehydration of the extract with anhydrous sodium sulfate, the extract was concentrated to 10 mL by RE. Hexane (20mL) was added to the concentrate and then the extract was concentrated to 1 mL with a RE. This procedure was carried out twice for a complete change of the solvent. The extract was applied to a silica−gel cartridge and was separated into three fractions by sequential elution of hexane (Fr−1), 5% acetone–hexane (Fr−2), and 30% acetone–hexane (Fr−3). Fr−1 was treated with copper powder to remove sulfur. Fr−3 was passed through an activated carbon column to remove colored substances (e.g. non−volatile pigments) that damage a GC column. Each fraction was concentrated to 1 mL with a RE and spiked with a IS solution (1μg) prior to instrumental analysis (GC–MS–TIM). Measurement conditions of GC–MS–TIM were shown in Table 2.2. Total ion current chromatograms obtained by a GC–MS–Scan were treated with AIQS–DB (Kadokami et al., 2005) that can determine the concentrations of the 940 OMPs. The MDL for the substances were estimated from concentration ratio (or, ratio of the dry weight of a sample to the volume of a final concentrate), and the instrument detection limit (IDL) of Scan (Table S2.1). The MDL of the chemicals in the database was ≤ 2 ng g^{-1} dry−wt.

2.4.2 Moisture Analysis

Ten gram (wet) of a sediment sample was placed in a plate and dried in an oven at 105 ^{o}C for 2 hrs. The moisture content of the sample was determined by measuring the loss of weight in subsample after drying, and the final result in a sediment sample are presented as concentration per unit dry weight basic of the sample (as µg kg^{-1} dry−wt).

$$\%\ \text{Moisture content} = \frac{(\text{A} - \text{B})\ \text{X}\ 100}{\text{A}}$$

Where: A = weight of wet sample, mg

B = weight of dried residue, mg

2.4.3 Volatile Solids

The dried residue from (2.4.2) was transferred to a cool muffle furnace and was heated at 550 ^{o}C for 2 hrs (Standard method, 2005). After cooling it in a desiccator, its weight was measured with a chemical balance. The total volatile solid contain was calculated as below:

$$\%\ \text{Volatile solid} = \frac{(\text{A} - \text{C})\ \text{X}\ 100}{\text{A} - \text{B}}$$

Where: A = weight of dried residue + dish, mg

B = weight of dish, mg

C = weight of residue + dish after ignition, mg

2.4.4 Quality control

In order to confirm the performance of the analytical method, the overall recovery test was carried out by spiking 119 MCs (1 μg), that representative of the OMP registered in the AIQS–DB, to sediment samples (10 g wet wt) collected from the mouth of Dokai Bay in Kitakyushu City (total organic carbon, 0.4%) (Kadokami et al., 2012). Recoveries of 80% of the MCs were ranged from 60 to 120% and 21 (mainly polar compounds) out of 119 MCs were recovered lower than 60%, which probably due to oxidation during LLE and silica–gel column chromatography. Some substances, such as n–alkanes, octanol and 4–n–nonylphenol, had recovery > 100% due to the effects of the contamination from a silica–gel cartridge column. The results of recovery test had confirmed that this method could analyze most OMPs in sediments except for polar substances.

In order to validate (check the accuracy and the precision) the analytical method, a standard reference material (SRM, NIST 1941b, Organics in Marine Sediment; National Institute of Standards and Technology, Gaithersburg, MD, USA) was analyzed. The pretreatment procedure of SRM–1941b was the same manner as those of environmental samples. Instrumental measurements were done by GC–MS–TIM/ SIM; PAHs were measured by TIM and quantified by the AIQS–DB; PCBs and OCPs were measured by a GC–MS–SIM and a GC–MS–MS–SRM and quantified by calibration curves in the AIQS–DB and conventional internal standard method, respectively. Although the number of compounds certified in the SRM–1941b is much smaller than compounds registered in the AIQS–DB, if analytical results agree with certificated concentrations, analytical results for other compounds (except for highly polar substances) can be assumed be close to true concentrations (Kadokami et al., 2012).

Table 2. 3 Organochlorine pesticides and PCBs concentrations in NIST SRM–1941b

No	Name	Recovery, %	RSD, %	No	Name	Recovery, %	RSD, %
1	Benzo(a)pyrene	32	29	26	PCB #101	70	4.2
2	Fluorene	40	0.3	27	PCB #201	78	7.4
3	Naphthalene	43	4.1	28	PCB #95	82	6.3
4	3-Methylphenanthrene	54	8.3	29	PCB #99	82	6.8
5	2-Methylphenanthrene	60	4.4	30	PCB #49	83	0.1
6	Benzo(ghi)perylene	62	30	31	PCB #18	83	0.1
7	Anthracene	63	3.9	32	PCB #110	85	5
8	Pyrene	68	8.9	33	PCB #8	86	12
9	Fluoranthene	69	8.9	34	PCB #180	87	13
10	Benzo(a)anthracene	70	11	35	PCB #44	88	3.8
11	Chrysene & Triphenylene	70	6.4	36	PCB #149	89	2
12	trans-Nonachlor	71	4.5	37	PCB #187	90	0
13	Phenanthrene	77	4.3	38	PCB #118	94	9.8
14	Benzo(j,b&k)fluoranthene	82	22	39	PCB #156	96	14
15	1-Methylnaphthalene	87	3.3	40	PCB #87	97	12
16	p,p'-DDD	91	1.3	41	PCB #138&158	97	2.3
17	Indeno(1,2,3-cd)pyrene	97	17	42	PCB #128	100	4.2
18	Dibenzo(a,h)anthracene	102	1.5	43	PCB #209	103	0
19	cis-Chlordane	102	11	44	PCB #52	105	4.6
20	cis-Nonachlor	108	10	45	PCB #206	106	6.2
21	p,p'-DDE	114	4	46	PCB #170	112	8.5
22	Hexachlorobenzene	118	2.1	47	PCB #105	112	3.6
23	trans-Chlordane	123	4	48	PCB #194	113	9.5
24	Perylene	143	23	49	PCB #153&168	117	1.5
25	Benzo(e)pyrene	175	24	50	PCB #183	121	1.4
				51	PCB #28	137	1.7

The results of SRM–1941b analysis were shown in Table 2.3. Total 51 of the 60 certified and registered substances were detected. The results of PCBs congeners were in good agreement with the certified. The average recoveries of PCBs congeners were ranged from 70– 137% with relative standard deviations (RSD) of were below 14%, indicating the method produced the results in a good reproducibility and repeatability. Similarly, 14 out of

18 detected PAHs showed good recovery rates except for 4 compounds (benzo(a)pyrene, fluorene, naphthalene and 3−methylphenanthrene) that were not recovered sufficiency (less than 60%). This was considered likely to decrease of the concentration of the sample itself due to evaporation during storage/concentration or decomposed by light during treatment processes. The average RSD of PAHs ranging between 0.3 – 30%. Good recoveries of 6 OCPs were obtained (ranged from 71 – 118%) with RSD of less than 11%. Overall, the results of recovery test for SRM–1941b demonstrated that although results for some of the substances differed from the certificated values and the accuracy of the comprehensive method is slightly lower than that of the conventional methods, but it is sufficient for environmental survey.

2.5 TARGET ANALYSIS

Table 2. 4 GC−MS−MS conditions for target analysis

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
Injector	250°C
Transfer line	300°C
Ion source	250°C
Injection method	splitless, 1 min for purge−off time
Carrier gas	He
Flow rate	1.2 ml m^{-1}, constant flow mode
Ionization method	EI
Emission current	50μA
Measurement method	1

The comprehensive analytical method for OMPs utilizing AIQS−DB involves simultaneous measurement of SIM and TIM (Scan), which enables collection of both SIM data and full scan data in a single sample injection. Target substances by SIM (Table S2.2) quantified by internal standard method was applied to persistent organic compounds such as PCBs, PAHs, OCPs and sterols. A measurement condition of GC for SIM was the same as those of TIM (Table 2.2). The MDL of PAHs, OCPs, sterols and PCBs measured by SIM for water samples were 1, 2, 8–320 and 0.4–1.6 ng L^{-1}, respectively. For sediment, the MDL of the substances was ≤ 0.2 ng g^{-1} dry−wt.

Precise analysis of PCBs and OCPs was carried out on GC–MS–MS–SRM (Table S2.3) and quantified by internal standard method because some chemicals cannot be measured correctly by SIM due to effects of interference substances. The GC conditions were the same as those of GC–MS–SIM/TIM (Table 2.4). The MDL of OCPs and PCBs measured by SRM for water samples ranged from 0.1–0.4 ng L^{-1}, while for sediment the MDL of the targets was ≤ 0.02 ng g^{-1} dry–wt.

If samples were measured by multiple methods (Scan, SIM and/or SRM), we preferentially used the results from SRM, followed by SIM and finally, Scan.

2.6 STATISTICAL ANALYSIS

Statistical analysis was performed using Microsoft Excel 2007 (Microsoft Japan, Tokyo, Japan) and IBM SPSS Statistics Ver. 20 (IBM Japan, Tokyo, Japan).Microsoft Excel 2007 was used to calculate basic statistical values. IBM SPSS Statistics was used to carry out two multivariate analyses: cluster analysis and principal component analysis.

Cluster analysis is one of the multivariate methods, which aims to classify a sample of subjects (or objects) on the basis of a set of measured variables into a number of different groups such that similar subjects are placed in the same group. In this study, cluster analysis with hierarchical agglomerative method (Ward’s method and squared Euclidean distance) was carried out on the investigated water (sediment) samples using the concentration of detected chemicals, in order to identify distinct groups which have the similar pollution characteristics or pollution sources.

Principal component analysis (PCA) is a multivariate method used for data reduction purposes. It represents a set of variables by a smaller number of variables called principal components. Once the principle components have been calculated, it is needed to decide how many to keep. For example, choose sufficient principle components to account for a particular percentage (e.g 75%) of the total variability in the data. Or use scree plot of the eigenvalues, this will indicate whether there is an obvious cut–off between large and small eigenvalues. In this study, PCA was applied using normalized concentrations of detected contaminants in order to evaluate if there were similarities in pollution sources among sampling locations. The number of components was selected based on the percentage (over 70%) of the total variability in the data.

CHAPTER III   STUDY AREAS AND SAMPLING

3.1 STUDY AREAS AND SAMPLING SITES

3.1.1 Hanoi

Hanoi is the capital of Vietnam and the country's second largest city with population is 7.067 million and covers a total area of 3324 km^2 (2014). It comprises 12 urban districts, one district–level town and 17 rural districts. Hanoi stands the second nationwide in population number and ranks the first in Vietnam in terms of area. It is the most important political centre, economy, and trade of Vietnam. Hanoi city is located on the right bank of the Red River and 1760 km away from the north of Ho Chi Minh City (HCM), the biggest city in Vietnam. Hanoi features a warm humid subtropical climate with plentiful precipitation. The city experiences the typical climate of northern Vietnam, where summers are hot and humid, and winters are, by national standards, relatively cold and dry (URL10).

Hanoi has a density river network with over 10 rivers which are flowing throughout the city. Among them, Red River is the biggest river in the North of Vietnam and the second largest river in the country, which plays an important role in the agricultural production in the Northern part of Vietnam. Five main rivers following through Hanoi (Tolich, Kim Nguu, Lu, Set) and apart of the Nhue river has become a black and stinky waste water drainage canal, and its water quality is extraordinarily bad due to untreated wastewater discharged from domestic and industrial activities of the city. It was reported that 95% of capital's wastewater effluents are discharged without treatment and an estimated 450000 m^3 day^{-1}, of which 57% is of industrial origin, 41% of domestic origin and 2% is discharged from hospital, are discharged untreated into the rivers, hue, Lu, Set, Tolich and Kim Nguu in Hanoi city (DOSTE, 2003; Hoai et al., 2010). These emission sources affect the self–cleaning ability of the river. Beside, the solid waste disposed from Hanoi city is piled up and obstructed the river flow; therefore, water of rivers is more and more polluted. Phosphate, nitrate, nitrite, ammonium, biological oxygen demand (BOD), chemical oxygen demand (COD) and dissolved oxygen (DO) are heavily polluted parameters which were observed on these river systems. These pollutants give adverse effects not only on the quality of stream, sediments in the river but also farming, breeding and the health of public in surrounding areas. On the other hand, the deterioration of city's river water quality may also negatively impacts on groundwater used for water for daily life of the local people. However, the investigations on wide–range organic micro–contaminants in this river water remains to be studied. Therefore, it is important to assess the water quality and extent of organic micro– contaminants in these rivers.

In this study, four representative rivers (Nhue, Tolich, Lu, Kim Nguu) receiving most of city's untreated domestic wastewater were selected for investigating occurrence of OMPs and PFAAs in water and sediment. Groundwaters were also taken from 26 wells distributed over Hanoi city for investigating the occurrence of OMPs and PFAAs. Detailed description of sampling sites was given in (Fig. 3.1 and Table 3.1)

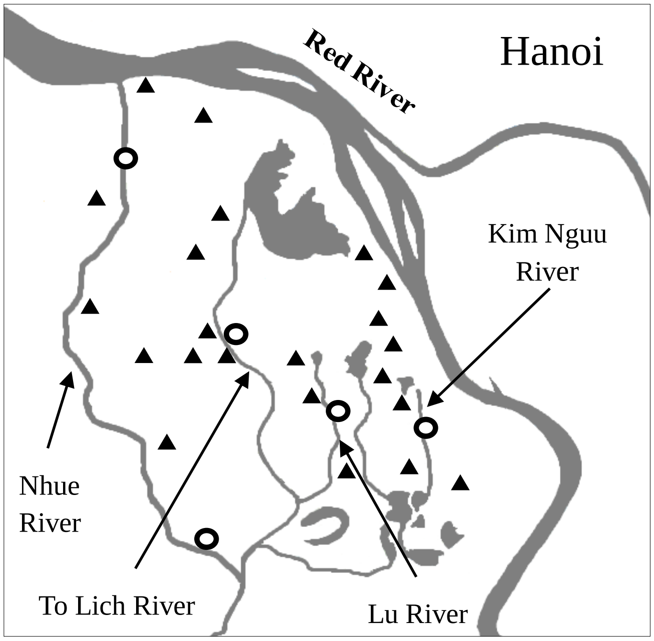


Fig. 3. 1 Surface, groundwater and surficial sediment collection points in Hanoi City

▲ Groundwater ○ surface water and sediment

Table 3. 1 Sampling locations of surface, groundwaters and sediments in this study

No.	Name of river (sampling bridge)/ Name of sampling location	Latitude	Longitude	Pollution of OMPs in environmental waters				Pollution of OMPs in sediments		Pollution of PFAAs in environmental waters	
				Surface water		Groundwater		No in Fig 5.1	Sampling time	No in Figs 6.1 and 3.2	Sampling time
				No in Fig 4.1	Sampling time	No in Fig 4.2	Sampling time				
	Hanoi										
	Surface water/sediment										
1	Nhue River (Noi bridge)	21° 3'41.69"N	105°46'20.50"E	HN1	Oct 2011 & Feb 2012	–	–	HN1	Oct 2011	HN4	Mar & Sep 2013
2	Nhue River (Mau Luong bridge)	20°57'39.81"N	105°47'46.65"E	HN2	Mar, Oct 2011 & Feb 2012	–	–	HN2	Oct 2011	HN5	Mar & Sep 2013
3	To Lich River (Moc bridge)	21° 0'31.89"N	105°48'48.58"E	HN3	Mar, Oct 2011 & Feb 2012	–	–	HN3	Oct 2011	HN3	Mar & Sep 2013
4	Lu River (Dinh Cong bridge)	20°58'58.77"N	105°50'5.18"E	HN4	Oct 2011 & Feb 2012	–	–	HN4	Oct 2011	HN2	Mar & Sep 2013
5	Kim Nguu River (Ku I bridge)	20°59'27.88"N	105°51'46.61"E	HN5	Oct 2011 & Feb 2012	–	–	HN5	Oct 2011	HN1	Mar & Sep 2013
6	Red River (Thanh Tri bridge)	20°59'37.09"N	105°54'5.66"E	HN6	Mar, Oct 2011 & Feb 2012	–	–	–	–	–	–
	Groundwater										
7	Quan Thanh ward, Ba Dinh district	21° 2'25.60"N	105°50'33.70"E	–	–	HN1	Sep 2013 & Aug 2014	–	–	No.1	Sep 2013
8	Chuong Duong ward, Hoan Kiem district	21° 1'53.80"N	105°51'24.70"E	–	–	HN2	Sep 2013 & Aug 2014	–	–	No.2	Sep 2013
9	Le Dai Hanh ward, Hai Ba Trung district	21° 0'49.50"N	105°50'57.10"E	–	–	HN3	Sep 2013	–	–	No.3	Sep 2013
10	Le Dai Hanh ward, Hai Ba Trung district	21° 1'13.14"N	105°51'8.84"E	–	–	HN3A	Aug 2014	–	–	–	–

Table 3.1 Sampling locations of surface, groundwaters and sediments in this study (continued)

No.	Name of river (sampling bridge)/ Name of sampling location	Latitude	Longitude	Pollution of OMPs in environmental waters				Pollution of OMPs in sediments		Pollution of PFAAs in environmental waters	
				Surface water		Groundwater		No in Fig 5.1	Sampling time	No in Figs 6.1 and 3.2	Sampling time
				No in Fig 4.1	Sampling time	No in Fig 4.2	Sampling time				
11	Le Dai Hanh ward, Hai Ba Trung district	21° 0'47.45"N	105°50'52.20"E	–	–	HN3B	Aug 2014	–	–	–	–
12	Thanh Nhan ward, Hai Ba Trung district	21° 0'10.30"N	105°51'27.70"E	–	–	HN4	Sep 2013 & Aug 2014	–	–	No.4	Sep 2013
13	Hoang Van Thu ward, Hoang Mai district	20°59'6.10"N	105°51'45.00"E	–	–	HN5	Sep 2013 & Aug 2014	–	–	No.5	Sep 2013
14	Linh Nam ward, Hoang Mai district	20°58'56.30"N	105°52'43.70"E	–	–	HN6	Sep 2013 & Aug 2014	–	–	No.6	Sep 2013
15	Nga Tu So ward, Dong Da district	21° 0'7.00"N	105°49'26.00"E	–	–	HN7	Sep 2013 & Aug 2014	–	–	No.7	Sep 2013
16	Dinh Cong ward, Hoang Mai district	20°59'24.50"N	105°49'42.7"E	–	–	HN8	Sep 2013 & Aug 2014	–	–	No.8	Sep 2013
17	Dinh Cong ward, Hoang Mai district	20°58'41.70"N	105°50'10.1"E	–	–	HN9	Sep 2013 & Aug 2014	–	–	No.9	Sep 2013
18	Co Nhue ward, Tu Liem district	21° 5'20.90"N	105°46'23.90"E	–	–	HN10	Sep 2013 & Aug 2014	–	–	No.10	Sep 2013
19	Xuan Dinh, Tu Liem district	21° 4'35.83"N	105°47'16.65"E	–	–	HN11	Sep 2013 & Aug 2014	–	–	No.11	Sep 2013
20	Nghia Do ward, Cau Giay district	21° 2'55.70"N	105°48'0.8"E	–	–	HN12	Sep 2013 & Aug 2014	–	–	No.12	Sep 2013
21	Dich Vong ward, Cau Giay district	21° 2'26.90"N	105°47'25.20"E	–	–	HN13	Sep 2013 & Aug 2014	–	–	No.13	Sep 2013
22	Nhan Chinh ward, Thanh Xuan district	21° 0'22.39"N	105°48'42.13"E	–	–	HN14	Sep 2013 & Aug 2014	–	–	No.14	Sep 2013
23	Nhan Chinh ward, Thanh Xuan district	21° 0'17.51"N	105°48'40.94"E	–	–	HN14A	Aug 2014	–	–	–	–

Table 3.1 Sampling locations of surface, groundwaters and sediments in this study (continued)

No.	Name of river (sampling bridge)/ Name of sampling location	Latitude	Longitude	Pollution of OMPs in environmental waters				Pollution of OMPs in sediments		Pollution of PFAAs in environmental waters	
				Surface water		Groundwater		No in Fig 5.1	Sampling time	No in Figs 6.1 and 3.2	Sampling time
				No in Fig 4.1	Sampling time	No in Fig 4.2	Sampling time				
24	Nhan Chinh ward, Thanh Xuan district	21° 0'20.07"N	105°48'49.36"E	–	–	HN14B	Aug 2014	–	–	–	–
25	Phu Dien ward, Tu Liem district	21° 3'15.59"N	105°45'44.99"E	–	–	HN15	Sep 2013 & Aug 2014	–	–	No.15	Sep 2013
26	Phu Do commune, Me Tri ward, Tu Liem district	21° 0'27.40"N	105°46'0.60"E	–	–	HN16	Sep 2013 & Aug 2014	–	–	No.16	Sep 2013
27	Me Tri ward, Tu Liem district	21° 0'11.10"N	105°46'55.80"E	–	–	HN17	Sep 2013 & Aug 2014	–	–	No.17	Sep 2013
28	Van Quan ward, Ha Dong district	20°58'39.74"N	105°47'24.20"E	–	–	HN18	Sep 2013 & Aug 2014	–	–	No.18	Sep 2013
	Ho Chi Minh City *Surface water/sediment*										
29	Sai Gon River (Sai Gon bridge)	10°47'56.04"N	106°43'37.94"E	HCM1	Mar, Oct 2011 & Feb 2012	–	–	HCM1	Oct 2011	HCM4	Mar and Sep 2013
30	Sai Gon River (Phu My bridge)	10°44'42.16"N	106°44'40.90"E	HCM2	Mar, Oct 2011 & Feb 2012	–	–	–	–	–	–
31	Dong Nai River (Dong Nai bridge)	10°54'5.71"N	106°50'20.80"E	HCM3	Mar, Oct 2011 & Feb 2012	–	–	HCM2	Oct 2011	HCM1	Mar and Sep 2013
32	Tham Luong-Vam Thuan Canal (Tham Luong bridge)	10°49'29.06"N	106°37'40.64"E	HCM4	Oct 2011 & Feb 2012	–	–	HCM3	Oct 2011	HCM7	Mar and Sep 2013
33	Nhieu Loc-Thi Nghe Canal (Le Van Sy bridge)	10°47'9.22"N	106°40'52.70"E	HCM5	Oct 2011 & Feb 2012	–	–	HCM4	Oct 2011	HCM8	Mar and Sep 2013

Table 3.1 Sampling locations of surface, groundwaters and sediments in this study (continued)

No.	Name of river (sampling bridge)/ Name of sampling location	Latitude	Longitude	Pollution of OMPs in environmental waters				Pollution of OMPs in sediments		Pollution of PFAAs in environmental waters	
				Surface water		Groundwater		No in Fig 5.1	Sampling time	No in Figs 6.1 and 3.2	Sampling time
				No in Fig 4.1	Sampling time	No in Fig 4.2	Sampling time				
34	Tan Hoa-Lo Gom Canal (Ong Buong bridge)	10°45'16.18"N	106°38'12.34"E	HCM6	Oct 2011 & Feb 2012	–	–	HCM5	Oct 2011	HCM9	Mar & Sep 2013
35	Doi-Te Canal (Chu Y bridge)	10°45'2.44"N	106°41'2.10"E	HCM7	Oct 2011 & Feb 2012	–	–	HCM6	Oct 2011	HCM10	Mar & Sep 2014
36	Sai Gon River (Ben Suc bridge)	11° 9'22.15"N	106°27'5.52"E	–	–	–	–	–	–	HCM2	Mar & Sep 2015
37	Sai Gon River (Phu Long bridge)	10°53'25.06"N	106°41'31.30"E	–	–	–	–	–	–	HCM3	Mar & Sep 2016
38	Sai Gon-Dong Nai River (Binh Khanh ferry)	10°40'1.60"N	106°46'27.41"E	–	–	–	–	–	–	HCM5	Mar & Sep 2017
39	Xang Canal (An Ha bridge)	10°55'5.56"N	106°33'46.86"E	–	–	–	–	–	–	HCM6	Mar & Sep 2018
40	Cho Dem River (Binh Dien bridge)	10°42'5.92"N	106°35'50.31"E	–	–	–	–	–	–	HCM11	Mar & Sep 2019
	Groundwater										
41	Hiep Binh Phuoc ward, Thu Duc district	10° 51'12.40"N	106°43'7.4"E	–	–	HCM1	Sep 2013	–	–	No.19	Sep 2013
42	Thanh Loc ward, District 12	10° 52'28.00"N	106°40'48.8"E	–	–	HCM2	Sep 2013	–	–	No.20	Sep 2013
43	Ward 14, Tan Binh District	10° 47'31.52"N	106°38'38.60"E	–	–	HCM3	Sep 2013	–	–	No.21	Sep 2013
44	Binh Tan District	10° 44'17.00"N	106°36'42.4"E	–	–	HCM4	Sep 2013	–	–	No.22	Sep 2013
	Hai Phong										
45	Re River (Re bridge)	20°52'1.53"N	106°36'47.48"E	HP1	Mar, Oct 2011 & Feb 2012	–	–	HP1	Oct 2011	–	–

Table 3.1 Sampling locations of surface, groundwaters and sediments in this study (continued)

No.	Name of river (sampling bridge)/ Name of sampling location	Latitude	Longitude	Pollution of OMPs in environmental waters				Pollution of OMPs in sediments		Pollution of PFAAs in environmental waters	
				Surface water		Groundwater		No in Fig 5.1	Sampling time	No in Figs 6.1 and 3.2	Sampling time
				No in Fig 4.1	Sampling time	No in Fig 4.2	Sampling time				
46	Chanh Duong River (Nhan Muc bridge)	20°41'6.82"N	106°28'52.15"E	HP2	Oct 2011 & Feb 2012	–	–	HP2	Oct 2011	–	–
47	Da Do River (Nguyet Ang bridge)	20°46'49.15"N	106°36'52.12"E	HP3	Oct 2011 & Feb 2012	–	–	HP3	Oct 2011	–	–
48	Tam Bac River (Quay bridge)	20°51'12.87"N	106°39'59.69"E	HP4	Mar, Oct 2011 & Feb 2012	–	–	–	–	–	–
49	Lach Tray River (Rao bridge)	20°49'41.04"N	106°41'58.48"E	HP5	Mar, Oct 2011 & Feb 2012	–	–	HP4	Oct 2011	–	–
	Hue										
50	Bo River (An Lo bridge)	16°32'39.42"N	107°27'19.69"E	–	–	–	–	–	–	HU1	Mar 2013
51	Bo River (Huong Can bridge)	16°31'2.93"N	107°32'6.48"E	–	–	–	–	–	–	HU2	Mar 2013
52	Huong River (Tuan bridge)	16°23'41.04"N	107°34'34.32"E	–	–	–	–	–	–	HU3	Mar 2013
53	Huong River (Cho Dinh bridge)	16°29'34.93"N	107°35'33.67"E	–	–	–	–	–	–	HU4	Mar 2013
54	Huong River (Thao Long dam)	16°32'49.99"N	107°37'1.40"E	–	–	–	–	–	–	HU5	Mar 2013
	Danang										
55	Trang River (Lien Chieu bridge)	16° 8'36.99"N	108° 7'18.43"E	DN1	Mar, Oct 2011 & Feb 2012	–	–	DN1	Oct 2011	DN1	Mar 2013
56	Cu De River (Nam O bridge)	16° 6'53.33"N	108° 6'16.53"E	–	–	–	–	–	–	DN2	Mar 2013
57	Phu Loc Canal	16° 4'8.48"N	108°10'52.61"E	DN5	Oct 2011 & Feb 2012	–	–	–	–	DN3	Mar 2013
58	Phu Loc Canal	16° 4'27.68"N	108°10'2.57"E	DN6	Oct 2011 & Feb 2012	–	–	–	–	–	–
59	A branch of Cam Le River (Tuy Loan bridge)	15°59'35.70"N	108° 8'37.90"E	DN2	Oct 2011 & Feb 2012	–	–	DN2	Oct 2011	DN4	Mar 2013

Table 3.1 Sampling locations of surface, groundwatersand sediments in this study (continued)

No.	Name of river (sampling bridge)/ Name of sampling location	Latitude	Longitude	Pollution of OMPs in environmental waters				Pollution of OMPs in sediments		Pollution of PFAAs in environmental waters	
				Surface water		Groundwater		No in Fig 5.1	Sampling time	No in Figs 6.1 and 3.2	Sampling time
				No in Fig 4.1	Sampling time	No in Fig 4.2	Sampling time				
60	Cam Le River (Cam Le bridge)	16° 0'30.72"N	108°12'25.51"E	DN3	Mar, Oct 2011 & Feb 2012	–	–	–	–	DN5	Mar 2013
61	A branch of Cai River (Qua Giang bridge)	15°58'20.54"N	108°12'31.99"E	–	–	–	–	–	–	DN6	Mar 2013
62	Han River (Han bridge)	16° 4'19.93"N	108°13'36.44"E	DN4	Oct 2011 & Feb 2012	–	–	–	–	DN7	Mar 2013
	Red River										
63	Lao Cai province (Coc Leu bridge)	22°30'11.61"N	103°58'6.90"E	–	–	–	–	–	–	Red 1	Mar 2013
64	Lao Cai province (Bao Ha bridge)	22°10'14.21"N	104°21'17.41"E	–	–	–	–	–	–	Red 2	Mar 2013
65	Yen Bai province (Yen Bai bridge)	21°41'41.45"N	104°52'13.90"E	–	–	–	–	–	–	Red 3	Mar 2013
66	Phu Tho province (Phong Chau bridge)	21°17'8.35"N	105°15'35.98"E	–	–	–	–	–	–	Red 4	Mar 2013
67	Phu Tho province (Trung Ha bridge)	21°14'4.15"N	105°21'4.61"E	–	–	–	–	–	–	Red 5	Mar 2013
68	Vinh Phuc province (Viet Tri bridge)	21°18'1.53"N	105°26'36.52"E	–	–	–	–	–	–	Red 6	Mar 2013
69	Vinh Phuc province (Vinh Thinh ferry)	21°10'0.39"N	105°29'7.40"E	–	–	–	–	–	–	Red 7	Mar 2013
70	Hanoi city (Thang Long bridge)	21° 5'57.33"N	105°47'11.22"E	–	–	–	–	–	–	Red 8	Mar 2013
71	Hanoi city (Thanh Tri bridge)	20°59'37.09"N	105°54'5.66"E	–	–	–	–	–	–	Red 9	Mar 2013
72	Hung Yen province (Chuong Duong ferry)	20°50'39.80"N	105°55'9.67"E	–	–	–	–	–	–	Red 10	Mar 2013
73	Ha Nam province (Yen Lenh bridge)	20°39'29.22"N	106° 2'5.38"E	–	–	–	–	–	–	Red 11	Mar 2013
74	Thai Binh province (Tan De bridge)	20°26'37.82"N	106°13'6.76"E	–	–	–	–	–	–	Red 12	Mar 2013
75	Thai Binh province (Sa Cao ferry)	20°22'12.39"N	106°20'38.83"E	–	–	–	–	–	–	Red 13	Mar 2013
76	Nam Dinh province (Ba Lat estuary)	20°17'29.68"N	106°32'57.05"E	–	–	–	–	–	–	Red 14	Mar 2013

3.1.2 Red River Delta

The Red River is the second largest river in Vietnam after Me Kong River (south Vietnam). It is an international river which rises in China and run through Vietnam before merging into the Gulf of Tonkin. The Red River delta is a main water supply source and important for agriculture activities in the Northern part of Vietnam, which has an important role in the agricultural production of the country. It had known as a heavy agricultural intensity area with almost three crops a year. The Red River delta is a typical example of a subtropical system experiencing high human pressure, which covers 8 provinces with two municipalities, the capital Hanoi and the port Hai Phong with a population of 19 million people (URL11). Surface water in the Red River is extensively used for not only irrigation but also it has been utilized for drinking and cooking by local residents. High density of industrial development and agriculture activities along the Red River basin may contribute pollutants to this river.

Total 14 river water samples (Red 1–14) were collected from 14 sites located at nine provinces along the Red River in March 2013 (Fig. 3.2, Table 3.1) for investigating the pollution of PFAAs in the river basin.

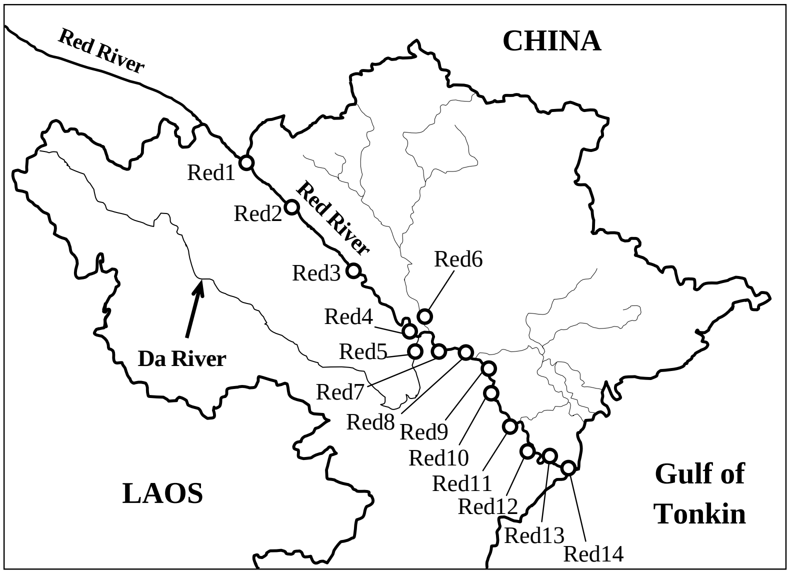


Fig. 3. 2 Surface water collection points on the Red River.

3.1.3 Hai Phong

Hai Phong (HP) is the third largest city and the second largest industrial centre in Vietnam with an area of 1527 km^2 and a population of 1.9 million by year 2013 (URL12). HP is a major port city, located in the east of Northern coastal area with the length of sea coast of about 125 km including the length of coast surrounding the offshore islands. The city is located in a convenient position for transportation to domestic provinces, and international networks via road network, railway, sea routes, and inland waterway. HP is located within the belt of tropical monsoons of Asia and adjoining the Eastern Sea, the climate can be divided into two distinct seasons, winter, and summer. The temperate is 1^{o}C warmer in winter and 1^{o}C cooler in summer than Hanoi.

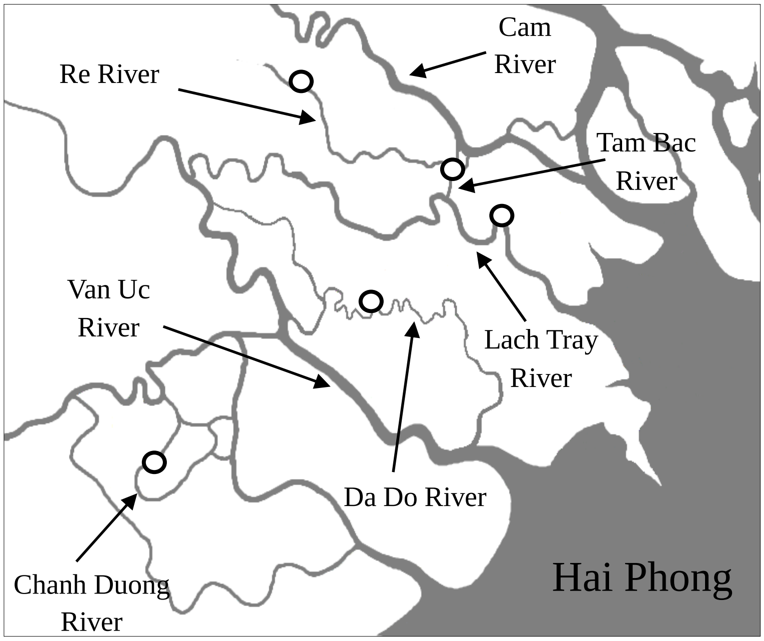


Fig. 3. 3Surface water and surficial sediment collection points in Hai Phong

○ surface water and sediment

HP has a dense network of rivers with an average density of 0.6 – 0.8 km of river per 1 km^2. All rivers in HP are tributaries of the Thai Binh River, which flows into the Gulf of Tonkin. There are 16 major rivers which spread over the entire territory of the city with the total length of more than 300 km. Lach Tray and Cam River are the main river flowing through the urban area and are main water source for agriculture activities of HP. Besides the major rivers, there are also many others small and medium river branches such as Gia River, Re River and Da Do River, which supply raw water sources for drinking water treatment plants in HP. However, these rivers are being encroached on both sides and pollution. River waters are polluted due to discharging of untreated domestic and industrial wastewater from thousand residences and industrial enterprises lying by these rivers. Agriculture activity is one of the major pollution sources contributing to the degradation of water quality at these rivers. In this study, five rivers (Tam Bac River, Lach Tray River, Re River, Da Do River, Chanh Duong River) were selected for investigating the occurrence of OMPs in water and sediment. Re River, Da Do River and Chanh Duong River are the important drinking water sources of HP while Tam Bac River is flowing through the city and is heavily polluted due to untreated industrial and domestic wastewater discharge. Five river water samples were collected from 5 rivers and four surficial river sediments were collected from four rivers except for Tam Bac River due to the dredging waterway. Detailed description of sampling sites was given in Fig. 3.3 and Table 3.1

3.1.4 Thua Thien Hue

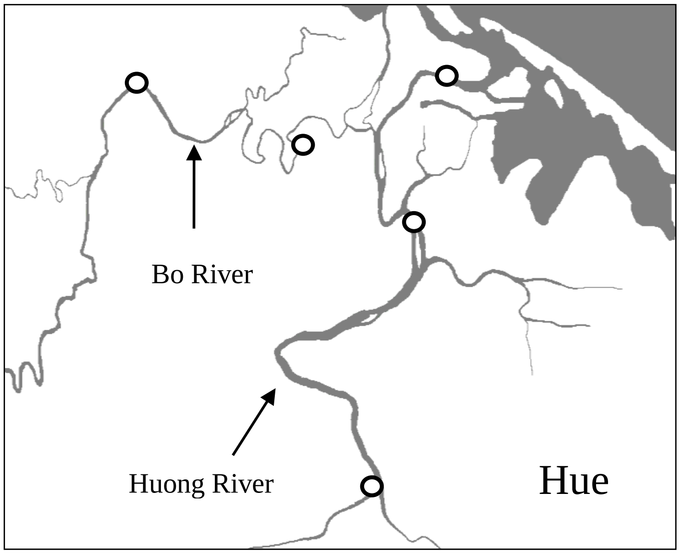


Fig. 3. 4 Surface water collection points in Hue

Hue (HU) is capital city of Thua Thien Hue province, which is located in central Vietnam developed in the flat land of the downstream basin of the Huong River (Perfume River). It is about 700 km south of Hanoi and about 1100 km north of HCM. The total area of the city is 72 km^2, including 27 urban wards with total population of 350000 in year 2013 (URL13). HU lies on the north–south transport axis of land, rail, sea, and air routes. It is located in the central key economic zones with the fast growing economy such as Chu Lai Open Economic Zone and Dung Quoc industrial zones with convenient transportation system that connects easily with Hanoi, HCM and other provinces in the country (URL13). HU features a tropical monsoon climate, the dry season is from March to August, and the rainy season is from August to January, with a flood season from October, onwards.

The Huong River, the largest river in Thua Thien Hue province, covers the majority area (56%) of Thua Thien Hue province that located in the east of Truong Son mountainous range and in the north of Bach Ma range. The Huong River mainstream originates from a high mountain area on the northwest of the Bach Ma range. The main flow of the Huong River has length of 104 km and a basin area of 2830 km^2 and playing an important role on water resource as well as inundation status of the province (Villegas, 2004). The Huong River has three main tributaries, namely the Ta Trach, the Huu Trach and the Bo.

In this study water samples were collected from a main stream of Huong River and a main tributary of Bo River to investigate the pollution of PFAAs. Total 5 sampling location were selected, in which 3 sites located in Huong River and 2 sites located in Bo River. Detailed information of the sampling locations is given in Fig. 3.4 and Tables 3.1.

3.1.5 Da Nang

Da Nang (DN) is a major port city in the South Central Coast of Vietnam, 764 km south of Hanoi and 964 km north of HCM. The total area of the city is 1256 km^2, including 6 urban districts (Cam Le, Hai Chau, Thanh Khe, Son Tra, Ngu Hanh Son, Lien Chieu) and 2 rural districts (Hoa Vang, Hoang Sa) with total population is 1100000 in (2014). DN borders with Thua Thien Hue Province in the north and Quang Nam Province in the south and the west, and the East Sea in the east. DN lies on the north–south transport axis of land, rail, sea and air routes (URL14) and has a 30 km coastline at the eastern part and considering as one of the important gateways to the sea of the central Highlands of Vietnam. DN is in a typical tropical monsoon zone with high temperature and equable climate. There are two seasons, the rainy season lasts from August to December, and the dry season from January to July.

There are two largest river basin systems in DN, they are Cu De and Tuy Loan river basin. Cu De river basin is located in the northern part of city and originates in Truong Son mountain and flows through Hoa Vang district to Lien Chieu district and finally flows into east sea at Nam O mouth. Tuy loan river basin rises in the western part of Hoa Vang district and flows west–east through Hoa Tien town and Hoa Vang district and finally joining by the Yen River to contribute Cau Do River. These river basins are very important that are supplying irrigation water for agricultural activities and aqua farming in DN. Beside these two important river basin systems, some canals flowing through the city are of public concerns recently due to its pollution. Phu Loc canal is the major city's canal which originates from Khanh Son, Hoa Khanh Nam Ward (Lien Chieu District) flowing through Hoa Minh Ward before merging into Da Nang Bay estuary. The canal is receiving wastewater from the canal tributaries systems. However, most of the canal tributaries have no collection systems therefore wastewater is discharged directly into the Phu Loc canal generates pollution, causing serious impacts on the environment.

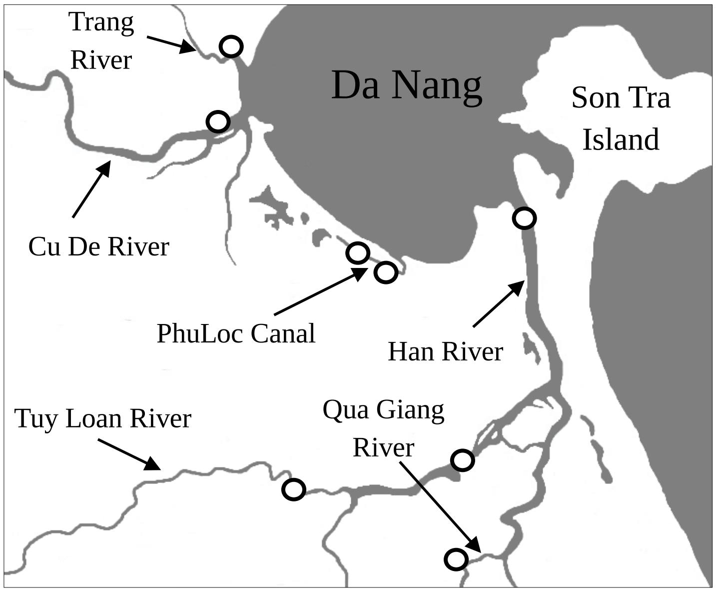


Fig. 3. 5 Surface water and surficial sediment collection points in Da Nang

Since DN has-been moving forward to urbanization and industrial expansion, environmental pollution by toxic chemicals has become serious. Therefore, monitoring water environment in this city is very important task to evaluate initial environmental condition of these rivers and find out the effective solution to prevent pollution in the future.

In this study, two largest river basin systems (Cu De and Tuy Loan) and a major canal (PhuLoc) in DN were selected to investigate occurrence of OMPs in water and sediment as well as the occurrence of PFAAs in water environment. Detailed description of sampling sites was given in (Fig. 3.5 and Table 3.1).

3.1.6 Ho Chi Minh City

Ho Chi Minh City (HCM) is the largest city in Vietnam with an area of approximately 2096 km^2 and population is nearly13 million in year 2014. It comprises 19 urban districts and 5 rural districts and stands the first nationwide in population number and ranks the second in

Vietnam in terms of area.HCM is located in the south of Vietnam from 10^o 10’–10^o 38’ North and 106^o22’–106^o54’ East. It is 1760km south of Hanoi and borders Tay Ninh Province and Binh Duong Province to the north, Dong Nai Province and Ba Ria–Vung Tau Province to the east, Long An Province to the west and the South China Sea to the south with a coast 15 km long (URL15). HCM is the economic center of Vietnam and accounts for a large proportion of the economy of the country. The city has a tropical climate, specifically a tropical wet and dry climate, with an average humidity of 75%. The year is divided into two distinct seasons. The rainy season, with an average rainfall of about 1800 mm annually (about 150 rainy days per year), usually begins in May and ends in late November. The dry season lasts from December to April. The average temperature is 28°C with little variation throughout the year. The highest temperature sometimes reaches 40°C in April, while the lowest may fall around 14°C in January (URL15).

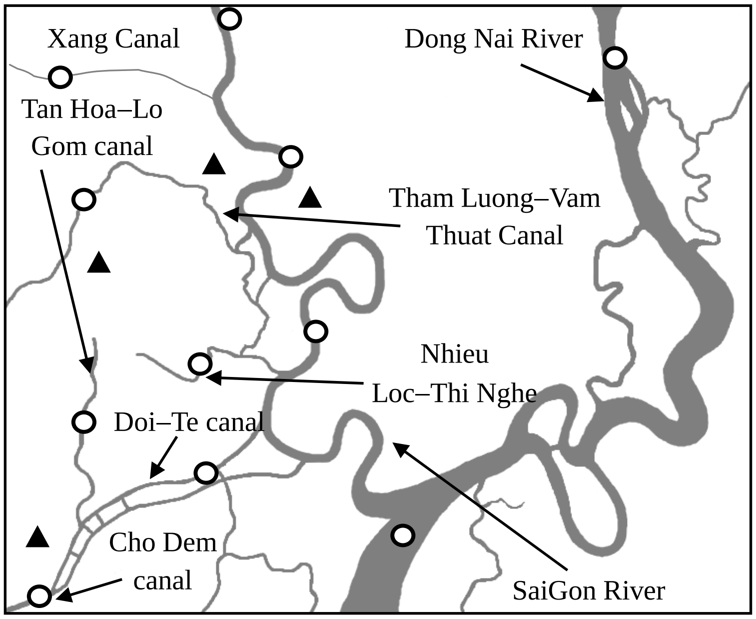


Fig. 3. 6 Surface, groundwater and surficial sediment collection points in Ho Chi Minh City

▲ Groundwater ○ surface water and sediment

HCM has a dense network of rivers and canals, hundreds of rivers and canals that flow through the city, in which Sai Gon and Dong Nai are two biggest river basins passing throughout the city. Dong Nai River basin and its surroundings cover the land of 11 provinces and cities (Dak Nong, Lam Dong, Ninh Thuan, Binh Thuan, Binh Phuoc, Binh Duong, Tay Ninh, Dong Nai, Long An, Ba Ria–Vung Tau and HCM), with the total area of about 48000 km^2, in which 47683 km^2 are in the country’s territory (99%). Only a small part (the river head of Be River, Sai Gon River and Vam Co River) lies in Cambodia. This river basin ranks the third largest basin after Mekong River and Red River in Vietnam. It has five major rivers: the Dong Nai mainstream, Be, Sai Gon, and La Nga River as major tributaries, and Vam Co Dong river system that joins the Dong Nai just before the outlet into the Sea. Dong Nai river basin is highly developed, with a relatively low share of agricultural GDP, relatively high income per capita, and a high population density, compared with other regions in Vietnam (Ringler and Nguyen, 2004, URL16). Saigon River Basin is located in southern Vietnam that rises near Phum Daung in southeastern Cambodia, flows south and south–southeast for about 225 km and combines with the Nha Be River which flows into the Sea after passing 20 km north–east of the Mekong Delta.

Saigon River is important to HCM as it is the main water supply as well as the host of Saigon Port. The Saigon River not only provides valuable water source to the HCM but also provides a great linking bridge for the country's trade and business. Saigon River flows through 40 industrial parks in Binh Duong, Binh Phuoc, Tay Ninh provinces and HCM. However, most of them do not have adequate industrial waste treatment system and most of the treated water released from facilities does not meet the quality required by environmental authorities. The Saigon River is also polluted by industrial and agricultural waste water from small–sized enterprises operating along the river.

Saigon and Dong Nai river basin has an important role in social and economic development in Vietnam since these basins encompasses the southern principal economic zone including HCM, Binh Duong, Dong Nai and Ba Ria–Vung Tau provinces. These provinces are the most predominant industrial area in Vietnam with a high rate economic growth. These rivers are the important sources of water for almost 7 million people living in the catchment areas. Large volumes of untreated municipal and industrial wastewater as well as accidental spills are released directly into the canal systems of the river. Beside, municipal solid wastes are dumped in open areas with poor management and, therefore, runoff from flood and rain events carry various toxic contaminants from these sites to the surface waters. Protection and remediation of the rivers from various pollutions caused by toxic discharges have become important tasks for sustainable development in this region, especially when demand for water supply has been increasing rapidly.

Beside two biggest river systems, the hundreds canals flowing through the city are seriously polluted due to untreated sewage discharge, especially in the densely populated areas. Therefore, in this study, two biggest river basins (Dong Nai and Sai Gon), six canals flowing through the city and four wells were selected for investigating occurrence of OMPs and PFAAs in water environment and sediment. Detailed description of sampling sites was given in (Fig. 3.6 and Table 3.1)

3.2. SAMPLING METHODS

3.2.1 Sampling for organic micro–pollutants

3.2.1.1 River water sample

River water at the center of a stream was sampled from a bridge by scooping the water with a stainless steel bucket, which was pre–cleaned with acetone, purified water and sample water. The water sample was then stored in a 1–L glass bottle, previously washed successively with a detergent, purified water, acetone, hexane, and water sample. The bottles containing water samples were kept in an ice–box and were transported to a laboratory. Water samples were stored in the dark at a temperature of $4^{o}C$ and extracted within 2 weeks after sampling.

3.2.1.2 Groundwater sample

Groundwater samples were mostly collected in drilled well at the depth from 16m to 35m (Table 3.1). Before samples were taken, each was pumped for 2 min in order to ensure that the water in the well is representative of the aquifer. Groundwater was stored in a 1–L glass bottle, previously washed successively with a detergent, purified water, acetone, hexane, and water sample. Samples labeled and stored in ice boxes were transported to a laboratory where then they were refrigerated until processed; processing was carried out within 1 to 2 days upon arrival at the laboratory.

3.2.1.3 Sediment sample

Surficial river sediment samples (5 cm depth) were collected using an Eckman–Bargegrab sampler (15 × 15 cm) previously pre–cleaned with acetone and water samples where the sediment samples were collected. The sediments collected were divided into three categories: (1) urban areas, (2) suburban areas and (3) rural districts. The samples labeled were stored in stainless steel bottles previously washed successively with a detergent, purified water, acetone and hexane and were transported to a laboratory in boxes packed with ice and kept at $-20\ ^{o}C$ until analysis.

3.2.2 Sampling for perfluoroalkyl acids

River water and groundwater sample:

Surface water samples from rivers and canals were collected at the center of a stream from a bridge with a stainless steel bucket, which was pre−cleaned with methanol, purified water and sample water. A water sample was stored in a 1 L polyethylene terephthalate (PET) bottle previously washed with methanol and purified water. Groundwater samples were mostly collected in drilled wells at the depth from 16m to 35m. Groundwater was pumped and discharged for 2 min in order to ensure that the water in the well is representative of the aquifer before it was taken into a clean PET bottle. The bottles containing surface and groundwater samples labeled were kept in an ice−box and were transported to a laboratory where then they were refrigerated until processed; processing was carried out within one week upon arrival at the laboratory.

CHAPTER IV POLLUTION OF ORGANIC MICRO–POLLUTANTS IN ENVIRONMENTAL WATERS

4.1 INTRODUCTION

Vietnam has being rapidly developing accompanied with extensive changes of its social and economic structure. Urbanization and industrial expansion cause the increase of urban populations, resulting in an increase in industrial and municipal waste, especially in highly industrialized and urbanized areas (eg. Hanoi, Hai Phong, Da Nang, HCM, etc.). There are high demands for fresh water and correspondingly large quantities of wastewater produced. The increasing contamination of water systems with domestic, industrial and agriculture compounds, which are released into the environment, have made Vietnam become an important subject for extensive studies dealing with environmental pollution during recent decades. In addition, the lack of adequate wastewater treatment facilities has lead chemicals released into environment via wastewater discharge. Hoai et al., (2010) reported that 95% of capital's wastewater effluents are discharged without treatment and an estimated 450000 m^3 day^{-1}, of which 57% is of industrial origin, 41% of domestic origin and 2% is discharged from hospital, are discharged into the rivers in Hanoi city. These emission sources affect the self–cleaning ability of the canals/ rivers. Phosphate, nitrate, nitrite, ammonium, COD, BOD, DO are heavily polluted parameters observed on Hanoi's river systems. It is perceptibly recognized that all canals in HCM have been heavily polluted due to the domestic wastewater discharge. The bad smell is frequently emitted and is worse at low tide; especially most canals in the inner city are affected by tide. IGES (2007) reported that, the daily wastewater quantity discharged into the canals in HCM was 710000 m^3 day^{-1} in 2000 and will be 2100000 m^3 day^{-1}in 2020. The BOD_5 load was 170 tons day^{-1} in 2000 and projected load will be 380 tons day^{-1} in 2020. In addition, the domestic and industrial wastewater of 729000 m^3 with a pollution load of more than 193000 kg in terms of BOD_5 is discharged daily to rivers and canals without any treatment. About 30000 m^3 day^{-1} of domestic wastewater and 15000 m^3 day^{-1} industrial wastewater from 5 of 15 industrial parks in HCM are conventionally treated.

There are eighty thousands of man–made chemicals that are currently used in today's society (Schaider et al., 2014) in vast quantities for a large of purposes including the production and preservation of food, industrial manufacturing processes, as well as for human and animal healthcare (Lapworth et al., 2012). In the last few decades there has been a growing interest in the occurrence of these "organic micro–pollutants" in the terrestrial and aquatic environment, their environmental fate and their potential toxicity (Clarke and Smith 2011; Kümmerer., 2009; Carrara et al., 2008; Kishida et al., 2007; Minh et al., 2006; Swartz et al., 2006; Kolpin et al., 2002; Nhan et al., 2001; Daughton and Ternes., 1999). There are a variety of pathways by which these OMPs can make their way into the aquatic environment such as direct discharge via wastewater treatment plants, landfills and land application of human and animal waste to farmland (Barnes et al., 2008). Groundwater may suffer pollution from many sources. For example, groundwater in urban areas is likely to be impacted by pollutants from sewage, industrial activities and diffuse leakages from reticulated sewer and septic systems (Ellis, 2006), while the main contributors to groundwater pollution in rural areas are probably fertilizers, agrochemicals and veterinary medicines related to agriculture, and animal waste (Boxall et al., 2004; Vàzquez–Suñé et al., 2010). However, the contamination of groundwater resources by OMPs is a growing concern and relatively poorly understood compared to other freshwater resources.

There are numerous investigations on pollution by chemicals in Vietnam that have been carried out in different environmental compartments: water, soil, sediment, food and biota, however the number of chemicals studied is limited, mainly focusing on specific chemical classes such as PCBs, OCPs, PAHs or dioxins (eg. polychlorinated dibenzodioxins, PCDDs) and their related compounds. Research has shown that many “emerging” persistent OCPs and PCBs enter the environment, disperse, persist to a greater extent and they have been found ubiquitously in water, soil and biota, not only in urban, industrialized areas but also in more remote environments. OCPs and PCBs were widely used in Vietnam since the 1960s for different purposes in agriculture, industry, and public health (Sinh et al., 1999; Thao et al., 1993a). Serious contamination by DDTs has been considered as a hot topic of concern due to its usage in huge quantities (Viet et al., 2000). Previous investigations that were conducted during the early 1990s dealing with various environmental media in Vietnam revealed that OCPs and DDTs contamination was apparent in soil, sediments and biota (Thao et al., 1993a; Iwata et al., 1994; Minh et al., 2006; Nhan et al., 2001; Monirith et al., 2003) and even in human breast milk (Minh et al., 2004). The contamination levels of these contaminants in Vietnam were in the high ranks among the developing countries and developed nations, which raise serious concern over the possible toxic impacts on human health.

The heavily pollution of surface water may affect aquifers via leaks in sewage canals, surface runoff or underground septic tanks, especially rural population of Vietnam is using groundwater pumped from individual private (family based) tube wells as sources for drinking water. In spite of this, to date there have been no comprehensive studies directed to the study of wide–spectrum organic pollutants in environmental waters in Vietnam, particularly in a wide–scale of study areas. In response to this situation, in the present study, a comprehensive monitoring survey has been conducted to examine great deal of OMPs in the water environment along Vietnam. Nine hundred and forty OMPs, comprising aliphatic compounds, benzenes, polycyclic compounds, PCBs, ethers, ketones, phenols, phthalates, fatty acid esters, aromatic amines, quinoline, nitro compounds, nitro amines, phosphoric esters, sterols, PPCPs and pesticides, representing a wide variety of uses and origins, were investigated (Table S2.1). To achieve this, an automated identification and quantification system with a GC–MS database and a developed comprehensive analytical method to fully utilize the AIQS–DB were used.

This method can be used for measuring a large number of chemicals simultaneously without the use of target standards, and the capability of identification and quantification were comparable with the conventional method using internal standards (Kadokani et al., 2004, 2005, 2009). Therefore, this valuable analytical tool should be widely applied in other developing countries, where the research on great deal of pollutants has not been thoroughly conducted due to the lack of facilities and investment as well as a good research approach. Once contamination levels of OMPs in water environment are determined, a whole pollution picture of OMPs that has not been known in Vietnam is able to be clarified. The main and high–risk identified substances in the first screening will be conducted in a detailed investigation.

4.2 SAMPLE COLLECTION

4.2.1 Surface water

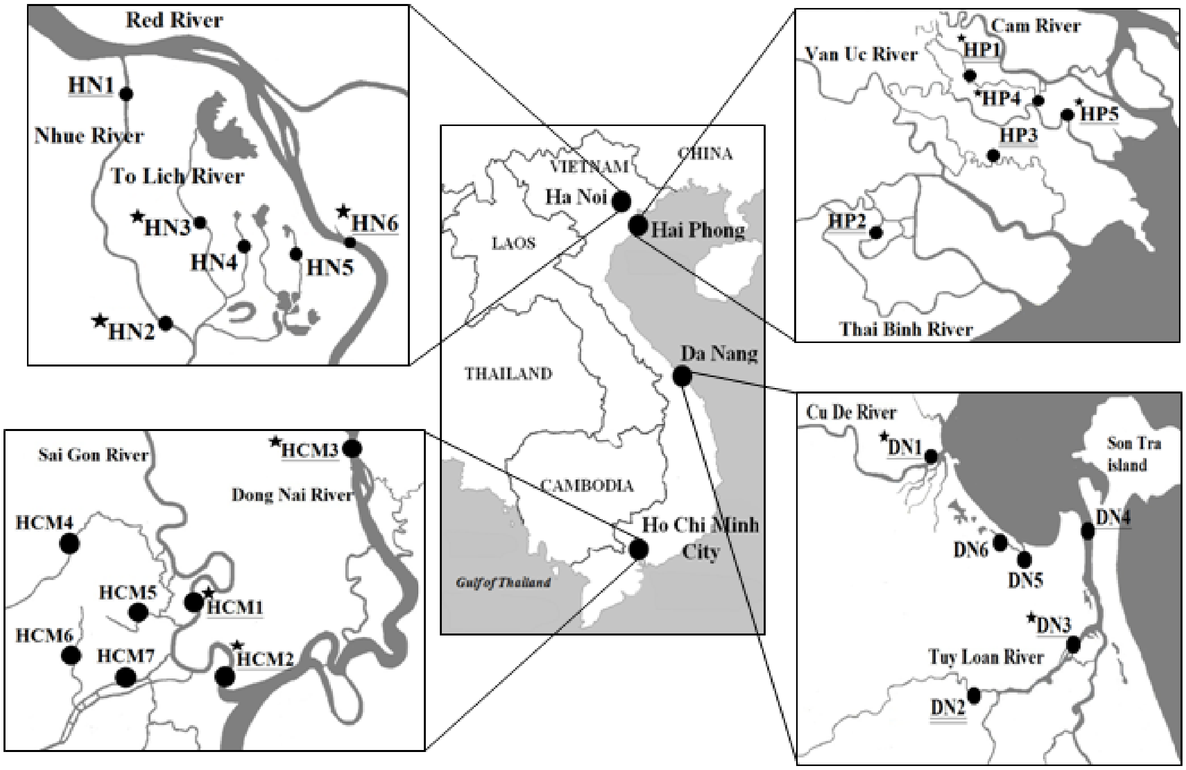


Fig. 4. 1 Location of 24 sampling sites in Hanoi, Haiphong, Danang and Ho Chi Minh City

Sites located in suburb and rural areas are indicated with a single and double underline whereas sites located in urban areas are indicated without an underline. Star symbols point out the sites that were sampled 3 times (March, October 2011 and February 2012), while others were sampled 2 times (October 2011 and February 2012).

In the dry (March, 2011 and February, 2012) and the rainy (October, 2011) seasons, 58 water samples were collected at 21 rivers and canals in towns, suburban districts and the center of four big cities: Ha Noi (5), Hai Phong (5), Da Nang (5) and Ho Chi Minh City (6) (Fig. 4.1). Sampling sites selected were representative of points that receive water discharged from human activities in the survey areas. The collection frequency of samples was described in Table 3.1. OMPs in surface water were extracted using liquid–liquid extraction method and the analytes were measured by AIQS–database using a GC–MS (TIM). Target analytes were also measured by GC–MS–SIM and GC–MS–MS–SRM.

4.2.2 Groundwater

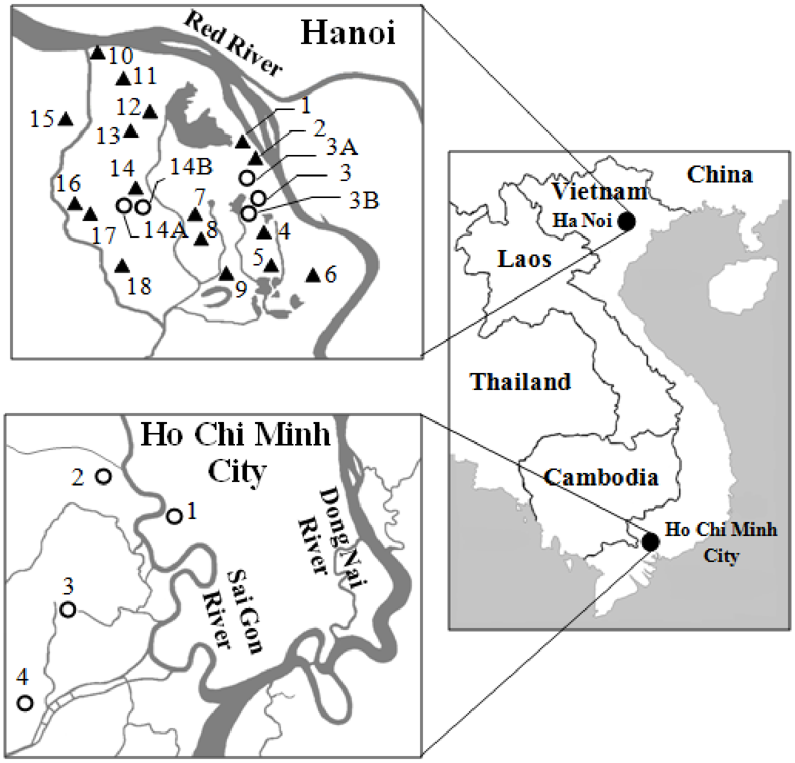


Fig. 4. 2 Locations of the 26 wells sampled in Hanoi and Ho Chi Minh City.

▲ two samples were collect ○ only one sample was collected.

Samples were collected from groundwater wells distributed over densely populated urban and suburban areas in HN and HCM (Fig. 4.2). The wells were not necessarily used for drinking water, but were close to sources of either unsewered household or industrial waste, which suggested that the water may be subject to organic pollution. Samples were collected twice in HN in the rainy seasons of 2013 and 2014 to examine if there was any variability in the occurrence and concentrations of the OMPs in the groundwater at different times of the year. A total of 22 samples were collected from 18 wells in HN and 4 wells in HCM in September 2013, while 21 samples were collected from 21 wells in HN (Fig.4.2, Table 3.1) in August 2014. Detailed information about the sampling locations is provided in Table 3.1 in the Supplementary data. OMPs in water were extracted using solid–phase extraction method and measured by GC–MS–AIQS–database, GC–MS–SIM and GC–MS–MS–SRM.

4.3 QUALITY CONTROL

Quality controls consisted of blank analysis, duplicate analysis and examining the recoveries of surrogates (deuterium–labeled internal standards), which were chosen as being representative of 940 compounds based on their physico–chemical properties. Thirty–eight and thirteen surrogates were spiked to surface and groundwaters, respectively, prior to extraction. Good recoveries (surface water, 70% – 127%) and (groundwater, 69% –115%) were obtained for most of surrogates except for highly polar and/or volatile compounds such as phenols (2–fluorophenol) and amines (2–animonaphthalene, 4–chloroaniline), which are difficult to extract. Tris(2–ethylhexyl)phosphate–d_{51}, fenitrothion–d_6, isofenphos oxon–d_6 showed high recovery rates, probably due to the matrix effect (Kadokami et al., 2012). Relative standard deviations of surrogates were mostly less than or equal to 21% (Table 4.1, 4.2), confirming that sample analyses were acceptably precise. Blank samples were processed regularly for every set of 10 samples (surface water) or/ 5 samples (groundwater) using 1–L of purified water, previously washed successively 3 times with dichloromethane (50 mL each) or/ passed through SPE disks (for groundwater). When reporting data, blank concentrations were subtracted from sample concentrations. Duplicate analyses were performed on the groundwater sample from well HN14 (Table S4.1), and the relative average deviations for 10 of the 13 detected substances were below 20%, indicating that the analyses gave results with good reproducibility and that the precision was sufficient for environmental surveys.

Table 4. 1 Recoveries (%) of surrogate compounds in spiked surface water samples (n=22)

No	Compound	Average recovery[a], %	RSD[b], %	Log Pow
1	1,2-Dichlorobenzene-d4	56	28	3.43
2	1,2-Diphenylhydrazine-d10	83	11	2.94
3	2,4,6-Tribromophenol	108	19	4.13
4	2,4-Dichlorophenol-d3	82	15	3.06
5	2-Aminonaphthalene-d7	0	0	2.28
6	2-Chlorophenol-d4	59	10	2.15
7	2-Fluorobiphenyl	73	13	–
8	2-Fluorophenol	27	24	–
9	2-Nitrophenol-d4	127	12	1.79
10	3,3'-Dichlorobenzidine-d6	46	59	3.51
11	4-Chloroaniline-d4	25	58	1.83

Table 4.1. Recoveries (%) of surrogate compounds in spiked surface water samples (n=22) (continued)

No	Compound	Average recovery[a], %	RSD[b], %	Log Pow
12	4-Methylphenol-d8	48	33	1.94
13	4-Nitrophenol-d4	64	29	1.91
14	Acetophenone-d5	74	17	1.58
15	Anthracene-d10	84	10	4.45
16	Benzidine-d8	42	50	1.34
17	Benzo(a)pyrene-d12	83	16	6.13
18	Benzophenone-d10	82	14	3.18
19	Bis(2-chloroethyl)ether-d8	82	21	1.29
20	Bisphenol A-d14	106	53	3.32
21	C20D42	83	14	–
22	C32D66	124	25	–
23	Dibenzothiophene-d8	81	10	4.38
24	Dimethylphthalate-d6	90	8	1.6
25	Diphenylamine-d10	70	26	3.5
26	Fenitrothion-d6	183	21	3.3
27	Fluorene-d10	92	16	4.18
28	Isofenphos oxon-d6	166	15	4.12
29	Isoxathion-d10	113	25	3.73
30	Nitrobenzene-d5	89	16	1.85
31	N-Nitrosodiphenylamine-d6	70	26	3.13
32	Pentachlorophenol-13C6	125	17	5.12
33	Phenol-d5	28	21	1.46
34	p-Terphenyl-d14	96	8	–
35	Pyrene-d10	102	14	4.88
36	Quinoline-d7	84	16	2.03
37	Simazine-d10	88	11	2.18
38	Tris(2-ethylhexyl)phosphate-d51	214	30	–

[a] One micro gram of each surrogate was added to the samples

[b] relative standard deviation.

Table 4. 2 Recoveries (%) of surrogate compounds in spiked groundwater samples (n=22).

No	Compound	Average recovery[a], %	RSD[b], %	Log Pow
1	2-Fluorophenol	42	18	–
2	1,2-Dichlorobenzene-d4	69	27	3.43
3	2,4-Dichlorophenol-d3	71	12	3.06
4	4-Chloroaniline-d4	96	7.3	1.83
5	Benzophenone-d10	75	18	3.18
6	Pentachlorophenol-13C6	93	6.0	5.12
7	4-Nonylphenol-d4	115	17	–
8	C20D42	69	22	–
9	BisphenolA-d14	81	25	3.32
10	p-Terphenyl-d14	60	20	–
11	4,4'-DDT-13C12	85	14	–
12	Tris(2-ethylhexyl)phosphate-d51	140	14	–
13	3,3'-Dichlorobenzidine-d6	85	20	3.51

[a] One micro gram of each surrogate was added to the samples

[b] relative standard deviation

4.4 RESULT AND DISCUSSION

4.4.1 Surface water

4.4.1.1 Occurrence of organic micro–pollutants

The number of detected chemical ranged from 29 to 103 (median 61 out of 940) with 235 analytes detected at least once. These detected compounds consist of a variety of chemical groups such as aliphatic hydrocarbons, benzenes, PAHs, PCBs, ketones, phenols, phthalates, aromatic amines, sterols, PPCPs, and pesticides. The number of compounds detected was higher in the rainy season (198) than in the dry season (177) (Table 4.3). This number of observations was higher than that observed in streams in Japan using the same method (188; Kadokami et al., 2009). The rivers in Hanoi (HN2 to 5) and Ho Chi Minh City(HCM4 to 7) produced the largest number of detected compounds as well as the highest concentrations (Fig. 4.3), particularly PAHs, PCBs, sterols, PPCPs and pesticide. The results indicated that the development of these cities with high population and dense industrial zones results in heavy pollution of rivers with untreated wastewater. Among ten sterol compounds analyzed: beta–sitosterol, campesterol, cholestane, cholestanol, cholesterol, coprostanol, coprostanone, epicoprostanol, ergosterol and stigmasterol, seven of them were found above 80% frequency except for cholestane (40%), ergosterol (9.0%) and stigmasterol (69%). Sterols contributed more than 40% of total concentrations at most sites (Fig. 4.3).

Thirty–eight out of the 457 pesticides in the database were found: 25 insecticides, 5 herbicides and 8 fungicides. Fenobucarb, an insecticide used in paddy fields, was the most frequently detected pesticide (84%) and was followed by metabolites from DDT (above 31%). Some banned pesticides, such as hexachlorocyclohexanes and chlordanes were also detected. Other than these, PAHs were detected at relatively low concentration, ranging from not detected to 4.6 μg L^{-1}. Nine of 14 PPCPs analyzed were detected, and caffeine was the most frequently detected compound (97%) at the highest concentration (92 μg L^{-1}), the following by diethyltoluamide (DEET, 86%) and L–menthol (71%). In general, chemicals from domestic sources were dominant in comparison with those from agricultural and industrial sources. This finding implies that untreated wastewater from domestic sources in highly populated urban areas was the main cause of river pollution.

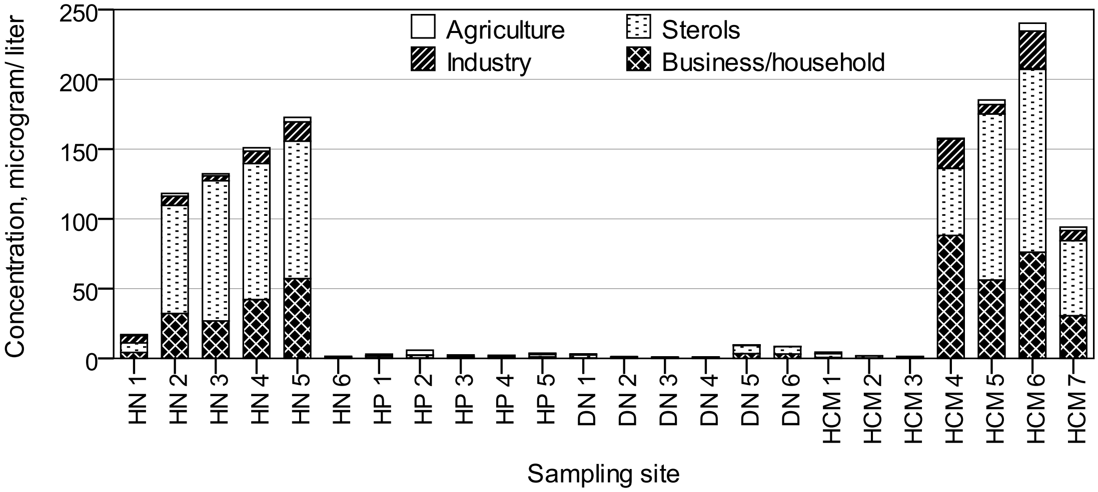
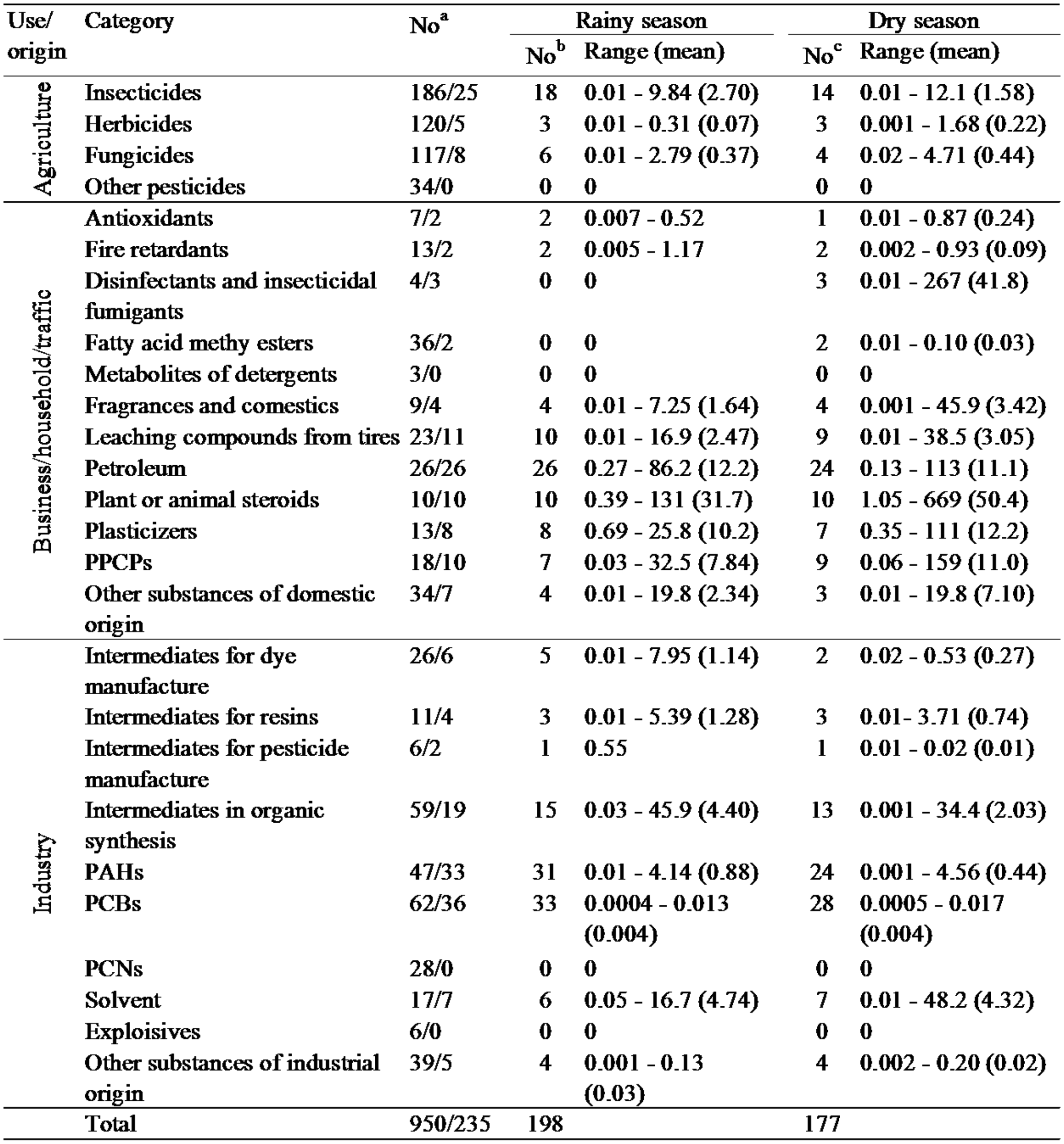


Fig. 4. 3 Concentrations (μg L^{-1}) and compounds categorized by origin at each site (rainy season)

[n–Alkanes and phthalates were excluded because these compounds were detected in reagent blanks. Figures above each column show the number of compounds detected. Contents of origins are referred to category in Table 4.3].

Table 4. 3 Concentrations (μg L^{-1}) of chemicals categorized by use or origin



Use/ origin	Category	No[a]	Rainy season		Dry season	
			No[b]	Range (mean)	No[c]	Range (mean)
Agriculture	Insecticides	186/25	18	0.01 - 9.84 (2.70)	14	0.01 - 12.1 (1.58)
	Herbicides	120/5	3	0.01 - 0.31 (0.07)	3	0.001 - 1.68 (0.22)
	Fungicides	117/8	6	0.01 - 2.79 (0.37)	4	0.02 - 4.71 (0.44)
	Other pesticides	34/0	0	0	0	0
Business/household/traffic	Antioxidants	7/2	2	0.007 - 0.52	1	0.01 - 0.87 (0.24)
	Fire retardants	13/2	2	0.005 - 1.17	2	0.002 - 0.93 (0.09)
	Disinfectants and insecticidal fumigants	4/3	0	0	3	0.01 - 267 (41.8)
	Fatty acid methy esters	36/2	0	0	2	0.01 - 0.10 (0.03)
	Metabolites of detergents	3/0	0	0	0	0
	Fragrances and comestics	9/4	4	0.01 - 7.25 (1.64)	4	0.001 - 45.9 (3.42)
	Leaching compounds from tires	23/11	10	0.01 - 16.9 (2.47)	9	0.01 - 38.5 (3.05)
	Petroleum	26/26	26	0.27 - 86.2 (12.2)	24	0.13 - 113 (11.1)
	Plant or animal steroids	10/10	10	0.39 - 131 (31.7)	10	1.05 - 669 (50.4)
	Plasticizers	13/8	8	0.69 - 25.8 (10.2)	7	0.35 - 111 (12.2)
	PPCPs	18/10	7	0.03 - 32.5 (7.84)	9	0.06 - 159 (11.0)
	Other substances of domestic origin	34/7	4	0.01 - 19.8 (2.34)	3	0.01 - 19.8 (7.10)
Industry	Intermediates for dye manufacture	26/6	5	0.01 - 7.95 (1.14)	2	0.02 - 0.53 (0.27)
	Intermediates for resins	11/4	3	0.01 - 5.39 (1.28)	3	0.01- 3.71 (0.74)
	Intermediates for pesticide manufacture	6/2	1	0.55	1	0.01 - 0.02 (0.01)
	Intermediates in organic synthesis	59/19	15	0.03 - 45.9 (4.40)	13	0.001 - 34.4 (2.03)
	PAHs	47/33	31	0.01 - 4.14 (0.88)	24	0.001 - 4.56 (0.44)
	PCBs	62/36	33	0.0004 - 0.013 (0.004)	28	0.0005 - 0.017 (0.004)
	PCNs	28/0	0	0	0	0
	Solvent	17/7	6	0.05 - 16.7 (4.74)	7	0.01 - 48.2 (4.32)
	Exploisives	6/0	0	0	0	0
	Other substances of industrial origin	39/5	4	0.001 - 0.13 (0.03)	4	0.002 - 0.20 (0.02)
	Total	950/235	198		177	

[a] The number of target compounds per the number of compounds detected at least once; [b]the number of compounds detected in the rainy season; [c]the number of compounds detected in the dry season; mean: average of detected concentrations; rainy season: October 2011; Dry seasons: March 2011 & February 2012.

4.4.1.2 Sterols and caffeine

Of the 10 sterols analyzed, β–sitosterol, campesterol, cholesterol, coprostanol and coprostanone were the most abundant, being observed in nearly 100% of samples (Table 4.4). The sum of sterol concentrations ranged from 0.39 μg L^{-1} (DN4, Oct 2011) to 669 μg L^{-1} (HN3, Mar 2011) with a mean value (43 μg L^{-1}). The total sterol concentrations in the dry season ranged from 1.05 to 669 μg L^{-1} while in the rainy season were 0.39 to 131 μg L^{-1}. The maximum concentrations of total sterols were around 2 times higher than those in Mekong Delta and about 10 times higher than in Tokyo (Takada et al., 2004). The canals flowing through densely population centers (e.g., Hanoi: HN2 – 5 and Ho Chi Minh: HCM4 – 7) were extremely polluted, with the average concentrations were 10 times higher than those in other rivers, suggesting that they are derived from sewage.

Table 4. 4 The range, mean (μg L^{-1}) and detection frequency (%) of sterols in water samples (n=58)

No	Compound	Min–Max (mean)	Detection frequency, %
1	beta-Sitosterol	ND – 50 (4.0)	98
2	Cholesterol	0.27 – 178 (12)	100
3	Coprostanol	ND – 189 (11)	98
4	Ergosterol	ND – 0.22 (0.17)	9.0
5	Stigmasterol	ND – 17 (1.6)	69
6	Cholestance	ND – 0.11 (0.04)	40
7	Epicoprostanol	ND – 89 (7.2)	74
8	Coprostanone	ND – 57 (3.1)	98
9	Cholestanol	ND – 59 (4.7)	88
10	Campesterol	ND – 31 (2.1)	97

ND represents “not detected”.
mean represents the average concentration of detected chemicals.

Coprostanol was first suggested as an indicator of fecal pollution in the late 1960s (Murtaugh & Bunch, 1967) and has been used as a powerful molecular marker for fecal pollution monitoring in several environmental matrices (Eganhouse et al., 1988; Leeming et al., 1996), which was the most dominant compound detected at 98% samples. The coprostanol concentrations ranged from not detected to 189 μg L^{-1} (mean 11 μg L^{-1}). The highest concentration of coprostanol (HN3, 189 μg L^{-1}) was observed at the sites located inside city areas in the dry season, which was higher than those reported in Japan in the 1970s (24 μg L^{-1}, Itoh and Tatsukawa, 1978) or in Canada (22 μg L^{-1}, Dougan and Tan, 1973). While the highest coprostanol concentration observed in the rainy season (HCM5, 37.7 µg L^{-1}) was higher than those reported in Malaysia in 1999 (11.5 µg L^{-1}) or in Mekong Delta (Vietnam) in 2000 (13.5 µg L^{-1}) and much higher than those in other urban center worldwide (Takada et al., 2002). The results demonstrated that rapid industrial development and urbanization expansion in recent decades accompanied with leakage of wastewater treatment facilities in Vietnam are the causes of heavy pollution in water environment, especially reviving water bodies at metropolitan areas. However, some sites located in rural areas and far away from river system receiving sewage released were observed at relatively low concentration of coprostanol. Therefore, in this case coprostanol was probably originated from biogenic sources such as cyanobacteria, microalgae, phytoplankton and zooplankton (Venkatesan and Santiago, 1989).

Cholesterol was found at all sampling sites with concentrations ranged from 0.27 µg L^{-1} to 178 µg L^{-1} (mean 12 µg L^{-1}). The highest concentration (178 µg L^{-1}) was observed in the dry season (Mar 2011) in highly populated area of Hanoi (HN3), where domestic wastewater from habitant living along watershed was direct discharged to the canal. Since cholesterol has a variety of potential sources including sewage disposal, terrestrial enrichment and contribution by algae and zooplankton (even though it is the main higher animal sterol) (Puglisi et al., 2003; Seguel et al., 2001). Consequently, this ubiquitous sterol has limitations in being used as independent marker, although it can be applied in the form of a ratio with other sterol (Masni et al., 2011). In addition, coprostanol has been proposed as a powerful molecular marker for fecal pollution monitoring and has been applied to several environmental matrices (Eganhouse et al., 1988; Venkatesan and Kaplan, 1990; Leeming et al., 1996). Therefore, the ratio of copostanol to cholesterol can be used to indicate sewage (>0.2, Grimalt et al., 1990) or human feces (>0.3, Glassmeyer et al., 2005). In this study, copostanol to cholesterol ratios over 0.8 were found in canals in Hanoi and Ho Chi Minh, with the high ratio confirming that human feces were discharged to the canals without treatment. However, all sampling sites in Hai Phong (HP1−5) and four sites in Da Nang (DN1−4) had low ratio values (<0.2), which suggested the less effect of sewage to these river basins due to the dilution of stream or these sites are located in rural areas and far away from river system receiving sewage released.

A coprostanol isomer, epicoprostanol, is widely used to assess sewage contamination in aquatic environments (Masni et al., 2011), which was detected in 74% samples with concentration ranged from not detected to 89 µg L^{-1} (mean 7.2 µg L^{-1}). The high epicoprostanol concentrations were detected at densely populated areas of HN and HCM in the dry seasons such as HN3 (89 µg L^{-1}, Mar 2011), HCM 6 (24 µg L^{-1}, Feb 2012) and HN5 (23 µg L^{-1}, Feb 2012). Epicoprostanol is only present in trace amounts in human sewage

(McCalley et al., 1981) and is formed from the microbial conversion from cholesterol to coprostanol and lastly to epicoprostanol during sewage treatment (Masni et al., 2011). In this study, the epicoprostanol identified at 74% sampling sites with high concentrations (mean 7.2 μg L^{-1}) in corresponding to cholesterol (100%, mean 12 μg L^{-1}) and coprostanol (98%, mean 11 μg L^{-1}), which indicated that there is no microbial conversion from cholesterol to coprostanol and epicoprostanol as well as there is no treated sewage in the study areas.

Caffeine has been detected in wastewater, surface water and groundwater worldwide (Buerge et al., 2003, 2006). This ubiquitous compound has been identified as an anthropogenic marker for wastewater contamination of surface waters or as an indicator of untreated wastewater (Nakada et al., 2008). Caffeine was found in 57 out of 58 samples at concentrations up to 92 μg L^{-1} (HN3, Mar 2011). These concentrations were much higher than maximum concentrations in Germany (0.13 μg L^{-1}; Prösch & Puchert, 1998) and Greece (0.16 μg L^{-1}; Patsias and Papadopoulou–Mourkidou, 2000). The distribution of caffeine in the aquatic environment in Vietnam is likely to correlate with population density; therefore, urban areas (Hanoi and Ho Chi Minh) were expected to be hotspots of such contamination due to the lack of wastewater treatment facilities. The high detection frequency of caffeine (98%) and coprostanol (98%) with high concentrations at most sites again verified that wastewater from domestic sources is a major cause of pollution in the rivers.

4.4.1.3 Pesticides

Thirty–eight out of the 457 pesticides in the database were found: 25 insecticides, 5 herbicides and 8 fungicides (Table 4.3). The most frequently detected pesticide was fenobucarb (84%), a carbamate insecticide widely used in paddy fields in Vietnam, followed by metabolites from DDT (above 31%), isoprothiolane (31%) and piperonyl butoxide (29%). Surprisingly, several organochlorine insecticides such as α–hexachlorocyclohexane (α–HCH), β–HCH, aldrin, endrin, DDT and its metabolites, dieldrin, trans–chlordane, cis–chlordane, heptachlorepoxide(B), that have been banned from use in Vietnam since 1990s (Hung and Thiemann, 2002), were detected in some studies areas but their concentrations were one–twentieth of those reported by Hung and Thiemann (2002) and were much lower than the allowable limit of Vietnamese standard for surface water (QCVN 08:2008/BTNMT/category B1) (Table 4.5).

p,p'–Dichlorodiphenyldichloroethylene (p,p'–DDE), o,p'–dichlorodiphenyldichloroethane (o,p'–DDD), p,p'–DDD which are breakdown product of p,p’–DDT were detected at 28, 21 and 32 out of 58 sampling sites at high concentrations up to 2.95 ng L^{-1} (HCM5) and 2.57 ng L^{-1} (HCM6), respectively. p,p’−DDT found at 12 out of 50 sampling sites with the highest concentration (0.71 ng L^{-1}, HCM5) just above detection limit (0.5 ng L^{-1}). Relatively high levels of p,p'–DDE, p,p'–DDD observed in this survey suggested that p,p'–DDT, a parent of these compounds, was applied in the study areas. α–HCH was only found at 14 sampling sites with the highest concentration up to 1.99 ng L^{-1} (HN5) while and β–HCH (0.30 ng L^{-1}) was found at only a site with level below detection limit (2 ng L^{-1}). Chlordane compounds have low detection frequency with contamination levels less than detection limit (2 ng L^{-1}). Aldrin and dieldrin were found at the highest mean values of 3.94 ng L^{-1} and 3.62 ng L^{-1}, respectively, compared with other banned insecticides detected in this study.

Table 4. 5 Temporal trend of banned pesticides (ng L^{-1})

Location	Year	n	HCHs	Drins	DDTs	References
Red River						
	1990	1	3.2	–	0.68	Iwata et al. (1994)
Dry season	1998/1999	11	28.3	27.4	65.7	Hung and Thiemann (2002)
Rainy season		11	29.8	23.8	48.6	
Dry season	2011/2012	1	ND	(0.33)	(0.10)	This study
Rainy season		1	ND	ND	ND	
Irrigation canals						
Dry season	1998/1999	6	7.19	11.4	58.6	Hung and Thiemann (2002)
Rainy season		6	17.3	11.0	49.7	
Dry season	2011/2012	5	(1.01)	(0.24)	1.34	This study
Rainy season		5	(0.66)	ND	1.94	
QCVN 08:2008/BTNMT (B1)			130^{a}	8^{b}	4^{c}	

n: The number of sample; ND: not detected; “()”: trace concentration (below the detection limit); HCHs: sum of α–, β–, γ–, δ– HCH; drins: sum of aldrin, dieldrin, endrin; DDTs: sum of p,p'–DDE, op'–DDE, p,p'–DDD, op'–DDD, p,p'–DDT, op'–DDT; QCVN 08:2008/BTNMT: National technical regulation on surface water quality. a: regulation value of HCHs; b: regulation value of (aldrin + dieldrin); c: regulation value of DDTs. These values are for category B1applied to surface water used for irrigation.

In terms of currently used pesticides, permethrin and its synergist (piperonyl butoxide) were the most dominant compounds detected in the rainy and the dry seasons, contributing more than 55% to total pesticide concentrations in urban areas such as Hanoi (HN1 to HN5) and Ho Chi Minh (HCM4 to HCM7). The highest concentration of permethrin–1 was found at HCM6 (4.39 μg L^{-1}) followed by HN3 (3.30 μg L^{-1}), HN5 (2.17 μg L^{-1}) and HCM5 (1.89 μg L^{-1}) in the rainy season (Oct 2011), indicating that they were used for hygiene purposes rather than crop protection. Fernobucarb was widely found at most sampling sites (49 out of 58 sample) with the contamination level up to 1.0 μg L^{-1} (HCM4, Feb 2012), indicating its popular used for paddy fields in Vietnam. Terbutryn was the most frequency detected herbicide (22%) and followed by atrazine (14%) with the highest concentrations up to 0.31 μg L^{-1} (HCM5, Oct 2011) and 0.04 μg L^{-1} (HN6, Oct, 2011), respectively. However, acetochlor was found at only 4 sites in the dry season with the highest level reach to 1.7 μg L^{-1} (HN2, March 2011).

Overall, total concentrations of pesticides were extremely high in canals located inside HN and HCM in both the rainy and the dry season, whereas the sites located in rural and suburban areas showed relatively low levels. Rivers in Da Nang city seem to be cleanest, none of pesticides were observed at remote areas such as DN1–3. However, some rivers (HP1–3) supplied raw water for drinking water treatment plants of Hai Phong city were contaminated at relatively high concentrations (1.1 μg L^{-1}, 3.5 μg L^{-1} and 0.87 μg L^{-1}, respectively) compared with other remote areas. Therefore, it is imperative to conduct a detailed survey of pesticides in these rivers as well as in tap water.

A larger number of pesticides (27) at higher concentrations were detected in the rainy season than those in the dry season (21) (Table 4.3), particularly in rural rivers (HP1 – 3), which may reflect that these pesticides were applied to areas near the sampling sites before sampling. Since storm–water run–off contains many kinds of chemicals such as metals, PAHs, PCBs pesticides, alkyl–phenols (Zgheib et al., 2012) and a large number of pesticides has indeed been reported in storm–water drain in developed countries (Phillips and Bode, 2004), intense rainfalls in Vietnam may bring various pollutants (including pesticides) to the receiving canals.

HCHs, chlordanes, drins, DDT and its metabolites have been banned from application for around 20 years in Vietnam, were determined significantly lower than those measured in a previous report (Hung and Thiemann, 2002). Concentration levels of DDTs and HCHs were over 20 times and 10 times lower than 10 years ago, respectively (Table 4.5). These results demonstrated that these persistent pesticides remain in the environment. The highest concentration of DDTs (0.71 ng L^{-1}) detected in this survey (HCM5) was much lower than their allowable limit of concentration in surface waters, which is accorded with criteria of Vietnam (QCVN 08:2008/BTNMT/ category B1) (DDTs < 4 ng L^{-1}). The highest detected concentrations of aldrin, dieldrin, endrin and chlordances were also lower than acceptable limit for surface water (QCVN 08:2008/BTNMT B1). The results reflect the contamination of the pesticides that have been naturally decreased due to by some processes such as dilution, degradation, washout, and evaporation, and there were no recent inputs of these pesticides in the study areas.

4.4.1.4 Polychlorinated biphenyls (PCBs)

Large numbers of PCBs were observed in the rainy season (33) than in the dry season (28) at relatively low concentrations (mostly lower than detection limit, 0.3 ng L^{-1}). In the rainy season, PCBs were only observed at sites in HN and HCM with total PCBs concentration ranged from not detected to 13 ng L^{-1}. The highest total concentration was observed at HN3 (13 ng L^{-1}) and followed by HCM7 (9.6 ng L^{-1}), HN4 (4.2 ng L^{-1}) and HCM6 (2.1 ng L^{-1}). The similar observation was seen in the dry season with the higher detection frequency and high concentrations were observed at canals in densely populated areas in HN and HCM. Total PCBs concentration in the dry season ranged from 0.05–17 ng L^{-1} with the highest total PCBs detected at HCM6 (17 ng L^{-1}), HCM7 (6.3 ng L^{-1}), HN5 (3.9 ng L^{-1}) and HCM5 (2.4 ng L^{-1}). These high concentrations seem to be related to industry, atmospheric deposition and domestic wastewater. Other than this, the leakages of PCBs from the PCBs–containing oils in old transformers and capacitors, especially recent PCBs–containing wastes can be one of the sources of PCBs in the Hanoi canals. These results agree well with those observed by Hoai et al. (2010), which showed that there are more than 11800 PCB–containing electric equipment in Vietnam, containing 7000 tons of PCB contaminated oils (MONRE, 2006). In addition, Toan et al. (2007) reported that PCBs could be used currently as components of lubricating oils for motor vehicles. In order to confirm the sources of PCBs in these study areas, sediment samples at the water sampling sites need to be examined.

4.4.1.5 Polycyclic aromatic hydrocarbons (PAHs)

PAHs detected in water samples at relatively low concentrations, ranged from not detected to 4560 ng L^{-1} (mean 570 ng L^{-1}), which indicated low to moderate contamination in relation to global levels. The distribution of PAHs was dominated by naphthalene, phenanthrene, pyrene and fluoranthene, which were detected over 65% of samples (Table 4.6). The highest total concentration of PAHs was observed at HN3 (4560 ng L^{-1}, Mar 2011) and followed by HCM6 (4095 ng L^{-1}, Oct 2011) and HN1 (3670 ng L^{-1}, Oct 2011). The maximum of total PAHs concentration observed in this study (4560 ng L^{-1}) was almost 5 times higher than those in Ulsan Bay (Korea) (Khim et al., 2001) and 1.7 times higher than those in Beiyun River (China) (Yu et al., 2004), whereas it was almost 3 times lower than those in Taizi River (China) (He et al., 2007).

Table 4. 6 Range, mean (ng L^{-1}) and detection frequency (%) of individual PAH in water samples (n=47)

No	PAH compounds	Detection frequency	Min	Max	Mean
1	Naphthalene	98	ND	874	88
2	Phenanthrene	72	ND	555	68
3	Pyrene	70	ND	339	38
4	Fluoranthene	66	ND	693	58
5	1-Methylnaphthalene	62	ND	312	49
6	Benzo(a)anthracene	62	ND	153	17
7	2-Methylnaphthalene	49	ND	609	95
8	Fluorene	47	ND	101	22
9	1,3-Dimethylnaphthalene	43	ND	794	206
10	Indeno(1,2,3-cd)pyrene	38	ND	72	23
11	2,6-Dimethylnaphthalene	36	ND	841	230
12	Acenaphthene	36	ND	40	13
13	Benzo(ghi)perylene	36	ND	65	13
14	Chrysene & Triphenylene	32	ND	309	49
15	3-Methylphenanthrene	30	ND	82	23
16	Benzo(a)pyrene	26	ND	113	10
17	Benzo(j&b)fluoranthene	26	ND	368	63
18	2-Methylphenanthrene	23	ND	105	32
19	Benzo(e)pylene	23	ND	630	128
20	9-Methylphenanthrene	19	ND	29	13
21	1,2-Dimethylnaphthalene	17	ND	167	56
22	Benzo(k)fluoranthene	15	ND	101	23
23	Acenaphthylene	13	ND	108	36
24	Dibenzo(a,h)anthracene	13	ND	18	7.2
25	Anthracene	6	ND	34	15

ND represents “not detected”; mean represents the average of detected concentrations.

In general, total concentrations of PAHs were higher in the center areas of HN and HCM compared to those in rural and suburban areas, especially the concentrations in the rainy season were higher than those in the dry season. In the rainy season, the averages of total PAHs concentration in HN, HP, DN, and HCM were 1713 ng L^{-1}, 64 ng L^{-1}, 18 ng L^{-1} and 1039 ng L^{-1}, respectively. While in the dry season, the averages of total PAHs

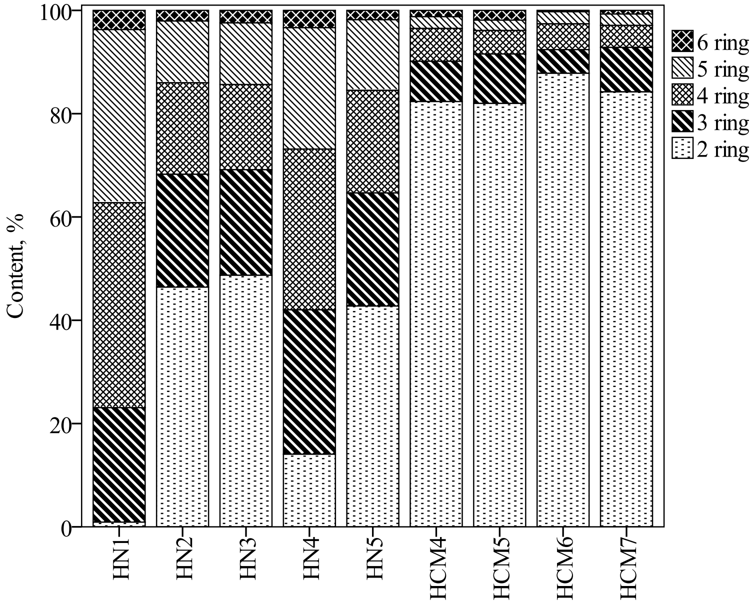


Fig. 4. 4 Profiles of 2– to 6– aromatic rings of PAHs in water samples in the rainy season (October 2011)

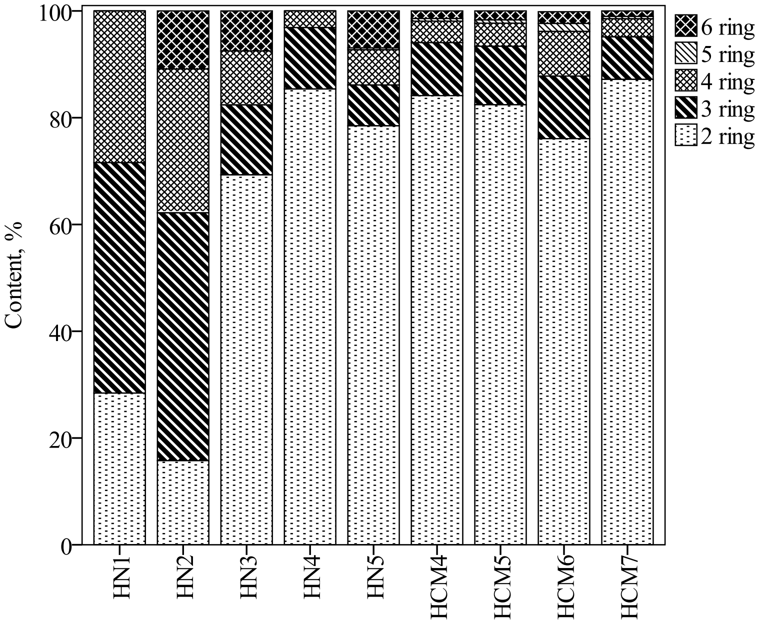


Fig. 4. 5 Profiles of 2– to 6– aromatic rings of PAHs in water samples in the dry season (February 2012)

concentration in these cities were 309 ng L^{-1}, 6.6 ng L^{-1}, 31 ng L^{-1}, and 1100 ng L^{-1}, respectively. The concentration levels of PAHs in HN and HP in the dry season were almost 6 times and 10 times lower than those observed in the rainy season, respectively, while, HCM had the similar trend. The abundance (>80%) of low molecular−weight PAHs (2 and 3 rings) observed in rivers in HN and HCM (Fig. 4.4 and Fig. 4.5) reflected the intensive inputs of petrogenic PAHs to the studied areas, primarily leakage of refined products from urban vehicle traffic. Some sites (e.g., HN1, 2, 4, and HCM4) had a mixed contamination pattern (pyrogenic and petrogenic inputs), probably due to urban runoff, wastewater discharges and vehicle exhaust gases, especially from motorcycles. In rural areas, pyrogenic contamination was the dominant source of PAHs, probably from the burning of rice straw after harvest.

4.4.1.6 Pharmaceuticals and personal care products (PPCPs)

Six PPCPs (carbamazepine, crotamiton, DEET, ibuprofen L−menthol and triclosan) well known as molecular markers of sewage contamination (Nakada et al., 2008), and three other PPCPs (nicotine, squalene and thymol) were detected. The most frequently detected compound was DEET (86%), followed by L−menthol (71%) and squalane (47%) at the detected concentrations of 0.01–1.1 μg L^{-1}, 0.01–61 μg L^{-1}, and 0.01–2.6 μg L^{-1}, respectively. The detection frequency, range, and mean concentration for PPCPs can be seen in Table 4.7. PPCPs concentration is higher in rivers running through highly populated areas such as HN (HN2−5) and HCM (HCM4−7), compared to other study sites, suggesting that they are derived from sewage. Total PPCPs concentrations (summed concentration of nine detected PPCPs) ranged from 0.001 μg L^{-1} (DN2, Oct 2011) to 68 μg L^{-1} (HN 3, Mar 2011) with median value (0.13 μg L^{-1}). The total PPCPs concentrations in the dry season (Feb 2012) ranged from 0.01 μg L^{-1} to 19 μg L^{-1} (median 0.26 μg L^{-1}) while those in the rainy season (Oct 2011) ranged from 0.001 to 18 μg L^{-1} (median 0.10 μg L^{-1}).

DEET was the most abundance chemical in the water samples appearing at 50 out of 58 water samples. High concentrations of DEET were observed in the dry season (Feb 2012), (eg., 1.1 μg L^{-1} at HCM6, followed by HCM4, 0.76 μg L^{-1} and HCM7, 0.69 μg L^{-1}). Lower values were seen in the rainy season, probably due to dilution. DEET was also observed at ground water of Tokyo's metropolitan area, suggesting wastewater leakage from decrepit sewers and this compound was not removed during passage through soil (Nakada et al., 2008).

Carbamazepine was found at 17 out of 58 water samples with concentration ranged from not detected to 3.7 μg L^{-1}. The maximum concentration (3.7 μg L^{-1}, HCM5) was much higher than those reported in Korea (0.59 μg L^{-1}, Kim et al., 2009), in Berlin (1.1 μg L^{-1}, Heberer, 2002), while it was lower than maximum concentration observed in EU rivers (11.6 μg L^{-1}) (Loos et al., 2009). However it is still lower compared with the lowest Predicted No Effect Concentration (25 μg L^{-1}) (PNEC) reported by Chen et al. (2008).

Table 4. 7 The detection frequency (%), range and mean concentration of PPCPs (μg L^{-1}) in water samples (n=58)

No	Compound	Detection frequency	Min	Max	Mean
1	Nicotine	2	ND	1.7	1.7
2	Carbamazepine	29	ND	3.7	0.41
3	Diethyltoluamide	86	ND	1.1	0.14
4	Ibuprofen	9	ND	2.0	1.0
5	L-Menthol	71	ND	61	4.6
6	Squalane	47	ND	2.6	0.31
7	Triclosan	16	ND	2.2	0.59
8	Crotamiton	12	ND	0.58	0.21
9	Thymol	3	ND	1.6	0.85

ND represents “not detected”.
mean represents the average of detected concentrations.

Ibuprofen was detected at 5 out of 58 samples at 3 sites in HCM (HCM5, 0.76 μg L^{-1}; HCM6, 2.0 μg L^{-1} and HCM7, 0.31 μg L^{-1}), while triclosan was detected in 9 out of 58 water samples in the dry season, with highest levels observed at HN3 (2.2 μg L^{-1}), followed by HN5 (0.83 μg L^{-1}), HCM7 (0.61 μg L^{-1}) and HCM6 (0.56 μg L^{-1}). Crotaminton was detected at 7 out of 58 samples in rives in DN in dry season (Feb 2012). The highest concentrations of crotaminton (<0.58 μg L^{-1}) was observed at sites located in rural and suburban areas of DN (DN1–4), while sites located inside city (DN5–6) showed relatively low concentration (0.05 μg L^{-1}). Squalene and L–menthol were the most frequency detected compounds (47% and 71%, respectively) with high concentrations of up to 2.6 μg L^{-1} and 61 μg L^{-1}, respectively.

Since crotaminton, carbamazepine, ibuprofen and DEET were found in ground water in Tokyo, implying wastewater leakage from decrepit sewers (Nakada et al., 2008). Moreover, Nakada (2008) indicated that crotaminton and carbamazepine were not removed during passage through soil, which demonstrated these compounds are stable and useful molecular markers for tracing sewage inputs to aquatic environments. Ibuprofen and thymol were removed by microbial degradation; triclosan was removed by a combination of microbial degradation, photodegradation and adsorption. Therefore, these persistent markers (crotaminton, carbamazepine) detected in surface water in Hanoi and Ho Chi Minh are proving the truth is that maintenance and operating sufficiency of the existing wastewater treatment plants (WWTPs) in Vietnam are necessary to treat entirely wastewater discharged and also to prevent the leakage of persistent PPCPs into the ground water. The amount of PPCPs consumed in Vietnam is unknown, although it is expected that there is direct discharge into river waters via untreated wastewater. The number of PPCPs identified in this study may be an underestimate since there are a limited number of PPCPs in the AIQS−DB (14 substances). Consequently, a more detailed survey on PPCPs in surface and ground water in Vietnam is required after new PPCPs are registered in the system's database.

4.4.1.7 Emerging contaminants (bisphenol A and nonylphenol)

Bisphenol A (BPA) is an endocrine disrupting chemical and has estrogenic potential even at low concentrations (Jin et al., 2004), which was found in 26 out of 47 samples at concentrations from 0.005 to 5.3 µg L^{-1} (mean 0.93 µg L^{-1}). These levels were higher than those in rivers in Japan (<0.50–0.90 µg L^{-1}; Kang & Kondo, 2006) and Europe (mean 0.025 µg L^{-1}; n = 122; Loos et al., 2009). BPA concentrations in Hanoi and Ho Chi Minh were 3 times higher than in other regions of Vietnam. The maximum concentration observed in this study (5.3 µg L^{-1}) was lower than PNEC for aquatic organisms (11 µg L^{-1}; MOE, 2001).

Nonylphenol (NP) is a degradation product of a nonylphenol polyethoxylates that are ubiquitous in industrial and household products (Derbalah et al., 2003). It was only found in canals in Hanoi (HN1 to HN5) and Ho Chi Minh (HCM4 to HCM7) at concentrations from 0.02–9.7 µg L^{-1} (mean 3.0 µg L^{-1}) and 2.0–20 µg L^{-1} (mean 9.7 µg L^{-1}), respectively. The mean values are much higher than those in European rivers (0.13 µg L^{-1}, n = 122; Loos et al., 2009) and surface waters (including river, lake and sea water) in Japan (0.17 µg L^{-1}, n =1574; MOE, 2001). Extremely high concentrations (20 µg L^{-1}, 16 µg L^{-1} and 9.7 µg L^{-1}) were observed at HCM4, HCM6 and HN5, respectively, probably due to the wide range of contamination sources and heavy use of household products near these sites. In this study, NP concentrations in 15 out of 17 samples were higher than the PNEC for aquatic organisms (0.21 µg L^{-1}; MOE, 2001), which implies that NP concentrations in rivers in Hanoi and Ho Chi Minh may be occasionally hazardous to aquatic organisms.

4.4.1.8 Conclusions

The results of investigating the pollution of 940 OMPs in surface waters throughout Vietnam have provided the first baseline data on a wide spectrum of OMPs in river water in

Vietnam. The main findings are that (1) 235 analytes from a range of chemical groups were detected, indicating that Vietnamese rivers are as polluted by numerous chemicals as developed countries; (2) sterols and PPCPs were detected at high concentrations, indicating that rivers are heavily polluted by domestic wastewater; (3) organochlorine pesticides still remain in the environment although they have been banned for 20 years; (4) some urban rivers were heavily contaminated by insecticides used for hygienic purposes. In addition, several sources of tap water were found to be contaminated by numerous pesticides, which implies a need for a detailed survey on pesticides in raw water and tap water. Bisphenol A and nonylphenol, endocrine disrupting chemicals, were found at elevated concentrations in metropolitan areas, implying needs for a further investigation of surface and ground water. The number and kinds of OMPs observed in Vietnam were similar to those found in developed countries, but the concentrations were much higher due to lack of wastewater treatment facilities. In addition, some compounds could be potentially threatening to human health and ecosystems. Therefore, the results indicate needs of in depth studies not only on the detected and related substances but also on effects to human and the aquatic ecosystem.

4.4.2 Groundwater

4.4.2.1 Occurrence of organic micro–pollutants

Of the 940 analytes, 74 that represent a variety of uses and origins were detected at least once (Table 4.8, Table S4.1). The maximum and the median number of compounds detected per well were 43 and 16, respectively. None of the samples was free of analytes; however, five of the samples contained less than ten compounds. Of the 43 samples examined, 20 had total detectable concentrations that were less than 3.0 µg L^{-1}, while 17 had values between 3 and 7 µg L^{-1}. OMPs occurred more frequently in groundwater samples collected in the first sampling round (62 compounds, Sep 2013) than in the second sampling round (37 compounds, Aug 2014), with 7 (Sep 2013) and 3 compounds (Aug 2014) detected in 100% wells, respectively. The total concentrations in the first sampling round were highest at HN1 and HN14 (8.0 µg L^{-1} and 16 µg L^{-1}, respectively), while the total concentrations in the second round were highest at HN6 (15 µg L^{-1}) and HN16 (10 µg L^{-1}). The OMPs with the highest concentrations (greater than or equal to 0.7 µg L^{-1}) were not necessarily among the most frequently detected compounds (Fig. 4.6). For example, although several compounds, such as di–n–butyl phthalate (DBP) and 4–cymene, were detected infrequently, their maximum concentrations exceeded 0.7 µg L^{-1} (Fig. 4.6, Table 4.8). Previous studies (Kolpin et al., 2002; Loos et al., 2010) have also demonstrated that the compounds that occur most frequently are not always those with the highest concentrations. The measured concentrations of individual chemicals were generally low, and 89% of concentrations were less than or equal to 0.5 μg L^{-1}. Bis(2–ethylhexyl)phthalate (DEHP), benzyl alcohol, cholesterol, DBP and stigmasterol (Fig. 4.6) were detected in the samples 27, 19, 9, 5 and 3 times, respectively, at concentrations exceeding 0.5 μg L^{-1}.

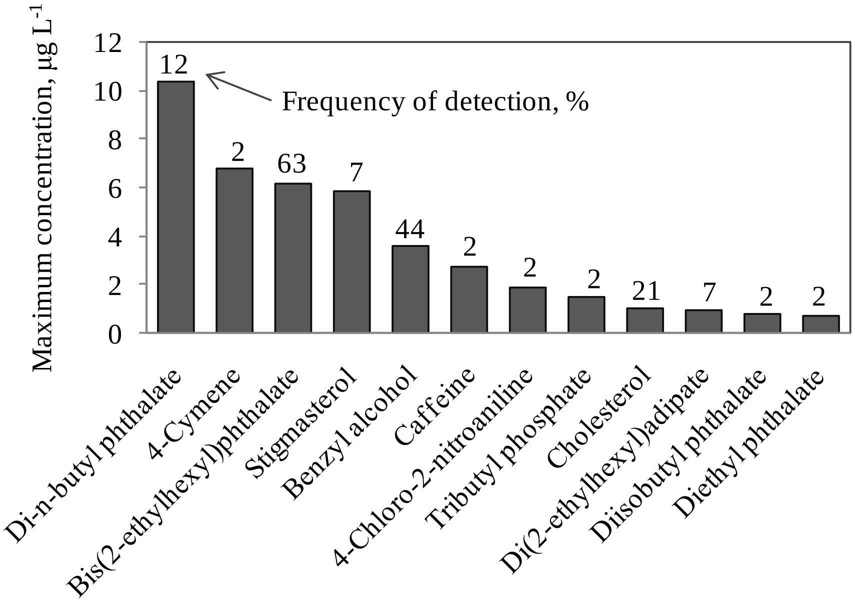


Fig. 4. 6 Maximum concentrations of compounds detected at concentrations greater than 0.7 μg L^{-1}.

Table 4. 8 Summary of analytical results of groundwater wells sampled for 940 OMPs in Hanoi and Ho Chi Minh City

No	Name	CAS number	LOD (μg L^{-1})	Number of detections		Maximum concentration (μg L^{-1})		Drinking water standards and health advisories (μg L^{-1})	Origin/ Source	Detector
				Sep–2013 (n=22)	Aug–2014 (n=21)	Sep–2013 (n=22)	Aug–2014 (n=21)			
	Sterol									
1	Campesterol	474-62-4	0.01	0	2	0	0.16	–	phytosterol	GC–MS/SIM
2	Cholestanol	80-97-7	0.01	0	1	0	0.35	–	animal sterol	GC–MS/SIM
3	Cholesterol	57-88-5	0.01	22	21	1.0	0.88	–	animal sterol	GC–MS/SIM
4	beta-Sitosterol	83-46-5	0.01	7	2	0.62	0.53	–	phytosterol	GC–MS/SIM
5	Stigmasterol	83-48-7	0.01	7	0	5.8	0	–	phytosterol	GC–MS/SIM
6	Ergosterol	57-87-4	0.01	0	1	0	0.34	–	phytosterol	GC–MS/SIM
	PPCPs									
7	L-Menthol	2216-51-5	0.01	18	4	0.06	0.02	–	PPCPs	GC–MS/TIM
8	Squalane	111-01-3	0.01	14	0	0.14	0	–	PPCPs	GC–MS/TIM
9	Diethyltoluamide	84-66-2	0.01	3	4	0.04	0.40	–	PPCPs	GC–MS/TIM
	Life-style compounds									
10	Caffeine	58-08-2	0.01	2	0	2.7	0	–	PPCPs	GC–MS/TIM
	Phtalates									
11	Diethyl phthalate (DEP)	84-66-2	0.01	22	15	0.09	0.71	[3]0.8; [4]30 000	plasticizer	GC–MS/TIM
12	Diisobutyl phthalate (DIBP)	84-69-5	0.01	22	0	0.80	0	–	plasticizer	GC–MS/TIM
13	Dimethyl phthalate (DMP)	131-11-3	0.01	4	3	0.02	0.04	–	plasticizer	GC–MS/TIM
14	Di-n-butyl phthalate (DBP)	84-74-2	0.01	22	16	0.39	10	[3]0.1; [4]4000	plasticizer	GC–MS/TIM
15	Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	0.01	22	8	3.6	6.2	[1]6.0; [3]0.02; [4]700; [5]300; [7]8.0	plasticizer	GC–MS/TIM

Table 4.8 Summary of analytical results of groundwater wells sampled for 940 OMPs in Hanoi and Ho Chi Minh City (continued)

No	Name	CAS number	LOD (µg L^{-1})	Number of detections		Maximum concentration (µg L^{-1})		Drinking water standards and health advisories (µg L^{-1})	Origin/ Source	Detector
				Sep–2013 (n=22)	Aug–2014 (n=21)	Sep–2013 (n=22)	Aug–2014 (n=21)			
16	Butyl benzyl phtalate	85-68-7	0.01	18	9	0.10	0.11	[3]0.2; [4]7000	plasticizer	GC–MS/TIM
	Other SVOC compounds									
17	3- & 4-tert-Butylphenol	585-34-	0.01	1	0	0.04	0	–	antioxidant	GC–MS/TIM
18	Acetophenone	98-86-2	0.01	17	7	0.12	0.07	[3]0.1	cosmetics/fragrance	GC–MS/TIM
19	alpha-Terpineol	10482-56-1	0.01	1	0	0.65	0	–	cosmetics/fragrance	GC–MS/TIM
20	Benzyl alcohol	100-51-6	0.01	15	21	3.6	0	–	cosmetics/fragrance	GC–MS/TIM
21	Phenylethyl alcohol	60-12-8	0.01	0	3	0	0.02	–	cosmetics/fragrance	GC–MS/TIM
22	Methyl palmitoleate	1120-25-8	0.01	0	1	0	0.13	–	fatty acid methy ester	GC–MS/TIM
23	Tributyl phosphate	126-73-8	0.01	11	1	0.50	1.4	–	fire retardant	GC–MS/TIM
24	4-Chloro-3-methylphenol	59-50-7	0.01	0	1	0	0.30	–	fungicide, paint	GC–MS/TIM
25	e-Caprolactam	105-60-2	0.01	0	19	0	0.11	[3]0.5	intermediate for fiber	GC–MS/TIM
26	Bisphenol A	80-05-7	0.01	5	0	0.04	0	[3]0.05	intermediate for resin	GC–MS/TIM
27	4-Chloro-2-nitroaniline	89-63-4	0.01	18	0	1.9	0	–	intermediate in organic synthesis	GC–MS/TIM
28	3,5-Dimethylphenol	108-68-9	0.01	0	21	0	0.38	–	intermediate in organic synthesis	GC–MS/TIM
29	Diphenylamine	122-39-4	0.01	0	5	0	0.07	[3]0.025	intermediate in organic synthesis	GC–MS/TIM
30	Nitrobenzene	98-95-3	0.01	0	1	0	0.10	[3]0.002	intermediate in organic synthesis	GC–MS/TIM
31	Safrole	94-59-7	0.01	1	0	0.69	0	–	intermediate in organic synthesis/preservative	GC–MS/TIM
32	2(3H)-Benzothiazolone	934-34-9	0.01	1	1	0	0.39	–	leaching from tire	GC–MS/TIM
33	2-(Methylthio)-benzothiazol	615-22-5	0.01	5	1	0.11	0.09	–	leaching from tire	GC–MS/TIM
34	Benzothiazole	95-16-9	0.01	12	4	0.04	0.13	–	leaching from tire	GC–MS/TIM
35	Ethanol, 2-phenoxy-	122-99-6	0.01	22	5	0.30	0.04	–	leaching from tire	GC–MS/TIM

Table 4.8 Summary of analytical results of groundwater wells sampled for 940 OMPs in Hanoi and Ho Chi Minh City (continued)

No	Name	CAS number	LOD (μg L^{-1})	Number of detections		Maximum concentration (μg L^{-1})		Drinking water standards and health advisories (μg L^{-1})	Origin/ Source	Detector
				Sep–2013 (n=22)	Aug–2014 (n=21)	Sep–2013 (n=22)	Aug–2014 (n=21)			
36	4-tert-Octylphenol	140-66-9	0.01	2	0	0.06	0	–	nonionic	GC–MS/TIM
37	Longifolene	475-20-7	0.01	4	0	0.09	0	–	other	GC–MS/TIM
38	2-Ethyl-1-hexanol	104-76-7	0.01	21	0	0.32	0	–	plasticizer	GC–MS/TIM
39	Bis(2-ethylhexyl) sebacate	122-62-3	0.01	2	1	0.02	0.13	–	plasticizer	GC–MS/TIM
40	Di(2-ethylhexyl)adipate	103-23-1	0.01	22	17	0.1	0.95	[1]400; [2]400; [3]0.6; [4]20 000; [5]3000	plasticizer	GC–MS/TIM
41	4-Cymene	99-87-6	0.01	5	0	6.8	0	–	solvent	GC–MS/TIM
42	trans-Decahydronaphthalene	493-02-7	0.01	21	0	0.34	0	–	solvent	GC–MS/TIM
43	Isophorone	78-59-1	0.01	5	8	0.02	0.20	[2]100; [3]0.2; [4]7000; [5]4000	solvent/paint	GC–MS/TIM
	Organochlorine pesticides [a]									
44	trans-Chlordane	5103-74-	0.4	1	0	3.0	0	–	insecticide	GC–MS–MS/SRM
45	cis-Chlordane	5103-71-	0.4	1	0	1.7	0	–	insecticide	GC–MS–MS/SRM
	Σchlordane							[1]2.0;[2]4.0; [3]0.0005; [4]20; [5]10; [7]0.2		
46	trans-Nonachlor	5103-73-	0.4	1	0	0.72	0	–	insecticide	GC–MS–MS/SRM
47	Endrin	72-20-8	0.4	4	7	1.3	1.7	[1]2.0; [2]2.0; [3]0.0003; [4]10	insecticide	GC–MS–MS/SRM
48	Dieldrin	60-57-1	0.4	2	0	2.8	0	[3]0.00005; [4]2.0; [5]0.2; [6]0.03	insecticide	GC–MS–MS/SRM
49	Hexachlorobenzene	118-74-1	0.1	2	0	0.35	0	[1] 1.0; [3]0.0008; [4]30; [5]2.0	by-product	GC–MS–MS/SRM

Table 4.8 Summary of analytical results of groundwater wells sampled for 940 OMPs in Hanoi and Ho Chi Minh City (continued)

No	Name	CAS number	LOD (μg L^{-1})	Number of detections		Maximum concentration (μg L^{-1})		Drinking water standards and health advisories (μg L^{-1})	Origin/ Source	Detector
				Sep–2013 (n=22)	Aug–2014 (n=21)	Sep–2013 (n=22)	Aug–2014 (n=21)			
50	Heptachlor epoxide (B)	1024-57-3	0.4	0	8	0	5.9	[1]0.2; [3]0.00001; [4]0.4; [5]0.4; [6]0.03	insecticide	GC–MS–MS/SRM
51	a-HCH	319-84-6	0.4	1	0	1.9	0	–	insecticide	GC–MS–MS/SRM
52	g-HCH	58-89-9	0.4	1	0	1.3	0	[1]0.2; [3]0.005; [4]200	insecticide	GC–MS–MS/SRM
53	p,p'-DDT	50-29-3	0.1	6	11	3.6	12	[3]0.0005; [7]1.0[b]	insecticide	GC–MS–MS/SRM
54	p,p'-DDE	72-55-9	0.1	1	1	0.11	0.33	–	insecticide	GC–MS–MS/SRM
55	p,p'-DDD	72-54-8	0.1	2	4	0.46	0.55	–	insecticide	GC–MS–MS/SRM
56	o,p'-DDT	789-02-6	0.2	2	2	0.38	1.3	–	insecticide	GC–MS–MS/SRM
57	o,p'-DDD	53-19-0	0.1	16	8	2.7	6.4	–	insecticide	GC–MS–MS/SRM
	Polychlorinated biphenyls[a]									
58	PCB#8	34883-43-7	0.1	3	0	0.35	0	–	PCB	GC–MS–MS/SRM
59	PCB#74	32690-93-0	0.1	2	0	0.13	0	–	PCB	GC–MS–MS/SRM
60	PCB#70	32598-11-1	0.1	2	0	0.11	0	–	PCB	GC–MS–MS/SRM
61	PCB#66	32598-10-0	0.1	2	0	0.12	0	–	PCB	GC–MS–MS/SRM
62	PCB#60	33025-41-1	0.1	5	7	1.1	0.33	–	PCB	GC–MS–MS/SRM
63	PCB#52	35693-99-3	0.1	2	0	0.46	0	–	PCB	GC–MS–MS/SRM
64	PCB#44	41464-39-5	0.1	2	0	0.25	0	–	PCB	GC–MS–MS/SRM
65	PCB#41	52663-59-9	0.1	2	0	0.34	0	–	PCB	GC–MS–MS/SRM
66	PCB#4&10	13029-08-	0.1	2	0	0.29	0	–	PCB	GC–MS–MS/SRM

Table 4.8 Summary of analytical results of groundwater wells sampled for 940 OMPs in Hanoi and Ho Chi Minh City (continued)

No	Name	CAS number	LOD (μg L^{-1})	Number of detections		Maximum concentration (μg L^{-1})		Drinking water standards and health advisories (μg L^{-1})	Origin/ Source	Detector
				Sep–2013 (n=22)	Aug–2014 (n=21)	Sep–2013 (n=22)	Aug–2014 (n=21)			
67	PCB#37	38444-90-5	0.2	1	0	0.20	0	–	PCB	GC–MS–MS/SRM
68	PCB#33	38444-86-9	0.1	3	0	0.40	0	–	PCB	GC–MS–MS/SRM
69	PCB#28	7012-37-5	0.1	4	0	1.8	0	–	PCB	GC–MS–MS/SRM
70	PCB#22	38444-85-8	0.2	2	0	0.30	0	–	PCB	GC–MS–MS/SRM
71	PCB#19	38444-73-4	0.1	1	0	0.15	0	–	PCB	GC–MS–MS/SRM
72	PCB#18	37680-65-2	0.1	4	0	0.78	0	–	PCB	GC–MS–MS/SRM
73	PCB#15	2050-68-2	0.1	2	0	0.19	0	–	PCB	GC–MS–MS/SRM
74	PCB#1	2051-60-7	0.1	1	0	0.11	0	–	PCB	GC–MS–MS/SRM
	ΣPCBs							[1]0.5; [5]10		GC–MS–MS/SRM

[a] Compounds presented concentrations in ng L^{-1};[b] Total DDT and metabolites concentration (μg L^{-1});"–" Represents values "not available"; Drinking Water Standards and Health Advisories:[1]U.S. EPA Maximum Contaminant Levels (MCL) (μg L^{-1}); [2]U.S. EPA Lifetime Health Advisory (μg L^{-1}); [3]U.S. EPA Reference Dose (RfD) (mg kg^{-1} day^{-1}); [4]U.S. EPA Drinking Water Equivalent Level (DWEL) (μg L^{-1}); [5]U.S. EPA 10^{-4} Cancer Risk (μg L^{-1}); [6]European Health–Based Chemical Standards (μg L^{-1}); http://www.doeni.gov.uk/niea/european_and_national_drinking_water_quality_standards_–_october_2011.pdf; [7]WHO Guidelines for Drinking–water Quality (μg L^{-1}).

4.4.2.2 Sterols and caffeine

The samples were screened for ten sterols, of which campesterol, cholestanol, cholesterol, beta–sitosterol, stigmasterol and ergosterol were detected. Cholesterol was observed in 100 % of wells, followed by beta–sitosterol (21%) and stigmasterol (16%), while cholestanol, ergosterol and campesterol were observed in only one, one and two wells, respectively (Table 4.8). Sterol appearances and concentrations in groundwater were highly variable across wells. Out of 43 samples investigated (both rounds), 33 were contaminated with only one sterol at detectable concentrations of less than 0.62 µg L^{-1} except for HCM3 (1.0 µg L^{-1}), while two, seven and one samples were polluted with two, three and five sterols, respectively (Table S4.1). The highest total concentrations of sterols were observed in HN2 (2.1 µg L^{-1}), HN1 (6.6 µg L^{-1}) and HN9 (1.1 µg L^{-1}) in the first sampling round, while HN6 was contaminated with high sterol concentrations in both rounds (Table S4.1). Stigmasterol and cholesterol were the only two sterols detected at concentrations greater than 1 µg L^{-1} (Table 4.8), whereas the other four remaining sterols were identified at concentrations that were lower than 0.88 µg L^{-1}. These results may indicate a high degree of heterogeneity in loadings from local sources and/or spatial differences in hydraulic conductivity and bio–geochemical conditions, as mentioned by Schaider et al. (2014).

Six sterols that were detected in groundwater were also abundant in surface waters and sediments collected in the same study areas of HN and HCM (Duong et al., 2014a,b). However, a fecal sterol (coprostanol) that was detected most often and at extremely high concentrations in HN and HCM's cities canals due to sewage contamination was not found in groundwater samples.

Caffeine was one of the most frequently detected compounds in other groundwater studies (Barnes et al., 2008; Focazio et al., 2008), and was detected in nearly 100% of surface waters in HN and HCM. In this study however, it was observed in only two (HN14 and HCM3) of the 43 groundwater samples. The maximum concentration that was detected in this study (2.7 µg L^{-1}) is about 20 times higher than the maximum detected in groundwater in the US (0.13 µg L^{-1}, Barnes et al., 2008), 14 times higher than the maximum concentration detected in groundwater in Europe (0.19 µg L^{-1}, Loos et al., 2010), and 10 times higher than the maximum value in untreated drinking water sources in the US (0.27 µg L^{-1}, Focazio et al., 2008). The presence of caffeine in shallow drinking water wells has been suggested as an indicator of wastewater impacts (Seiler et al., 1999) and it is thought that it is attenuated in oxic subsurface conditions (Schaider et al., 2014). Moreover, it persists in anaerobic conditions in groundwater (Ying et al., 2003). Therefore, the presence of caffeine in two wells probably reflects direct entry of leachate from surface water, leaks in sewage canals or underground septic tanks.

4.4.2.3 Emerging chemicals

Of the 14 PPCPs analyzed, DEET, L–menthol and squalane were detected in groundwater samples at maximum concentrations of 0.40, 0.06 and 0.14 μg L^{-1}, respectively (Table 4.8, Table S4.1). L–menthol and DEET, which are well–known molecular markers of sewage contamination (Nakada et al., 2008), were detected in 22 and 7 groundwater samples (in both sampling rounds), respectively, while squalane, which is used in numerous vaccine and drug delivery emulsions (Fox, 2009), was only detected in 14 out of 22 groundwater samples in the first sampling round (Table 4.8, Table S4.1). DEET was the most frequently detected compound in groundwater in the US at maximum concentrations of 13.5 μg L^{-1} (Barnes et al., 2008), 34 times higher than those of this study. However, the maximum levels of DEET in this study were 6 times higher than those (0.07 μg L^{-1}) in groundwater from the metropolitan area of Tokyo (Nakada et al., 2008).

The three detected PPCPs in groundwater samples were the most abundant in surface water of HN and HCM that was contaminated with sewage, which demonstrates the ubiquitous use of these PPCPs; the fact that they exist in the water environment in Vietnam reflects the lack of adequate wastewater treatment facilities. Nakada et al. (2008) reported that DEET and other PPCPs were also detected in groundwater in Tokyo as the consequence of sewage leakage from decrepit sewers. Therefore, the presence of PPCPs in groundwater in this study is probably the result of a combination of leaking underground septic tanks, infiltration of untreated wastewater through old sewer canal systems, and urban storm water recharge/runoff. Furthermore, because a large number of PPCPs are known to be found in domestic wastewater, it is thought that groundwater is polluted by many PPCPs. However, the number of PPCPs (14) registered in the AIQS database is very limited, so a more detailed survey on PPCPs should be carried out after new PPCPs are registered in the database.

Two phenolic endocrine disrupting chemicals (EDCs), BPA and 4–tert–octylphenol (OP), deserve particular attention because of their estrogenic activity and widespread application and ubiquity in the environment (Kuch and Ballschmiter, 2001; Meesters and Schroder, 2002). There is evidence that BPA has estrogenic potential even at low concentrations (Jin et al., 2004) and OP can cause estrogenic effects in fish and other aquatic organisms (Jobling et al., 1996). BPA was detected in 5 wells, while OP was detected in 2 wells of the 22 wells sampled in the first round at concentrations that ranged from 0.02 to 0.04 μg L^{-1} and 0.02 to 0.06 μg L^{-1}, respectively (Table S4.1). The maximum BPA concentration (0.04 µg L^{-1}) was 64 and 57 times lower than those in groundwater in the US (2.55 µg L^{-1}, Barnes et al., 2008) and in Europe (2.3 µg L^{-1}, Loos et al., 2010), respectively, and the maximum OP concentration was 14 times lower than those reported in Oxford, England (0.83 µg L^{-1}, Stuart et al., 2014) and 1.5 times higher than those in European groundwater (0.04 µg L^{-1}, Loos et al., 2010). The concentrations of BPA detected in this study are much lower than the human health–based guideline values (100 µg L^{-1}) for exposure to BPA in groundwater proposed by the Minnesota Department of Health (URL17).

Of the six phthalate compounds detected, diethyl phthalate (DEP), DBP, and DEHP were detected in over 70% of the sampled wells with maximum concentrations of 0.71, 10 and 6.2 µg L^{-1}, respectively (Table 4.8, Table S4.1). These compounds have been detected in groundwater in England; however, the concentrations in this study were more than 2.5 times lower than those reported in Boxford, but more than 1.5 times higher than those reported in Oxford (Stuart et al., 2014). Dimethyl phthalate (DMP) was found in scattered wells in this study at trace concentrations of less than 0.04 µg L^{-1}, and was detected only once in groundwater from Maresme, Spain, at a concentration of 0.12 µg L^{-1} (Sánchez–Avila et al., 2009). The highest concentration of DEHP (6.2 µg L^{-1}), an EDC (Akingbemi et al., 2004), was comparable with the concentration detected in the Llobreg at River aquifers, Spain (5.67 µg L^{-1}, López–Roldán et al., 2004).

4.4.2.4 Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs)

Pollution from OCPs and PCBs in surface waters and sediments has been extensively researched in Vietnam (Nhan et al., 2001; Minh et al., 2006; Hoai et al., 2010). However, they are of little concern as groundwater contaminants because they are relatively insoluble in water and are retained strongly by soil. Our previous study on OMPs pollution in surface waters in Vietnam (Duong et al., 2014a) showed that PCBs and OCPs still remain in the aquatic environment and most of the banned OCPs can still be found in high concentrations in the environment throughout Vietnam (e.g. Kishida et al., 2007; Minh et al., 2007a, b; Hoai et al., 2010). In addition, Belfroid et al. (1998) demonstrated that many pesticides entered the aquatic environment via soil percolation, air drift or surface runoff and eventually ended up in groundwater, where their transformation products could remain for years.

In this study, 14 OCPs and 17 PCBs were detected, and the detection frequency was higher in the first sampling round than in the second round (Table 4.8, Table S4.1). Of the 43 samples, 17 and 33 contained at least one of the OCP and PCB congeners, respectively. o,p'–DDD, p,p'–DDT and endrin were the most frequently detected OCPs with maximum concentrations of 6.4 ng L^{-1}, 12 ng L^{-1} and 1.7 ng L^{-1}, respectively. trans–Chlordane was detected in one well, and dieldrin was detected in two wells, and their concentrations reached around 3 ng L^{-1} (Table 4.8, Table S4.1). As was observed for PCBs, none of the PCBs were detected in the groundwater samples from the second sampling round except for PCB #60, which was the most abundant PCB congener and had the highest occurrence in both rounds. The highest concentrations of individual PCB congeners were generally less than 0.5 ng L^{-1} except for PCB #28 (1.8 ng L^{-1}), followed by PCB #60 (1.1 ng L^{-1}) and PCB #18 (0.78 ng L^{-1}) (Table S4.1). Well HCM2 was seriously polluted by PCBs and OCPs with a total concentration of 20 ng L^{-1}, while HN3A, HN4 and HN5 were heavily polluted by OCPs and had total detected concentrations of 16 ng L^{-1}, 14 ng L^{-1} and 9.4 ng L^{-1}, respectively (Table S4.1). This is not surprising, as the surface waters collected at these sites were also extremely polluted by elevated levels of OCPs and PCBs (Duong et al., 2014a). OCPs such as α–, β–, γ–, δ–hexachlorocyclohexane (HCH), aldrin, dieldrin, heptachlor and DDT and its metabolites have been detected in groundwater in India (Sankararamakrishnan et al., 2005; Shukla et al., 2006; Lari et al., 2014); Syria (Jamal, 2011); and in Beijing, China (He et al., 2011). However, the pathways by which these contaminants can make their way into the groundwater are still unclear. For example, Jabbar et al. (1993) demonstrated that the principle mechanism by which OCPs are transported from soil to groundwater is via downward percolation of water containing dissolved pesticides, while Cerejeira et al. (2003) indicated that because of drift, runoff, drainage and their leaching potential, OCPs caused contamination of surface and groundwater. However, more detailed studies need to be carried out to gain an improved understanding of the leaching behavior of OCPs and PCBs in ground water.

4.4.2.5 Organic micro–pollutant compound groups

The 74 OMPs can be divided into 18 groups based on general use category or type of compound (Fig. 4.7). n–Alkanes were excluded from the pollution profile because of their widespread existence in environmental samples. However, it should be noted that the uses of any given compound can vary widely; therefore, the tabulated use categories are presented for illustrative purposes and may not be all–inclusive. The frequency of detection was calculated as the ratio of the measured detection to the total measurement. Although these groupings are composed of unequal numbers of compounds, the detection frequency of the compound group is not controlled by the number of compounds in the group. The phthalate group, consisting of six compounds, had the greatest detection frequency and accounted for the highest percentage of the total concentrations in the first round, while the fiber group contained only e–caprolactam, which was detected in 19 out of 21 samples in the second sampling round at relatively low concentrations. A total of 9 out of 16 groups in the first sampling round had a detection frequency exceeding 40%, and two groups (phthalates and sterols) accounted for over 60% of the total concentrations. While detection frequencies that exceeded 40% were reported for five groups in the second sampling round, three groups (cosmetics/fragrance, phthalate, sterol) accounted for 80% of the total concentrations (Fig. 4.7).

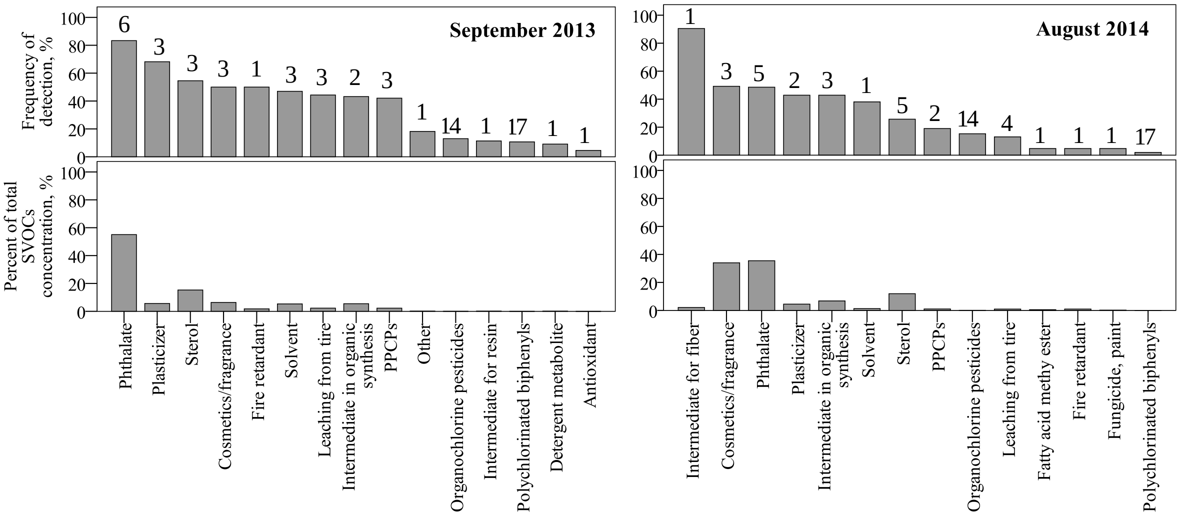


Fig. 4. 7 (1) Detection frequency of SVOCs by general use category and (2) percent of total concentration of SVOCs by general use category in the first round (Sep 2013) and the second round (Aug 2014). Number of compound in each category is shown above the bar.

4.4.2.6 General comparison with the surface water study

Data collected for groundwater in this study can be qualitatively compared with data collected for the surface waters (Duong et al., 2014a). This is a valid comparison because the same analytical method was used for this study and the previous surface water study, although fewer surface water samples were collected (26 surface water samples compared with 43 groundwater samples). Because a large number of chemicals that originated from domestic wastewater were detected in surface waters and sediments (Duong et al., 2014a,b), it was thought that groundwater would also be contaminated with many chemicals. Therefore, the groundwater sampling sites were close to the surface water sampling sites. Overall, fewer contaminants were detected in groundwater, and only 74 of the 940 analytes were detected in groundwater, while 235 were detected in surface waters. All of the compounds that were detected in groundwater samples were also detected in the surface water samples. Although similar compounds were detected in the groundwater, the number of compounds having a detection frequency exceeding 70% in groundwater (six compounds) was much smaller compared with surface water (42 compounds). The concentrations of pollutants in surface water were higher than those in groundwater. Total concentrations of the detected pollutants in 12 out of the 43 groundwater wells exceeded 5 µg L^{-1}, with three wells having total concentrations higher than 10 µg L^{-1}. The total concentrations in 50% of the surface waters were greater than 120 µg L^{-1} (from 120 to 440 µg L^{-1}) while the levels were below 10 µg L^{-1} in only six samples. Coprostanol and coprostanone were detected at extremely high concentrations in all surface water samples in HN and HCM, but were not detected in groundwater samples. While surface waters in HN and HCM were heavily contaminated by permethrin and carbamate insecticide (fenobucarb), these compounds were not detected in any of the groundwater wells. This is most likely because of their hydrophobic properties (log K_{ow}6.1 and 2.79, respectively) and their tendency to adsorb onto organic matter and sediment/soil, meaning it is difficult for them to reach the aquifer. In addition, Sharom and Solomon (1981) and Kim et al. (2014) demonstrated that permethrin and fenobucarb are biodegraded in aqueous systems and soils, so they were not present in aquifers.

4.4.2.7 Identification of potential sources of contamination

Information about the aquifer conditions, such as hydrogeological processes, aquifer characteristics (gravel, chalk, hyporheic zone), kinetics, groundwater flow velocity and information on the well depth, was not available for all the wells sampled. Therefore, an evaluation of the characteristics of chemicals detected in groundwater in this study may provide a useful insight into the factors that control the presence of organic contamination in the aquifers of HN and HCM. The sampled groundwater wells were close to the surface water and sediment sampling sites. As such, heavily polluted surface waters may influence aquifers via numerous processes, including concentrations at the source, dilution, adsorption, and degradation (Jurado et al., 2012). The largest number of contaminants (27 compounds) and the highest total concentration (18 µg L^{-1}) were detected at HN14. In addition, 4–cymene, caffeine and DEHP were the main contributors to pollution at this well. Out of these, caffeine, an indicator of wastewater impacts in shallow drinking water wells (Seiler et al., 1999), was only detected in two out of 43 wells. Therefore, it is thought that this well may be impacted by point sources, such as direct influences from the surface or leaks from underground septic systems. Three other wells (HN13, HN16 and HN17), located close to the most polluted canals in HN, had elevated total concentrations of 9.0 µg L^{-1}, 9.7 µg L^{-1} and 8.3 µg L^{-1}, respectively, and a similar range of chemicals contributed to the high total concentrations at each of these sites. The leakage of surface water contaminated by sewage from the decrepit sewer canals to the aquifers is probably the cause of the pollution at these wells. The total concentrations in the remaining wells were less than 6 µg L^{-1}. At 20 of the sites, the total concentrations were lower than 3 µg L^{-1} and fewer than 20 compounds were detected; these sites were possibly influenced by non−point source pollution. There are multiple possible sources of non−point pollution to aquifers, such as storm water and urban runoff, leakages from urban sewerage systems, diffuse aerial deposition (Nakada et al., 2008; Buerge et al., 2011; Vulliet et al., 2008), or intentional and unintentional recharge of wastewater sources (Drewes, 2009). However, the possibility of contaminant leakages from septic systems is not excluded because it was reported that about 32% of HN's population is served by septic tanks (World Bank, 1996). In addition, several case studies in the US and Canada have reported a range of emerging organic contaminants in groundwater impacted by septic tanks (Carrara et al., 2008; Swartz et al., 2006). Hence, further research is needed to clarify the major source of detected contaminants as well as to determine the primary fate, degradation, transformation and transport processes in impacted aquifers.

4.4.2.8 Risk assessment

Well water sampled in this study is not used for drinking purposes; however, more than half of the population of HN get their tap water from groundwater sources. Hence, the presence of contaminants in HN and HCM's groundwater raises human health concerns even though most of the detected contaminants are not currently regulated in drinking water or were present at low levels. Therefore, in this context we were not able to evaluate the potential health implications of all the detected contaminants because of a lack of toxicity information for many organic pollutants (Stephenson, 2009) and limited testing requirements (Schaider et al., 2014). Further, while this study included a diverse list of 940 organic pollutants, there are about 80000 chemicals currently in use (Schaider et al., 2014), suggesting that other organic pollutants, as well as their metabolites, were also present in our samples. Consequently, we have assessed the health risk for 19 out of the 74 detected contaminants, for which health−based guidelines are available, by comparing the measured concentrations with the drinking water standards or health advisories (Table 4.8) proposed by the US−EPA, European Commission, and the WHO. None of the detected concentrations exceeded the maximum contaminant levels, drinking water equivalent levels or lifetime health advisory proposed by the US−EPA (Table 4.8), or the health−based chemical standards and guideline values for drinking water issued by EU and WHO, respectively. A non−carcinogenic assessment of some chemicals was carried out based on the exposure of a 50 kg adult consuming 2 liters of water per day by dividing the reference dose (US−EPA). The risk quotients for the 18 investigated pollutants were much smaller than 1, which demonstrates that there is no risk to humans from these detected contaminants.

4.4.2.9 Conclusions

This is the first comprehensive study of OMPs in groundwater in Vietnam, and as such, this study provides new baseline knowledge about the occurrence and levels of organic contaminants in groundwater. Key findings are as follows: (1) Out of 940 analytes, 74 were detected, which represented about one−third of the number of contaminants that were detected in surface waters. (2) Cholesterol, di(2−ethylhexyl)adipate, DBP, DEP, DEHP and benzyl alcohol were the most frequently detected compounds and were found in over 80% of samples. The total concentrations in 75% of the groundwater samples were less than 5.0 μg L^{-1}. (3) Many of the wells and aquifers are probably influenced by non−point source pollution, such as leaks from the urban sewer system or recharge by wastewater. (4) There is concern for human health related to the presence of pollutants in groundwater in HN and HCM, even though most detected contaminants are not currently regulated in drinking water or were present at low levels. A health risk assessment for 19 detected contaminants showed that there were no risks to humans from these contaminants.

This study was carried out over a limited time period (Sep 2013 and Aug 2014) with a limited number of sampling events. The number of sampling sites was particularly limited in HCM, which means that we only have limited information on the occurrence of OMPs in groundwater in HCM. In spite of the limited information, these initial results can be used as baseline data and will form the basis for further intensive studies on the occurrence of OMPs in groundwater in HCM, and on the primary fate, degradation, and transport processes of OMPs in impacted aquifers. A full evaluation of the potential risks of detected contaminants should also be carried out.

CHAPTER V POLLUTION OF ORGANIC MICRO–POLLUTANTS IN SEDIMENTS

5.1 INTRODUCTION

Four large cities HN, HP, DN and HCM are considered to be the most highly industrialized and urbanized in Vietnam. The rapid development of industry and high population growth in conjunction with lack of proper wastewater treatment facilities have led to toxic chemicals entering the rivers of the cities via wastewater discharged from industrial, medical and domestic activities. Most of domestic wastewaters HN and HCM are not treated and directly discharged into its rivers/canals. World Bank (1996) have reported that there are three types of systems for domestic wastewater disposal in Hanoi; about 32% of Hanoi's population is served by septic tank, 21% by double vault latrines and 23% by on–site systems. The remaining 24% are not served by any system at all. In addition the previous study dealing with OMPs pollution in aquatic environment in Vietnam (Duong et al., 2014a; Duong et al., 2015) revealed that a wide range of OMPs contaminates the Vietnamese aquatic environment, greater attention has been focused on man–made chemicals originating from households, such as sterols, EDCs, PPCPs. Sterols (coprostanol and cholesterol) and PPCPs (caffeine and L–menthol) were found in nearly 100% of surface water samples, indicating that rivers are heavily polluted by untreated domestic wastewater. EDCs (BPA, NP) were found at elevated concentrations in river water in metropolitan areas, and some sites have values exceeding the predicted no–effect concentration for aquatic organisms (MOE, 2001). BPA and OP were detected in groundwaters in HN and HCM. The existence of legacy persistent organic pollutants, such as OCPs and PCBs in sediments in Vietnam, is still of concern because of their persistence, accumulation in sediments, high bioaccumulation potential and harmful biological effects (Iwata et al., 1994). Previous study on OCPs in environmental waters (Duong et al., 2014a; Duong et al., 2015) showed that some OCPs still remain in the water environment although they were banned 20 years ago. In addition, most of the banned OCPs can still be found in relatively high concentrations in the environment throughout Vietnam (e.g. see Viet et al., 2000; Kishida et al., 2007; Minh et al., 2006, 2007a,b; Hoai et al., 2010) and their concentrations are higher than those in other Southeast Asian countries (Monirith et al., 2003; Minh et al., 2006). Although a number of studies have indicated that sediment contamination by banned OCPs in Vietnam has continued until recently (Nhan et al., 2001; Minh et al., 2007a) and some researches on PCB contamination have been conducted in several regions in Vietnam, a complete picture of their contamination in Vietnam has not yet to be compiled.

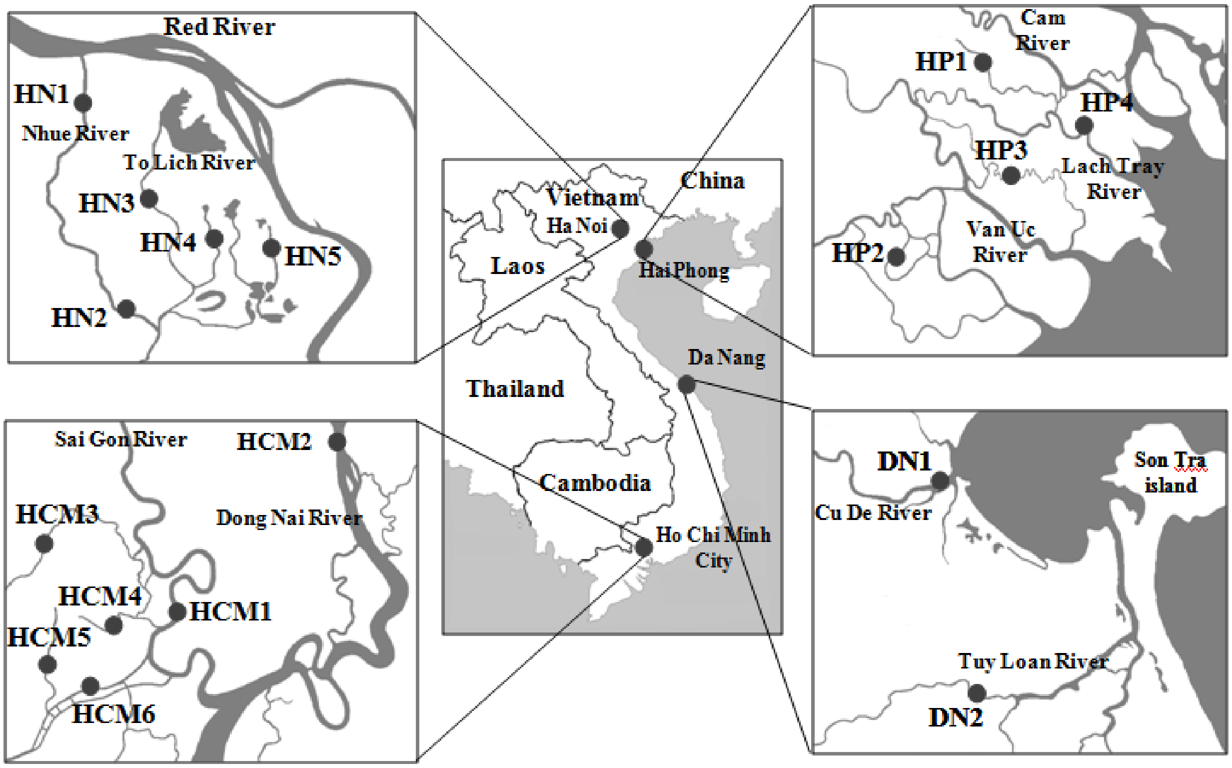


Fig. 5. 1 Location of 17 sampling sites in Hanoi, Hai Phong, Da Nang and Ho Chi Minh City

To manage the effects of such contaminants, information on chemical concentrations is ultimately required. In order to analyze a large number of contaminants in the sediments, an Automated Identification and Quantification System with a GC–MS Database (AIQS–DB) (Kadokami et al., 2004, 2005) that can determine the concentrations of 940 semi–volatile organic compounds, and comprehensive analytical methods for various environmental substrates by making full use of the AIQS–DB are useful. The AIQS–DB was successfully applied to water samples throughout Vietnam in our previous study as well as the water samples from 11 Japanese rivers (Kadokami et al., 2009). Large numbers of chemicals detected in surface (235) and groundwaters (74) in Vietnam implied that these contaminants were mainly discharged from domestic sources due to lack of wastewater treatment facilities. Contamination levels in groundwaters were generally low, however some groundwater wells are influenced by pollution sources from surface such as the leaks from sewerage system/or recharge by untreated wastewater.

An understanding of the contamination status of chemicals, as well as their sources and potential toxic effects on aquatic organisms in Vietnam, is required to provide information for the public and environmental authorities to protect the environment and ecological system. Therefore, this research on a wide variety of OMPs (940) in 17 river and canal bed sediments collected from urban, suburban and rural areas of the four biggest cities in Vietnam was conducted in order: (1) to produce a more complete picture of pollution in Vietnamese rivers, (2) to clarify the main emission sources, (3) to clarify the pollution characteristics of contaminants at each river, (4) to identify chemicals having the potential to pose adverse effects on aquatic organisms, and (5) to assess the long–term temporal trends of pollutants by comparing data with previous studies.

5.2 SAMPLE COLLECTION

In the rainy season of 2011 (October), surficial river sediment samples (5 cm depth) were collected at 17 sites from 16 rivers in four cities: HN, HP, DN and HCM (Fig. 5.1). The 17 sampling sites were divided into three categories: (1) urban areas (HN2, HN3, HN4, HN5, HCM3, HCM4, HCM5, HCM6), (2) suburban areas (HN1, HP4, DN1, HCM1, HCM2) and (3) rural districts (HP1, HP2, HP3, DN2). Detailed information about the sampling locations is provided in Table 3.1. Moisture contents of sediments and volatile solid were analyzed according to methods that were described in 2.4.2 and 2.4.3. OMPs in sediment were extracted by the method that was described in 2.4.1. The analytes were measured by AIQS–database using a GC–MS (TIM). Target analysis were carried out on GC–MS–SIM and GC–MS–MS–SRM.

5.3 QUALITY CONTROLS

Quality controls were performed by blank analysis and examining the recoveries of surrogates (deuterium–labeled internal standards), which were chosen as being representative of 940 compounds based on their physico–chemical properties. Laboratory blank samples were carried out for every batch of six samples for cross–verification. Prior to extraction, sediment and blank samples were spiked with 38 surrogate compounds (Table 5.1), which have the same range of broad physico–chemical properties as found among the OMPs measured, and were used to assess whether recoveries of targets OMPs are acceptable or not. Good recoveries (73–126%) were obtained for 23 out of 38 surrogate compounds except for six highly polar compounds, which are poorly extracted with dichloromethane (Kadokami et al., 2012). Two compounds, benzidine–d_8, 3,3'–dichlorobenzidine–d_6, were not recovered even in blank samples due to oxidative losses during concentration steps (EPA–8270D, 2007). Six surrogate compounds showed high recovery rates (over 150%) probably due to the matrix effect (Kadokami et al., 2012). Relative standard deviations of 31 surrogates were below 20% (Table 5.1), confirming that sample analyses were acceptably precise. When reporting data, blank concentrations were subtracted from sample concentrations. The reported concentrations were not corrected for recovery values.

Duplicate analysis was performed using the sample from HCM4 (Table S5.1). The relative average deviations of 152 out of the 158 detected substances were below 20%, indicating that the sample analysis produced results with good reproducibility and was sufficient for environmental surveys.

Table 5. 1 Recoveries of surrogate compounds (n=8)

No	Compound	Average recovery[a], %	RSD[b], %
1	2–Aminonaphthalene–d_7	0	–
2	Benzidine–d_8	0	–
3	3,3'–Dichlorobenzidine–d_6	0	–
4	4-Chloroaniline–d_4	19	38
5	2–Fluorophenol	26	17
6	Bis(2-chloroethyl)ether–d_8	48	20
7	1,2–Dichlorobenzene–d_4	51	8.8
8	2–Chlorophenol–d_4	62	11
9	Acetophenone–d_5	73	8.6
10	2–Fluorobiphenyl	74	19
11	Nitrobenzene–d_5	74	9.3
12	4–Methylphenol–d_8	76	10
13	2,4,6–Tribromophenol	83	11
14	Benzo(a)pyrene–d_{12}	83	18
15	Simazine–d_{10}	85	8.0
16	Dibenzothiophene–d_8	87	7.0
17	Phenol–d_5	88	24
18	Quinoline–d_7	88	7.2
19	Anthracene–d_{10}	91	4.0
20	Fluorene–d_{10}	94	6.2
21	2,4–Dichlorophenol–d_3	94	9.1
22	Diphenylamine–d_{10}	95	8.5
23	$C_{20}D_{42}$	97	15
24	Benzophenone–d_{10}	98	5.4
25	N–Nitrosodiphenylamine–d_6	100	9.1
26	Dimethylphthalate–d_6	101	4.8
27	p–Terphenyl–d_{14}	104	15
28	Pyrene–d_{10}	108	14
29	1,2–Diphenylhydrazine–d_{10}	108	8.4
30	Pentachlorophenol–$^{13}C_6$	114	14
31	2–Nitrophenol–d_4	126	17

Table 5. 1 Recoveries of surrogate compounds (n=8) (continued)

No	Compound	Average recovery[a], %	RSD[b], %
32	$C_{32}D_{66}$	147	24
33	Isoxathion–d_{10}	150	19
34	Isofenphos oxon–d_6	192	5.4
35	Fenitrothion–d_6	207	5.9
36	Bisphenol A–d_{14}	288	28
37	4–Nitrophenol–d_4	306	12
38	Tris(2–ethylhexyl)phosphate–d_{51}	358	16

[a] One micro gram of each surrogate was added to the samples.

[b] Relative standard deviation.

5.4 RESULTS AND DISCUSSIONS

5.4.1 Occurrence of organic micro–pollutants

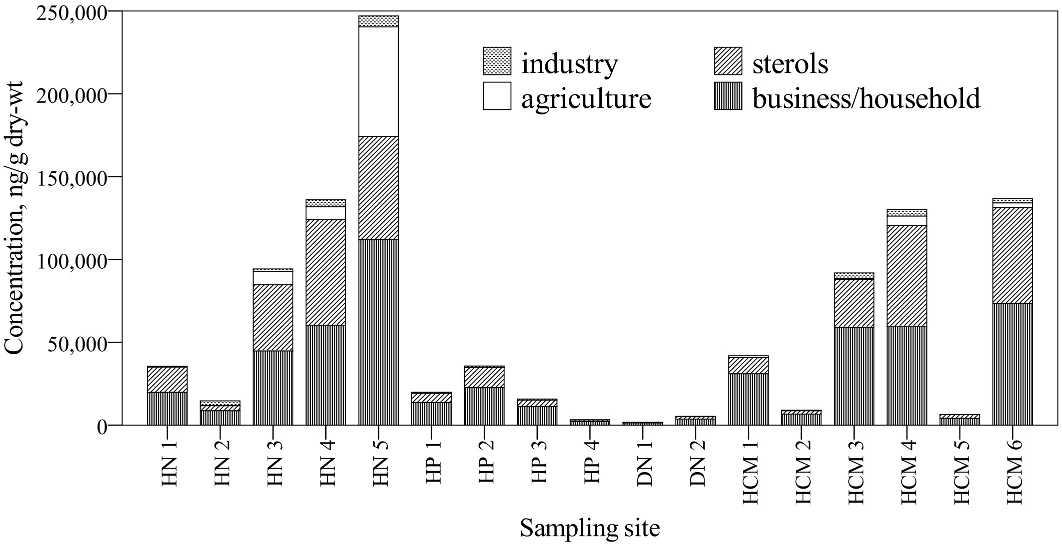


Fig. 5. 2 Concentration (ng g^{-1} dry–wt) from different emission sources at each site

One hundred and eighty–five of the 940 analytes, belonging to 26 different chemical groups were detected at least once (Tables S5.1 and Table 5.2). This number of observations was similar to those (184) detected in sediments in Japan using the same method (Kadokami et al., 2013). The sum of the concentrations of detected compounds varied from 1600 ng g^{-1} dry–wt (DN1) to 247000 ng g^{-1} dry–wt (HN5). Contamination levels in sediments from highly populated urban areas (HN3–5, HCM3–4 and HCM6) were over 5 times higher than those in suburban and rural areas (Fig. 5.2).

Chemicals originating from domestic sources and sterols compounds were the most dominant, contributing over 90% of total concentration in sediment samples (Fig. 5.2). Sterol compounds were observed in almost 100% of sampling sites at the greatest levels with sum of sterols concentrations ranging from 335 to 92400 ng g^{-1} dry–wt. We observed the similar contamination pattern in river water at the same sampling sites (Duong et al., 2014a), clearly indicating the discharge of untreated sewage from municipal areas to the rivers. Cluster analysis of pollutants was carried out on 17 sites using the standardized concentrations of 185 identified compounds. The results highlight clear differences between the sampling sites (Fig. 5.3). For instance, HN5 is clearly different from other sites, probably due to the extremely high contamination levels. A very tight group composed of the sites located inside city areas (HN1, HN3–4, HCM3–4 and HCM6) implies similar pollution characteristics, while the other suburban sites represent the third group (HN2, HP1–3, DN2 and HCM1–2). Sites HP4, DN1 and HCM5 were identified as a separate group due to their low contaminants concentrations. In addition, the observation of contamination levels and categories of chemicals detected in urban sediments in HN and HCM revealed that, although there is a large latitudinal gap between two cities, a similar pollution profile was still observed in sediments of these cities, perhaps as a result of their similar social features. Low concentration level of urban sediment (HCM5) is the consequence of low volatile organic contents (Table S5.1).

5.4.2 Sterols

Nine out of the 10 sterols analyzed were detected in all the sediment samples. Coprostanol, cholestanol and cholesterol appeared at the highest mean concentration values (7100, 4700, and 4300 ng g^{-1} dry–wt, respectively). Total sterol concentrations (summed concentrations of 9 detected sterols) ranged from 335 (DN1) to 92400 ng g^{-1} dry–wt (HN5) (median 12400 ng g^{-1} dry–wt) (Table 5.3), and contributed the highest proportion of total detected chemicals in these sediment samples. Elevated concentrations of total sterols were observed in the metropolitan areas (HN3–5, HCM3–4, HCM6) (Fig. 5.2); these levels are about 2 times higher than those in other Asian developing countries (Isobe et al., 2002), clearly indicating their derivation from untreated municipal sewage.

Among 9 sterols observed in this study, coprostanol, cholesterol and cholestanol were only sterols quantified for evaluating sewage effects (Writer et al., 1995), which were

Table 5. 2 Sediment concentrations (ng g^{-1} dry–wt) and the number of chemicals belonging to different chemical categories and origins at each sampling site

Origin	Category	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4	HCM 5	HCM 6
Agriculture	Insecticides (187)	6.6 (7)	0.55 (4)	7908 (13)	7721 (12)	66131 (12)	12 (10)	29 (9)	5.2 (9)	0.49 (6)	0.02 (1)	0.84 (6)	3.9 (5)	0.84 (6)	605 (7)	5557 (19)	0 (0)	2810 (16)
	Herbicides (117)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
	Fungicides (112)	0.05 (1)	0 (0)	2.9 (1)	3.8 (1)	0.79 (1)	0 (0)	0.02 (1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0.19 (1)	1.6 (1)	0 (0)	1.4 (1)
	Other pesticides (36)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Business/household/traffic	Antioxidants (8)	406 (4)	391 (3)	447 (4)	490 (3)	703 (3)	254 (4)	172 (3)	32 (1)	177 (3)	24 (2)	95 (2)	284 (3)	191 (3)	152 (3)	629 (4)	75 (3)	1182 (3)
	Fire retardants (13)	3.8 (1)	0 (0)	0 (0)	115 (1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	41 (1)	0 (0)	0 (0)	0 (0)	0 (0)	119 (1)
	Disinfectants and insecticidal (2)	3.5 (1)	2.2 (1)	38 (2)	6.3 (2)	35 (2)	0.37 (1)	0 (0)	0.77 (1)	1.2 (1)	0 (0)	0.58 (1)	0.86 (1)	0.50 (1)	13 (2)	4.4 (1)	0.84 (1)	0.64 (1)
	Fatty acid methyl esters (34)	67 (2)	7.9 (3)	10 (2)	210 (1)	0 (0)	124 (2)	296 (2)	77 (2)	24 (3)	3.2 (2)	9.0 (3)	113 (3)	1.4 (1)	0 (0)	208 (1)	19 (2)	290 (1)
	Metabolites of detergents (3)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
	Fragrances and cosmetics (13)	1.3 (1)	6.7 (2)	72 (2)	110 (3)	71 (2)	0 (0)	22 (1)	12 (1)	0 (0)	0 (0)	8.0 (1)	43 (3)	0.99 (1)	42 (2)	44 (1)	0.91 (1)	44 (2)
	Leaching compounds from tires (21)	10 (2)	0 (0)	145 (2)	0 (0)	174 (2)	0 (0)	9.0 (1)	0 (0)	0 (0)	0 (0)	0 (0)	8.8 (1)	1.8 (1)	39 (2)	43 (2)	0 (0)	0 (0)
	Petroleum (26)	6859 (22)	5964 (19)	12019 (23)	24809 (23)	61839 (25)	9566 (18)	15345 (22)	9305 (19)	1139 (15)	1056 (14)	2254 (18)	22319 (22)	5408 (18)	27329 (25)	27612 (24)	2002 (16)	34794 (23)
	Plant or animal steroids (10)	23354 (9)	4409 (8)	59763 (9)	85426 (9)	92444 (9)	7576 (9)	16997 (9)	5113 (9)	1209 (8)	335 (9)	1741 (8)	12373 (9)	2403 (9)	46494 (9)	79103 (9)	3142 (9)	83307 (9)

Table 5.2 Sediment concentrations (ng g^{-1} dry–wt) and the number of chemicals belonging to different chemical categories and origins at each sampling site (continued)

Origin	Category	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4	HCM 5	HCM 6
Business/household/traffic	Plasticizers (14)	4107 (6)	764 (6)	11886 (7)	6880 (7)	9983 (5)	1659 (6)	1939 (5)	529 (6)	475 (5)	177 (4)	870 (6)	3987 (7)	622 (5)	8475 (8)	8562 (6)	1056 (8)	6395 (7)
	PPCPs (19)	176 (1)	93 (1)	210 (1)	1361 (1)	1094 (1)	0 (0)	0 (0)	0 (0)	67 (1)	0 (0)	70 (1)	310 (1)	0 (0)	0 (0)	211 (1)	3.5 (1)	889 (1)
	Other substances of domestic (29)	8.3 (1)	0 (0)	47 (1)	4558 (3)	7869 (3)	3.7 (1)	11 (2)	0 (0)	6.8 (1)	0 (0)	7.4 (1)	501 (2)	0 (0)	5263 (3)	4112 (3)	45 (1)	4246 (1)
Industry	Intermediates for dye (24)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	12 (1)	0 (0)	0 (0)	0 (0)	0 (0)	18 (1)	3.1 (1)	0 (0)	0 (0)	0 (0)	0 (0)
	Intermediates for resins (9)	0.98 (1)	8.2 (2)	0 (0)	2.5 (1)	0 (0)	0 (0)	0.67 (1)	0.57 (1)	0 (0)	0 (0)	0 (0)	716 (2)	0 (0)	3.8 (1)	0 (0)	0 (0)	4.5 (1)
	Intermediates for pesticide (5)	0 (0)	0 (0)	0 (0)	0.63 (1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0.55 (1)	0 (0)	0.46 (1)
	Intermediates in organic (57)	28 (3)	23 (2)	88 (2)	132 (3)	156 (3)	13 (2)	19 (2)	33 (3)	0 (0)	0 (0)	4.9 (2)	42 (3)	5.9 (3)	117 (2)	82 (3)	8.8 (2)	31 (2)
	PAHs (50)	475 (27)	2951 (25)	1417 (26)	3060 (26)	5811 (28)	661 (25)	640 (28)	645 (27)	35 (22)	10 (17)	180 (24)	1021 (24)	364 (23)	3025 (27)	3305 (27)	28 (16)	2221 (26)
	PCBs (59)	1.2 (22)	0.07 (3)	35 (44)	42 (36)	39 (40)	0.40 (13)	0.12 (5)	0.16 (4)	0.08 (3)	0 (0)	0 (0)	4.7 (36)	0.64 (12)	12 (32)	103 (49)	N.Q. N.Q.	57 (49)
	PCNs (27)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
	Solvent (11)	60 (4)	33 (3)	197 (4)	389 (5)	542 (2)	25 (2)	206 (3)	10 (3)	51 (1)	0 (0)	62 (3)	71 (5)	47 (2)	189 (3)	301 (3)	7.7 (1)	140 (5)
	Exploisives (6)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
	Other substances of industrial (48)	11 (2)	1.2 (1)	13 (2)	702 (2)	150 (2)	0 (0)	1.7 (1)	2.1 (1)	2.6 (2)	0 (0)	1.4 (1)	30 (2)	0 (0)	130 (2)	243 (3)	2.5 (2)	185 (3)
Total (940)		35577 (117)	14656 (83)	94296 (145)	136019 (140)	247043 (140)	19895 (93)	35701 (96)	15764 (87)	3187 (71)	1604 (49)	5305 (77)	41888 (131)	9051 (86)	91890 (129)	130120 (158)	6392 (63)	136716 (153)

Parentheses show the number of chemicals.

N.Q. represents “not quantified”.

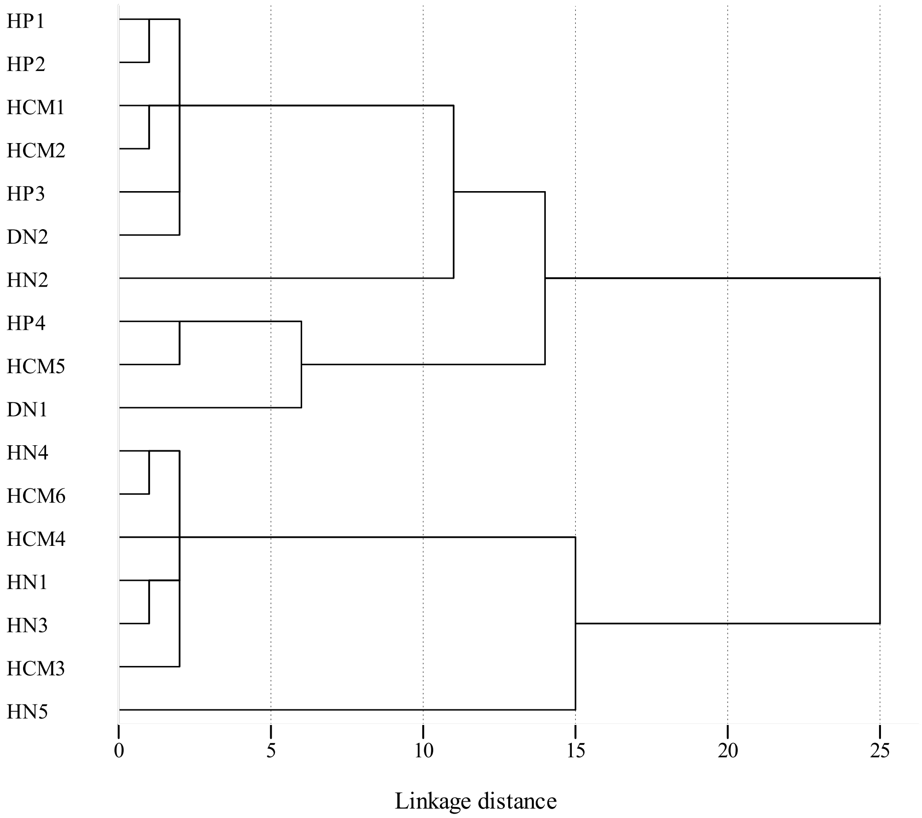


Fig. 5. 3 Hierarchical dendrogram of sampling sites obtained by cluster analysis (Ward's method and squared Euclidean distance) using standardized concentrations of 185 substances at 17 sites.

observed at all sampling sites at the highest concentrations. The concentrations of these compounds ranged from 64 ng g^{-1} dry–wt (DN1) to 23000 ng g^{-1} dry–wt (HN4) (mean 7600 ng g^{-1} dry–wt), 79 ng g^{-1} dry–wt (DN1) to 18000 ng g^{-1} dry–wt (HCM4) (mean 5100 ng g^{-1} dry–wt), 78 ng g^{-1} dry–wt (DN1) to 16 500 ng g^{-1} dry–wt (HCM6) (mean 5200 ng g^{-1} dry–wt), respectively (Table 5.3). Beta–Sitosterol, stigmasterol, epicoprostanol, coprostanone and campesterol were also observed at all sampling sites but at lower contamination levels. Coprostanol concentrations in the sediment samples at the sites located close to the populated cities had higher levels (Table 5.3). In Hanoi, elevated concentrations were found at HN4 (23000 ng g^{-1} dry–wt), HN5 (21000 ng g^{-1} dry–wt) and HN3 (15000 ng g^{-1} dry–wt). In Ho Chi Minh City, the highest concentration (19000 ng g^{-1} dry–wt) was observed in inner city canals (HCM4 and HCM6), followed by HCM3 (8400 ng g^{-1} dry–wt). The maximum level of coprostanol observed in this study was higher than those reported in

Mekong Delta (Vietnam) (4500 ng g^{-1} dry–wt) and in Malaysia (15500 ng g^{-1} dry–wt) (Hideshige et al., 2002).

Writer et al. (1995) proposed using a ratio of coprostanol (sewage sources) to sum of cholestanol with cholesterol (sewage and non–sewage sources) to predict sewage sources. This ratio is independent of organic carbon percentage of sediments, whereas the coprostanol concentration increases with increasing organic carbon percentage (Table 5.3). Since cholesterol is transformed in anoxic sediments and produced coprostanol and cholestanol, evaluation fecal pollution through sedimentary coprostanol concentrations, in–situ productions of coprostanol from cholesterol should be taken into account (Takada et al., 2002). Grimalt et al. (1990) had demonstrated that, a ratio of copostanol to cholesterol (>0.2) indicates sewage or Glassmeyer et al. (2005) indicated that the value of higher than 0.3 implied human feces. In this study, values >0.4 were seen at all sampling sites, and values greater than 1 were observed in 10 out of 17 sites in urban areas, suggesting these studied rivers were seriously contaminated by raw sewage (Quéméneur and Marty, 1994). A higher percentage of coprostanol relative to total sterols (%Cop) indicates greater contributions of fecal matter of human origin to fecal pollution (Hatcher and McGillivary, 1979; Isobe et al., 2002). The %Cop (>20%) was higher in sediments from urban canals (HN1–5, HCM4–6) than those in rural and suburban areas, which suggests the direct input of human feces to urban canals.

5.4.3 Pesticides

Twenty–five out of the 457 pesticides in the database were detected, which included 4 current use insecticides (chlorpyrifos, deltamethrin, permethrin–1, permethrin–2), 19 banned insecticides, one fungicide (hexachlorobenzene) and a synergist, piperonyl–butoxide (Table 5.4). The most frequently detected pesticides were DDT metabolites (more than 80% of samples), followed by lindane (γ–HCH) (60%) and dieldrin (60%). In terms of currently used pesticides, pyrethroid insecticides (such as permethrin–1 and –2) and their synergist (piperonyl–butoxide) were the most dominant and contributed more than 98% of total concentration of detected pesticides. These insecticides were only found in sediments from urban areas of HN and HCM, with the highest concentration up to 6400 ng g^{-1} dry–wt, 1900 ng g^{-1} dry–wt and 64 ng g^{-1} dry–wt, respectively (Table 5.4). These results agree well with those observed in surface water samples taken in the same sampling sites in this study (Duong et al., 2014a). It has been reported that pyrethroids are one of the most widely used classes of insecticides for various uses such as agriculture, in the home and/or garden and have been steadily increasing in use in urban areas (Sourlock and Lee, 2008).

Table 5. 3 Concentrations (ng g^{-1} dry–wt) of sterol compounds and volatile organic contents (%) in sediment at each site

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM4–2	HCM 5	HCM 6
1	Cholestane	10	N.D.	118	165	171	1	1	2	N.D.	6	N.D.	27	1	184	233	256	3	65
2	beta-Sitosterol	2810	184	5377	7820	11698	934	2181	538	115	48	274	1378	373	4173	7930	7803	153	4300
3	Stigmasterol	1521	265	4532	8636	5938	992	1758	726	97	20	272	1958	377	4340	6500	6225	275	6587
4	Cholesterol	2481	487	7836	9217	11477	1387	3160	1125	273	79	372	1787	534	5237	16522	18157	497	11186
5	Cholestanol	2662	754	7498	14462	11713	1253	2652	1085	220	78	288	2617	423	6493	10594	14176	551	16506
6	Coprostanol	5747	1347	14566	23398	21397	1011	2490	508	266	64	189	1975	246	8391	19063	16403	804	19143
7	Epicoprostanol	3514	591	7594	7300	10840	627	1531	331	124	21	113	952	113	6016	10148	10789	417	10845
8	Coprostanone	3452	700	7734	9048	10412	317	1055	238	59	3	84	675	104	8952	1973	1823	244	11092
9	Campesterol	1156	82	4508	5381	8797	1053	2168	560	55	16	149	1004	232	2709	6140	6606	198	3583
Total concentration		23354	4409	59763	85426	92444	7576	16997	5113	1209	335	1741	12373	2403	46494	79103	82237	3142	83307
Volatile organic, %		6.6	7.3	12	10	17	5.9	7.7	7.1	1.4	1.0	1.6	11	11	7.3	10	10	3.4	13

N.D. represents “not detected”.

Table 5. 4 Concentrations (ng g^{-1} dry–wt) of pesticides at each site

No	Name	DL	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6	QCVN15: 2008/ BTNMT
	Current use insecticides																				
1	Chlorpyrifos	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	9.4	25	3.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
2	Deltamethrin	0.2	N.D.	N.D.	N.D.	N.D.	59714	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
3	Permethrin 1	0.2	N.D.	N.D.	6410	6346	4433	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	435	3990	3702	N.D.	2308	
4	Permethrin 2	0.2	N.D.	N.D.	1444	1296	1874	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	162	1404	1320	N.D.	473	
5	Piperonyl butoxide	0.2	N.D.	N.D.	12	33	64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.3	27	29	N.D.	9.2	
	Banned insecticides																				
6	α–HCH	0.2	(0.1)	N.D.	0.87	0.66	0.89	(0.03)	(0.02)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.85	0.88	N.Q.	0.39	
7	β–HCH	0.2	N.D.	N.D.	N.D.	(0.04)	0.28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.04)	(0.04)	N.Q.	N.D.	

Table 5.4 Concentrations (ng g^{-1} dry–wt) of pesticides at each site (continued)

No	Name	DL	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6	QCVN15: 2008/ BTNMT
8	γ–HCH	0.2	N.D.	N.D.	2.0	0.70	N.D.	0.44	(0.16)	0.29	N.D.	N.D.	N.D.	N.D.	(0.18)	1.2	1.6	1.3	N.Q.	2.8	100
9	Aldrin	0.1	N.D.	N.D.	0.12	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.02)	N.D.	N.D.	N.D.	N.D.	0.13	0.18	N.Q.	N.D.	100
10	Endrin	0.2	0.5	(0.12)	N.D.	N.D.	N.D.	N.D.	N.D.	0.35	(0.19)	N.D.	0.23	(0.10)	N.D.	N.D.	N.D.	N.D.	N.Q.	0.43	100
11	Dieldrin	0.2	N.D.	(0.05)	3.1	N.D.	N.D.	(0.15)	0.27	0.26	(0.14)	N.D.	(0.11)	N.D.	0.22	N.D.	4.7	4.0	N.Q.	N.D.	100
12	oxy-Chlordane	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.Q.	0.28	
13	trans–Chlordane	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.24	0.25	N.Q.	0.31	
14	cis–Chlordane	0.2	N.D.	N.D.	(0.10)	N.D.	(0.03)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.90	0.82	N.Q.	0.50	100^a
15	trans–Nonachlor	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.47	0.33	N.Q.	0.21	
16	cis–Nonachlor	0.2	N.D.	N.D.	N.D.	N.D.	(0.02)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.03)	0.38	0.41	N.Q.	(0.07)	
17	Heptachlor	0.1	N.D.	N.D.	N.D.	(0.02)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.02)	(0.02)	N.Q.	N.D.	100
18	Heptachlorepoxide(	0.2	N.D.	N.D.	0.4	(0.10)	N.D.	(0.07)	N.D.	N.D.	(0.05)	N.D.	(0.09)	N.D.	(0.10)	N.D.	(0.08)	(0.08)	N.Q.	1.4	
19	o,p'–DDE	0.1	0.11	N.D.	0.45	0.73	0.88	(0.04)	(0.04)	N.D.	N.D.	N.D.	N.D.	0.11	N.D.	(0.03)	3.3	3.0	N.Q.	0.24	
20	p,p'–DDE	0.1	4.1	0.25	17	27	26	0.66	0.93	0.40	(0.03)	N.D.	0.29	2.1	0.20	1.3	62	54	N.Q.	6.7	
21	o,p'–DDD	0.1	0.34	N.D.	5.7	4.9	2.3	0.15	0.36	(0.07)	(0.02)	N.D.	(0.03)	0.39	(0.02)	N.D.	8.0	6.5	N.Q.	1.2	
22	p,p'–DDD	0.1	1.4	0.12	13	12	15	0.63	2.4	0.40	(0.06)	N.D.	(0.09)	1.2	0.11	N.D.	52	49	N.Q.	5.1	
23	o,p'–DDT	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.02)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.Q.	N.D.	
24	p,p'–DDT	0.1	0.1	N.D.	N.D.	N.D.	N.D.	(0.06)	0.11	0.13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.6	2.4	N.Q.	N.D.	100^b
	Fungicide																				
25	Hexachlorobenzene	0.1	(0.05)	N.D.	2.9	3.8	0.79	N.D.	(0.02)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.19	1.6	1.4	N.Q.	1.4	100
	Volatile organic, %		6.6	7.3	12	10	17	5.9	7.7	7.1	1.4	1.0	1.6	11	11	7.3	10	10	3.4	13	

N.Q. represents “not quantified”; N.D. represents “ not detected”; DL represents “detection limit”; QCVN 15:2008/BTNMT: National technical regulation on the pesticide residues in the soils issued by Ministry of Natural Resources and Environment, Vietnam; “()” represents value below detection limit; [a] Limitation of chlordanes; [b] Limitation of DDTs.

Since these pyrethroids were found in only the center of HN and HCM, these seem to be used for vector controls such as mosquitoes and flies. An elevated concentration of deltamethrin was only found at HN5 (60000 ng g^{-1} dry−wt), contributing over 90% of total pesticides in the sample (Table 5.4). The emission source of deltamethrin is currently unknown, however, it has been hypothesized that the inputs of this compound are due to an accidental release before our sampling, which demonstrates the need for additional monitoring. The high concentrations of pyrethroids observed in stream sediments in USA resulted in the highest pyrethroids toxic units and contributed to sediment toxicity (Kuivila et al., 2012). The pyrethroid contamination levels in sediments in this study were over 70 times higher than those reported in USA (Kuivila et al., 2012), and so probably pose significant potential toxicity to benthic animals. An organophosphorus insecticide, chlorpyrifos, was found in agriculture areas close to water supply sources for HP (HP1−3) (Table 5.4) at concentration up to 25 ng g^{-1} dry−wt, indicating their wide spread use in paddy fields in Vietnam.

In term of banned pesticides, chlordane compounds such as oxy−chlordane, trans−chlordane and cis−chlordane were mostly detected at concentrations lower than the detection limit (0.2 ng g^{-1} dry−wt) except for those detected at site HCM6. Similar observation was seen for heptachlor, heptachlorepoxide (B), trans− and cis−nonachlor, which were not detected or detected at trace concentrations of less than 0.5 ng g^{-1} dry−wt in most of sediment samples (Table 5.4), except for heptachlorepoxide (B) (1.4 ng g^{-1} dry−wt, HCM6). The detected concentrations of chlordane compounds and heptachlor were much lower than limitation values of pesticide residues in the soils (100 ng g^{-1} dry−wt, QCVN15:2008/ BTNMT) issued by Ministry of Natural Resources and Environment, Vietnamese (Table 5.4), implying that there were no recent use of these compounds in Vietnam.

DDT has been used in large quantities for agricultural and public health purposes in Vietnam over the last few decades (Viet et al., 2000), and are the most abundant OCPs detected in the environment in Vietnam, although the prohibition of DDTs has been implemented in Vietnam since 1995. This chemical perhaps is continuously used until recent years (Minh et al., 2007a, b), yet DDTs residue levels were highly variable among sampling sites, ranging from not detected (DN1) to 127 ng g^{-1} dry−wt (HCM4) (Table 5.4). This range was similar to those reported by Minh et al. (2007b) (<0.01–110 ng g^{-1} dry−wt), however it was several times lower in comparing with those in early 1990s (Table 5.5). DDTs concentration levels in Hanoi and Ho Chi Minh City urban areas (127 ng g^{-1} dry−wt, HCM4; 13 ng g^{-1} dry−wt, HCM6; 36 ng g^{-1} dry−wt, HN3; 45 ng g^{-1} dry−wt, HN4; 44 ng g^{-1} dry−wt,HN5) were over 10 times higher than those in other locations. DDTs presented at lower

Table 5. 5 Comparison of organochlorines in Vietnamese sediments with those reported elsewhere in Asia[a]

Country	Year	n	PCBs[b]	DDTs[c]	HCHs[d]	HCB[e]	CHLs[f]	Reference
A – Vietnam								
Hochiminh (urban areas)	1990	5	7.6–630	47–790	0.97–12	–	0.46–20	Iwata et al. (1994)
	2004	6	46–150	12–72	<0.05	<0.1–18	0.6–4.5	Minh el al. (2007a)
	2012	4	15–121	1.4–127	1.2–3.1	0.19–1.6	0.03–2.0	Present study
Hochiminh (outskirt)	2003–2004	22	0.04–9.2	<0.01–110	<0.02–1.3	–	–	Minh et al. (2007b)
	2004	9	0.33–22	0.21–23	<0.01–0.03	<0.001–0.6	0.016–1.0	Minh el al. (2007a)
	2012	2	0.85–5.5	0.34–3.8	0–0.18	N.D.	N.D.	Present study
Hanoi (urban areas)	1997	12	0.67–40[g]	7.3–73	0.07–3.1	–	–	Nhan et al. (2001)
	2006	16	1.3–328[h]	6.4–1100	–	<0.2–22	–	Hoai et al. (2010)
	2012	4	0.13–55	0.38–45	0-2.8	0–3.8	0–0.51	Present study
Hanoi (outskirt)	1995–1996	2	2.2–11[g]	7.0–14	–	–	–	Nhan et al. (1998)
	2012	1	1.7	6.0	0.11	0.05	N.D.	Present study
B – World								
China (Pearl River Estuary)	1996–1997	20	0.18–1.82	1.36–8.99	0.28–1.23	–	–	Hong et al. (1999)
China (Minjiang River)	1999	9	15.1–57.9	1.5–13	2.9–16	–	–	Zhang et al. (2003)
Taiwan (Wu–Shi River)	1997–1998	19	–	0.53–11.4	0.99–14.5	–	–	Doong et al. (2002)
India (urban and suburban area)	1989	6	4.8–1000	8–450	0.58–38	–	0.47–130	Iwata et al. (1994)
Thailand (urban and industrial area)	1990	4	11–520	4.8–170	0.48–3.1	–	1.4–210	Iwata et al. (1994)
Indonesia (urban and residential area)	1991	4	5.9–220	3.4–42	0.035–0.1	–	0.16–38	Iwata et al. (1994)
Japan (urban area)	1990	3	63–240	2.5–12	4.5–6.2	–	0.66–2.1	Iwata et al. (1994)
Taiwan (urban and suburban area)	1990	3	2.3–230	0.39–11	0.29–0.79	–	0.14–5.6	Iwata et al. (1994)

"–" represents the data is not available; N.D. represents “not detected”.

[a] Concentration in ng g^{-1} dry–wt.

[b] Sum of 24 PCB congeners (PCB 8, 18, 31, 28, 33, 52, 44, 70, 66, 95, 101, 110, 118, 105, 149, 138, 153, 187, 174, 180, 170, 199, 196, 194) by multiplication with the value of 1.64 [percentage contribution of 24 major congeners (in average = 60.9%) to total PCBs in KC−MIX formulation] (Takasuga et al., 2006).

[c] Sum of 6 DDTs (o,p'−DDE, p,p'−DDE, o,p'−DDD, p,p' DDD, o,p'− DDT, p,p'−DDT).

[d] Sum of 3 HCH isomers (α−HCH, β−HCH, γ−HCH).

[e] Hexachlorobenzene.

[f] Sum of 4 CHLs (trans−chlordane, cis−chlordane, trans−nonachlor, cis−nonachlor).

[g] As alochlor 1254 mixture.

[h] Sum of 7 PCB congeners (28, 52, 101, 118, 138, 153, 180) by multiplication with the value of four (Froescheis et al., 2000).

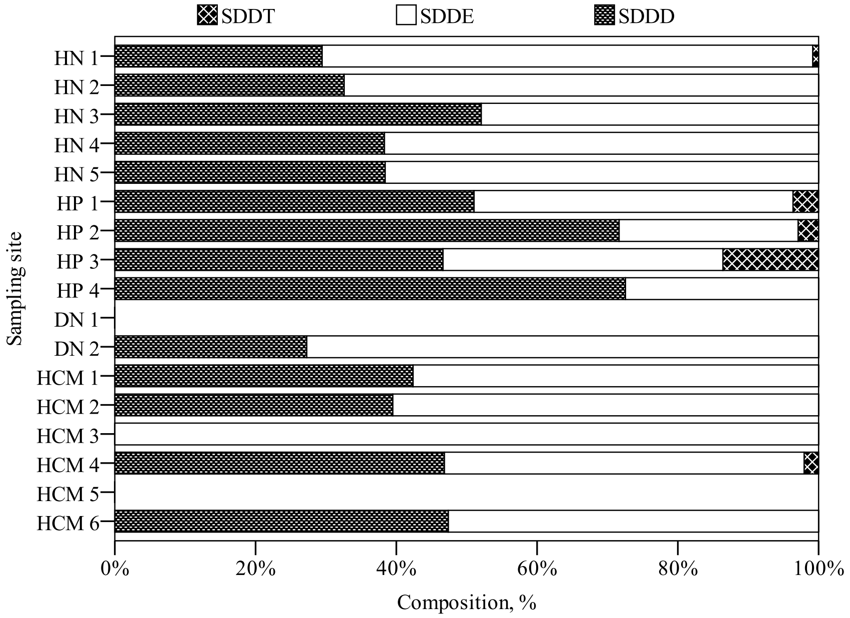


Fig. 5. 4 DDTs composition in sediments at each site. SDDT = o,p'–DDT + p,p'–DDT; SDDE = o,p'–DDE + p,p'–DDE; SDDD = o,p'–DDD + p,p'–DDD

concentrations in sediments collected in remote and suburban areas such as DN2 (0.29 ng g^{-1} dry–wt), HCM2 (0.31 ng g^{-1} dry–wt) and HN2 (0.37 ng g^{-1} dry–wt). This supports the hypothesis that the usage of the insecticide dicofol, which contains DDTs as by products, may be a pollution source of DDTs. However, so far the accurate data of usage of dicofol in Vietnam is not available, although Minh et al. (2006) suggested that this chemical might be have been used in Vietnam recent years. Perhaps further studies regarding the characterization of DDT pollution in Vietnam is necessary.

The ratios of the three major compounds, DDT, DDE, and DDD, can be used to understand the chronology of input of DDT in the environment. For instance, the ratio of DDT/DDE can be used to indicate recent input of DDT (>0.5) or past input (<0.3) (Strandberg et al., 1998). In addition, the ratio of (DDE + DDD) to total DDTs ((DDE + DDD)/ΣDDTs) can be used to indicate old DDTs residues (>0.5) or recent input (<0.5) (Hong et al., 1999; Zhang et al., 1999). In this study, the high proportion (>80%) of DDE and DDD to ΣDDTs (Fig. 5.4) in conjunction with the ratio of (DDE + DDD)/ΣDDTs and DDT/DDE were higher than 0.5, and less than 0.3, respectively, clearly demonstrating that there have been no recent inputs of DDT in the study areas.

In view of the fact that DDT has been used in large quantities for agricultural and public health purposes in Vietnam over last many years (Viet et al., 2000). The low concentration levels of this compound observed in water and sediment samples indicating that there is degradation of DDT in the environment. The risk assessment of these compounds was carried out based on the guidelines issued by Canadian Council of the Ministers of the Environment (URL18). Accordingly, nine urban sediments in the present study exceeded the Probable Effect Level (PEL) value and three had levels over the Interim Sediment Quality Guideline (ISQG) for DDD and DDE (Table 5.6). This implies there is a potential risk from DDTs to aquatic organism in the rivers.

The spatial distribution of HCHs was similar to that of DDTs. Total HCHs concentration (ΣHCHs) ranged from not detected (HN2, HP4, DN1–2, HCM1) to 3.1 ng g^{-1} dry–wt (HCM6), which is around 20 times lower than ΣDDTs (Table 5.5). The lower concentrations of HCHs compared to DDTs are probably due to the short environmental half–lives of HCHs in soils ($T_{1/2}$ of hours to weeks), lower log K_{ow} 3.6–3.8 and higher water solubility which is 3 to 4 orders of magnitude higher than that of DDTs (Howard, 1989). In addition, the rapid mineralization and formation of organic volatile compounds of HCHs (Nhan et al., 2001) are probably the causes of lower concentrations of HCHs compared to DDTs in sediments. Although the concentrations of ΣHCHs in HN and HCM appear to have decreased from 1990 to 2004, their concentration in some sediment samples was still higher than those reported in 2004 (Table 5.5), suggesting recent input of HCHs to the environment. On a global scale, the highest ΣHCHs concentrations in urban sediments in HN and HCM were comparable with those in Thailand, whilst less than half of those reported in Japan and India, and much higher than those in Indonesia and Taiwan (Table 5.5). Nhan et al. (2001) indicated that, in the technical HCH mixture, α–HCH usually contributes to about 50%, β–HCH to about 20% and γ–HCH usually accounts for about 30%. Lindane (γ –HCH), only isomer with insecticidal properties, became available in Vietnam under the trade name of "666" (Nhan et al., 2001) was found at higher concentration compared to other HCH isomers in sediments (Table 5.4). In particular, four sediments had γ –HCH values beyond the ISQG and three of them had values exceeding PEL (URL18) (Table 5.6), again suggesting recent use of lindane and potential toxicological stress on aquatic biota of the rivers.

Similar to HCHs compounds, the concentration levels of drins (aldrin, endrin and dieldrin) were low compared with DDTs in this study (Table 5.4). Aldrin, endrin and dieldrin were sporadically found in some sampling sites. Total drins concentrations appear higher in HCM than those in HN, perhaps due to the high use amount of drins in HCM than HN. However, further work is required to test the hypothesis that there are differences in contamination levels between two cities. The concentration of dieldrin at two urban sediments (HN3 and HCM4) was slightly higher than the ISQG (Table 5.6), again suggesting the potential risk of dieldrin to aquatic organism in the rivers.

Table 5. 6 Comparison between measured concentrations (ng g^{-1} dry–wt) and Canadian Environmental Quality Guideline for protection of aquatic life, issued by Canadian Council of the Ministers of the Environment (URL18)

No	Compound	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4	HCM 5	HCM 6	ISQG[a]	PEL[b]
1	Naphthalene	6.5	0.10	56	73	125	0.26	5.0	0.91	0	0	0	6.8	0.34	166	66	0.24	17	34.6	391
2	Acenaphthene	1.2	0	7.3	12	16	3.4	1.5	0	0	0.06	0.42	3.3	0	13	13	0	7.3	6.71	88.9
3	Anthracene	1.7	0.23	6.8	17	35	3.5	2.6	0.87	0.10	0.10	0.20	2.4	0.29	15	17	0.14	11	46.9	245
4	Fluorene	3.4	0.78	8.2	26	31	3.7	4.4	2.2	0.22	0	0.86	5.2	0.60	24	22	0.21	15	21.2	144
5	Phenanthrene	13	1.5	53	136	272	16	16	5.7	0.40	0	2.1	14	2.2	128	115	1.7	73	41.9	515
6	Benzo(a)anthracene	4.1	1.5	43	57	223	23	13	1.4	0.31	0.32	0.54	5.5	0.86	36	103	0.72	56	31.7	385
7	Chrysene & Triphenylene	7.5	2.7	87	125	258	21	16	2.4	0.27	0.10	0.62	9.7	1.4	67	132	0.76	80	57.1	862
8	Fluoranthene	12	2.0	89	237	447	44	31	6.7	0.46	0.19	2.5	20	2.8	161	200	2.1	142	111	2355
9	Pyrene	9.3	5.4	114	267	459	34	24	4.3	0.49	0.27	1.6	30	2.3	183	209	2.1	139	53	875
10	Benzo(a)pyrene	4.6	0.96	42	86	275	25	12	1.6	0.13	0.15	0.47	6.2	0.39	38	148	0	53	31.9	782
11	Chlordane	0	0	0.10	0	0.03	0	0	0	0	0	0	0	0	0	1.1	0.19	1.1	4.5	8.87
12	DDD[c]	1.8	0.12	**19**	**17**	**17**	0.78	2.7	0.47	0.08	0	0.11	1.6	0.13	0	**60**	N.Q.	6.3	3.54	8.51
13	DDE[c]	4.2	0.25	**17**	**28**	**27**	0.69	0.97	0.40	0.03	0	0.29	2.2	0.20	1.4	**65**	N.Q.	**7.0**	1.42	6.75
14	Dieldrin	0	0.05	3.1	0	0	0.15	0.27	0.26	0.14	0	0.11	0	0.22	0	4.7	N.Q.	0	2.85	6.67
15	Endrin	0.46	0.12	0	0	0	0	0	0.35	0.19	0	0.23	0.10	0	0	0	N.Q.	0.43	2.67	62.4
16	Heptachlorepoxide(B)	0	0	0.40	0.10	0	0.07	0	0	0.05	0	0.09	0	0.10	0	0.08	N.Q.	1.4	0.6	2.74
17	Hexachlorocyclohexane (γ HCH)	0	0	**2.0**	0.70	0	0.44	0.16	0.29	0	0	0	0	0.18	1.2	**1.6**	N.Q.	**2.8**	0.94	1.38
18	Total PCBs[d]	1.7	0.13	43	55	50	0.60	0.21	0.26	0.20	0	0	5.5	0.85	15	121	N.Q.	67	34.1	277

[a] Interim Sediment Quality Guideline; [b] Probable Effect Level; [c] Sum of o,p' and p,p' isomers; [d] Sum of 24 PCB congeners (PCB 8, 18, 31, 28, 33, 52, 44, 70, 66, 95, 101, 110, 118, 105, 149, 138, 153, 187, 174, 180, 170, 199, 196, 194) by multiplication with the value of 1.64 [percentage contribution of 24 major congeners (in average = 60.9%) to total PCBs in KC–MIX formulation] (Takasuga et al., 2006); N.Q.: not quantified; Grey highlight indicated the values higher than interim sediment quality guideline, in which adverse biological effects occasionally occur; Thick box border point out the probable effect concentration in which adverse biological effects frequently occur.

5.4.4 Polychlorinated biphenyls (PCBs)

The concentrations of individual PCB congeners measured in sediments collected from rivers/canals in HN, HP, DN and HCM were shown in Table S5.1. An estimation of the total PCB burden (ΣPCBs) of sample was calculated by the multiplication of the sum concentrations of 24 congeners by a factor of 1.64 (percentage contribution of 24 congeners (in average = 60.9%) to total PCBs in KC−MIX formulation) (Table 5.6). PCBs were detected in most of the sediment samples, ranged from 0.13 ng g^{-1} dry−wt (HN2) to 121 ng g^{-1} dry−wt (HCM4) except for 2 sites in rural areas in Da Nang city (DN1−2), where none of PCB congeners was detected (Table 5.6). The concentrations of PCBs in soils from Vietnam have been reported to range from 0.61 to 320 ng g^{-1} dry−wt, with the highest concentrations usually measured in the large cities such as Hanoi and Ho Chi Minh City (Thao et al., 1993b). Similarity, in this study, ΣPCB concentrations observed in the canals inside Hanoi (HN3−5) and Ho Chi Minh City (HCM3−4 and HCM6) were almost 100 times higher than those from agricultural areas (e.g. HP2−4) (Table 5.6), which suggested that the metropolitan areas are the major sources of PCBs pollution to the rivers. Comparing the ΣPCBs values with the Canadian Environmental Quality Guideline for protection of aquatic life (URL18), it was known that concentrations of 5 out of 17 sediments are much higher than the ISQG values (Table 5.6), suggesting possible toxicological effect caused by PCBs contamination in the sediment of these rivers.

In urban areas of HN, PCBs levels were comparable to those in previous study in 1997 (Nhan et al., 2001), but lower than observed in 2006 (Hoai et al., 2010) (Table 5.5). This observation can be explained by the sampling time; since the sediment samples were collected in the rainy season in this study and at the end of the dry season in 2006, the intense rainfall brings large amount of water drained through the canal system, which might affect the washout of suspended particle containing PCBs. A similar trend in PCB contamination was also observed in HCM where urban areas (HCM3−4, HCM6) had extremely high PCBs levels compared to those in suburban areas (HCM1−2) (Table 5.6). However, none of PCBs was detected at HCM5 located in high densely populated areas probably due to the low organic contents. PCB concentrations in urban areas and outskirts of HCM were around 2 times lower than those reported in 2004 (Minh et al., 2007a), whilst over 5 times lower compared to early 1990s (Iwata et al., 1994) (Table 5.5), which implies a decreasing trend of PCBs in the river system in HCM. It is interesting to notify that in Ho Chi Minh City, PCB concentrations in sediments decrease from Ho Chi Minh City canals to the outskirt rivers such as Saigon and Dong Nai River. The high PCB concentrations in the large cities were attributed to the uncontrolled waste discharge by industries and motor repair workshops (Nhan et al., 2001; Minh et al., 2007a).

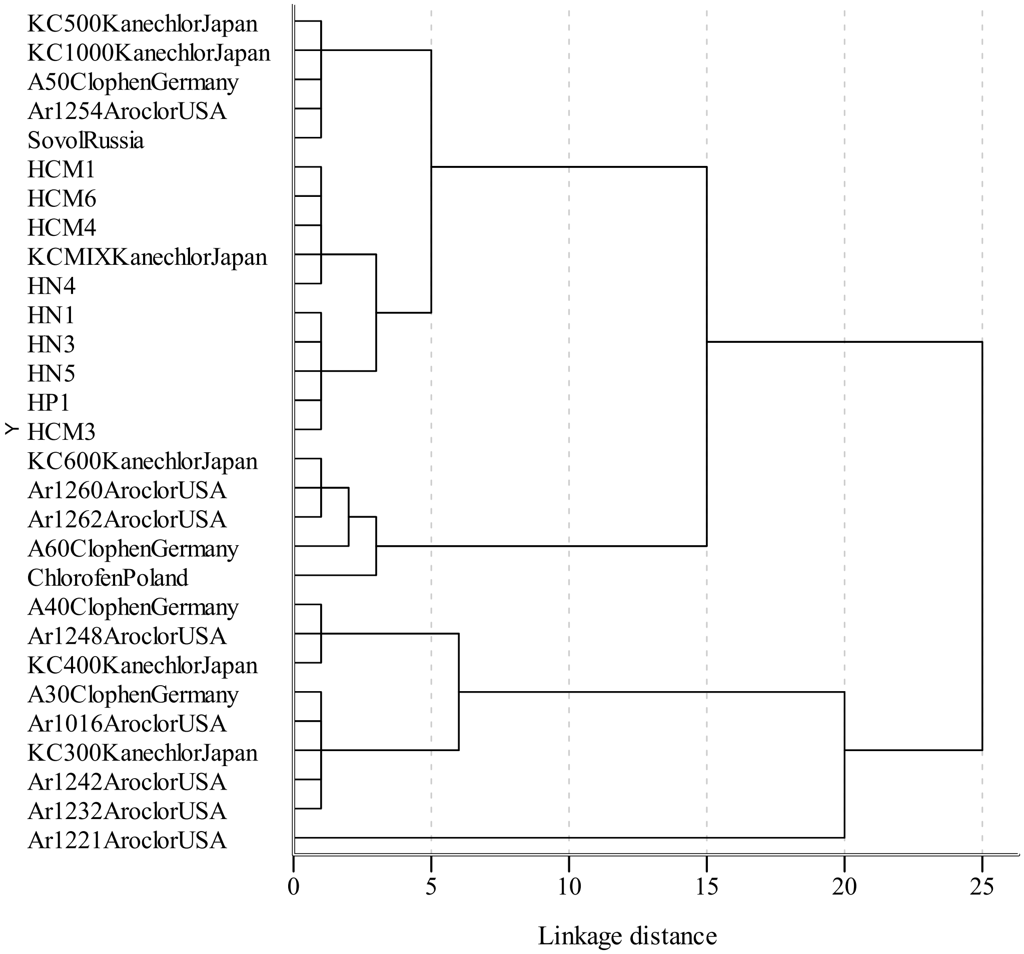


Fig. 5. 5 Hierarchical dendrogram of sampling sites obtained by cluster analysis (Ward's method and squared Euclidean distance) using ratios of 24 PCB congeners of 5 commercial formulations (Takasuga et al., 2006)

Comparing the PCB contamination levels in this study with those reported in the global scale, the result showed that PCBs levels in the city's canals in HN and HCM were similar to those in the Minjiang River (Zhang et al., 2003), but more than 20 times higher than those in the Pearl River estuary (China) (Table 5.5). However, the present range of PCBs in Vietnamese sediments was several times lower than those in sediments collected in other Asian countries (India, Thailand, Japan and Taiwan) in 1990s (Iwata et al., 1994) (Table 5.5). This trend implying the local source of PCBs in Vietnam is less than the other above countries. Since Viet et al. (2000) indicated that PCB contamination in developing countries is not so serious as compared with developed nations where the PCB production and usage is deemed heavier. However, greater residues were occasionally found in some places in this study indicating that point sources of PCBs in Vietnam are still remaining.

The cluster analysis was carried out on 9 sites (except for DN1− 2 and HCM5 where PCBs were not detected and HN2, HP2−4 and HCM2 where less PCB congeners were detected) using composition ratios of 24 PCB congeners of 5 commercial formulations reported by Takasuga et al. (2006) (Fig. 5.5). As a result, all analyzed sites are classified into the same group of KC−MIX, which indicates the inputs of PCBs into the environment possible originated from technical KC−MIX mixture.

5.4.5 Polycyclic aromatic hydrocarbons (PAHs)

Twenty−eight PAHs were detected (Table S5.1), with mean total PAHs concentrations (except for perylene which is naturally occurring (Hites et al., 1980; Boonyatumanond et al., 2006)) in HN, HP, DN and HCM being 2700, 500, 100 and 1700 ng g^{-1} dry−wt, respectively. Total PAHs in urban areas (median 3000 ng g^{-1} dry−wt) were higher than those in outskirts (median 420 ng g^{-1} dry−wt). Similar to the distribution patterns of PAHs in water samples, relatively low concentrations of total PAHs were detected in sediments collected from DN1−2, HP1−4, HCM2 and HCM5 with concentrations of less than 700 ng g^{-1} dry−wt; while high concentrations of total PAHs were observed at sites located inside cities such as HN4−5, HCM3−4 and HCM6 with concentrations of higher than 2000 ng g^{-1} dry−wt. However, relatively low contamination levels of PAHs were detected in sediments at HN1 and HCM5 even though they were observed at high concentration levels in water samples. These results are in accordance with the quality of sediments. The lower organic matter contents in proportion to lower concentration of pollutants in sediment samples because hydrophobic substances such as PAHs adsorb on organic matters (Table S5.1). The concentrations of naphthalene, acenaphthene, fluorene, phenanthrene, benzo(a)anthracene, chrysene and triphenylene, fluoranthene, pyrene and benzo(a)pyrene in six sediments located in urban sites were extremely high, exceeding the ISQG values for protection of aquatic life (Table 5.6). These results demonstrate the toxicological stress of these compounds on aquatic biota in the rivers and require further monitoring for sediments observed at greater values than ISQG.

In terms of PAH composition pattern by ring size, the detected concentrations ranged between 4.5−11560 ng g^{-1} dry−wt (mean 323 ng g^{-1} dry−wt) for 2−ring PAHs; 0.62−951 ng g^{-1} dry−wt (mean 218 ng g^{-1} dry−wt) for 3−ring PAHs; 0.88−1613 ng g^{-1} dry−wt (mean 320 ng g^{-1} dry−wt) for 4−ring PAHs, 1.1−1328 ng g^{-1} dry−wt (mean 266 ng g^{-1} dry−wt) for 5−ring PAHs (subtracting perylene) and 0−242 ng g^{-1} dry−wt (mean 49 ng g^{-1} dry−wt) for 6−ring PAHs (Table 5.7). The detection frequencies of 28 individual PAHs (from 2−ring to 6−ring) were above 77% except for 1−methylphenanthrene and 2−methylnaphthalene which

Table 5. 7 Concentrations (ng g^{-1} dry–wt) of the detected PAHs and volatile organic contents (%) at each site

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
1	1,3–Dimethylnaphthalene	10	3.2	6.9	250	340	3.4	11	5.0	2.1	0.96	3.0	21	2.4	378	205	198	4.9	162
2	1,4–&2,3–Dimethylnaphthalene	6.1	1.9	25	35	172	1.8	5.2	2.7	0.98	0.70	1.3	20	0.92	176	100	105	2.6	55
3	1–Methylphenanthrene	N.D.	N.D.	N.D.	35	125	N.D.	4.2	1.7	0.39	N.D.	N.D.	N.D.	0.85	48	27	27	N.D.	11
4	Naphthalene	6.5	0.10	56	73	125	0.26	5.0	0.91	N.D.	N.D.	N.D.	6.8	0.34	166	66	70	0.24	17
5	2,6–Diisopropylnaphthalene	10	6.3	N.D.	35	26	3.2	3.4	6.8	2.5	3.9	3.1	94	N.D.	N.D.	N.D.	N.D.	6.2	111
6	2,6–Dimethylnaphthalene	20	5.0	24	499	305	19	30	9.3	2.6	N.D.	2.9	45	N.D.	290	245	235	4.6	243
7	2–Methylnaphthalene	4.0	N.D.	29	65	63	N.D.	3.5	1.5	N.D.	N.D.	N.D.	3.4	N.D.	44	47	45	0.60	30
	Total 2 rings[a)]	**56**	**17**	**141**	**991**	**1156**	**28**	**63**	**28**	**8.6**	**5.6**	**10**	**191**	**4.5**	**1102**	**690**	**681**	**19**	**631**
8	1–Methylnaphthalene	1.7	0.19	10	31	36	0.25	1.7	0.60	0.08	0.10	0.07	1.5	0.10	28	25	23	0.40	14
9	2–Methylphenanthrene	5.5	0.62	39	75	160	3.9	5.2	2.1	0.19	N.D.	0.34	N.D.	0.91	56	57	56	N.D.	41
10	2–Phenylnaphthalene	6.0	1.1	7.2	72	135	9.0	7.4	3.7	N.D.	N.D.	0.70	5.3	1.1	565	61	59	N.D.	40
11	3–Methylphenanthrene	4.4	0.38	36	84	139	2.6	3.8	0.85	N.D.	0.36	0.14	N.D.	0.27	50	57	50	N.D.	34
12	9–Methylphenanthrene	2.7	1.3	26	122	127	N.D.	2.3	0.64	0.15	N.D.	0.22	N.D.	0.37	48	43	36	N.D.	28
13	Acenaphthene	1.2	N.D.	7.3	12	16	3.4	1.5	N.D.	N.D.	0.06	0.42	3.3	N.D.	13	13	11	N.D.	7.3
14	Anthracene	1.7	0.23	6.8	17	35	3.5	2.6	0.87	0.10	0.10	0.20	2.4	0.29	15	17	15	0.14	11
15	Fluorene	3.4	0.78	8.2	26	31	3.7	4.4	2.2	0.22	N.D.	0.86	5.2	0.60	24	22	26	0.21	15
16	Phenanthrene	13	1.5	53	136	272	16	16	5.7	0.40	N.D.	2.1	14	2.2	128	115	130	1.7	73
	Total 3 rings[b)]	**40**	**6.1**	**194**	**576**	**951**	**42**	**45**	**17**	**1.1**	**0.62**	**5.1**	**31**	**5.9**	**929**	**411**	**405**	**2.4**	**264**
17	Chrysene & Triphenylene	7.5	2.7	87	125	258	21	16	2.4	0.27	0.10	0.62	10	1.4	67	132	153	0.76	80
18	Fluoranthene	12	2.0	89	237	447	44	31	6.7	0.46	0.19	2.5	20	2.8	161	200	168	2.1	142
19	2,3–Benzofluorene	7.2	4.2	8.6	129	227	20	8.6	5.0	N.D.	N.D.	N.D.	9.3	N.D.	93	146	157	N.D.	84
20	Benzo(a)anthracene	4.1	1.5	43	57	223	23	13	1.4	0.31	0.32	0.54	5.5	0.86	36	103	96	0.72	56
21	Pyrene	9.3	5.4	114	267	459	34	24	4.3	0.49	0.27	1.6	30	2.3	183	209	184	2.1	139
	Total 4 rings[c)]	**40**	**16**	**342**	**814**	**1613**	**142**	**93**	**20**	**1.5**	**0.88**	**5.2**	**74**	**7.4**	**539**	**790**	**758**	**5.8**	**502**

Table 5.7 Concentrations (ng g^{-1} dry–wt) of the detected PAHs and volatile organic contents (%) at each site (continued)

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
22	Benzo(a)pyrene	4.6	1.0	42	86	275	25	12	1.6	0.13	0.15	0.47	6.2	0.39	38	148	154	N.D.	53
23	Benzo(e)pylene	21	7.2	279	324	669	61	41	7.9	1.2	1.0	1.5	24	3.4	169	374	304	N.D.	173
24	Benzo(j&b)fluoranthene	10	5.7	105	146	310	30	24	4.3	0.44	0.41	0.90	11	2.1	78	187	180	0.86	89
25	Benzo(k)fluoranthene	1.9	0.35	21	33	74	10	7.5	0.51	0.07	0.12	0.21	1.4	0.28	11	52	57	0.23	26
26	Perylene	293	2896	188	90	521	301	337	562	22	0.98	155	670	339	86	454	420	N.D.	484
	Total 5 rings[d)]	**330**	**2910**	**634**	**679**	**1850**	**426**	**422**	**577**	**24**	**2.7**	**159**	**713**	**345**	**383**	**1214**	**1114**	**1.1**	**824**
27	Benzo(ghi)perylene	5	1	60	N.D.	115	10	6	2	0	0	0	5	1	43	108	96	N.D.	N.D.
28	Indeno(1,2,3–cd)pyrene	4.4	1.5	45	N.D.	127	13	10	2.0	0.19	N.D.	0.58	6.8	0.99	30	92	87	N.D.	N.D.
	Total 6 rings[e)]	**9.0**	**2.4**	**106**	**0**	**242**	**23**	**17**	**3.6**	**0.35**	**0.13**	**1.0**	**12**	**1.9**	**73**	**200**	**183**	**0**	**0**
Total PAHs[f)]		475	2951	1417	3060	5811	661	640	645	35.2	9.88	180	1021	364	3025	3305	3141	28.5	2221
Volatile organic, %		6.6	7.3	12	10	17	5.9	7.7	7.1	1.4	1.0	1.6	11	11	7.3	10	10	3.4	13

N.Q. represents “not quantified”.

N.D. represents “not detected).

[a)] Sum of 2–ring PAH compound concentrations.

[b)] Sum of 3–ring PAH compound concentrations.

[c)] Sum of 4–ring PAH compound concentrations.

[d)] Sum of 5–ring PAH compound concentrations.

[e)] Sum of 6–ring PAH compound concentrations.

[f)] Sum of 2– through 6–ring PAH compound concentrations.

were detected at 9 and 11, respectively, out of 17 sediment samples. 1,3–Dimethylnaphthalene, 1,4–&2,3–dimethylnaphthalene, anthracene, benzo(a)anthracene, benzo(j&b)fluoranthene, chrysene & triphenylene,, fluoranthene, pyrene, 1–methylnaphthalene, and benzo(k)fluoranthene were detected at 100% sediment samples.

The composition profiles of 2– to 6–ring PAHs (except for perylene) in the 17 sediment samples were similar among the sites (Fig. 5.6), while obviously different from those detected in waters (Duong et al., 2014a). 2– and 3–ring PAHs were the most abundant in water samples whilst in sediments, the composition of 2– to 5–ring PAHs varied. This is probably due to different PAH inputs and the characteristic of PAH. First, river water receives direct PAH inputs from various sources including wastewater discharge, runoff, atmospheric fallout and so on. Second, concentration of smaller molecular PAHs gradually decreases by degradation and evaporation in the high temperatures of a tropical region, such that only large molecular PAHs are sufficiently resistant to degradation that they can survive to reach the sediment bed (Guo et al., 2007). Third, compels water current condition in flood season changed the state of water column process including dissolution, adsorption, desorption, degradation and deposition. As a result, the water and sediment samples had different composition of PAHs (He et al., 2007). The abundance of 4– and 5–ring PAHs in sediments observed in this study probably due to long–term contamination and the resistant of these compounds in sediments.

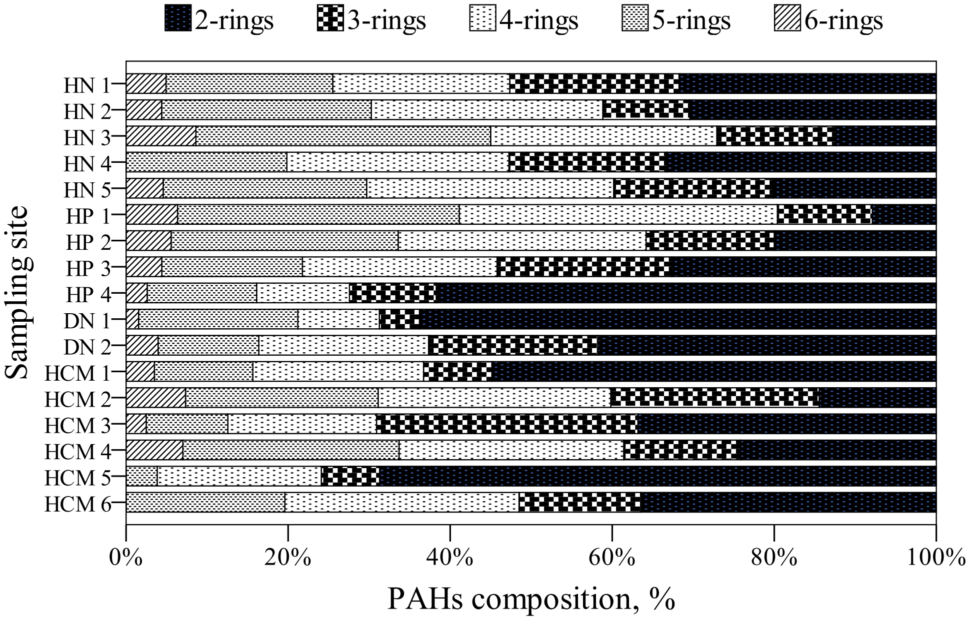


Fig. 5. 6 Profiles of 2– to 6– aromatic rings of PAHs (except perylene) at each site

The sources of PAHs are generally categorized into two origins: pyrogenic (from combustion) and petrogenic (from petrochemical) (Takada et al., 2006). There is several of molecular ratios of PAH could be used to assess the possible origins of PAHs. For example, the abundance ratio 2− to 3−ring PAHs to 4− to 6−ring PAHs (low molecular weight/ high molecular weight, LMW/HMW), fluoranthene/pyrene (Flu/Pyr), fluoranthene/fluoranthene plus pyrene (Flu/(Flu+Pyr)), total methylphenanthrene isomers to that of phenanthrene (ΣMPhens/Phen), phenanthrene/anthracene(Phen/Ant), chrysene/benz(a)anthracene (Chr/BaA), naphthalene/fluoranthene (Nap/Flu), anthracene/anthracene plus phenanthrene (Ant/(Ant+Phen)), (Sirce et al., 1997; Budzinski et al., 1997; Yunker et al., 2002; Doong an Lin, 2004).

ΣMPhens/Phen ratio has been successfully used to distinguish petrogenic and pyrolytic sources of PAHs. ΣMPhens/Phen ratios measured in combustion products are generally <0.5, whereas unburned fossil PAH mixtures typically ranged from 2 to 6 (Garrigues et al., 1995). Ratios of ΣMPhens/Phen above 1.6 were observed in high densely populated urban areas, such as HN2−5, HCM3 and HCM6 (Table 5.8), indicating that PAHs pollution was mainly caused by uncombusted petroleum (i.e. of petrogenic origin) (Zakaria et al., 2002). This finding is in contrasts with results in industrialized countries where pyrogenic PAHs are dominant in urban aquatic environments (Garrigues et al., 1995; Budzinski et al., 1997; Stout et al., 2004; Notar et al., 2001).This is probably a common phenomenon in Southeast Asia countries because petrogenic PAHs inputs to urban sediments were also observed in Malaysia and Thailand (Zakaria et al., 2002; Boonyatumanond et al., 2006). Whereas, values of ΣMPhens/Phen less than 1 were observed in suburban and rural areas, such as HN1, HP1−3, DN2 and HCM2 (Table 5.8), suggesting the pyrogenic PAHs inputs (Zakaria et al., 2002). This result agrees well with previous research (Kishida et al., 2007) that indicates that the combustion of fossil fuels and/or biomass such as rice straw after harvest is probably major sources of pyrogenic PAHs in rural and suburban areas. Similar findings were also observed with Flu/Pyrand Flu/(Flu + Pyr) ratios (Table 5.8). Ratios of Flu/(Flu+Pyr) were greater than 0.5 at remote and suburban areas (HN1, HP1−3, DN2, HCM2) implying the pyrolytic PAHs sources, whereas the petrogenic PAHs sources were observed in the remaining sites (ratios less than 0.5). However, some inner city sites (HN3−5 and HCM3−6) showed the values of Flu/(Flu + Pyr) between 0.4 and 0.5, suggesting the existence of liquid fossil fuel (vehicle and crude oil) combustion (Yunker et al., 2002). HP4 and DN1 located in suburban areas are also contaminated by petrogenic PAHs. In fact, two heavily industrial parks are located in the proximity of the estuary of the Trang River (DN1) therefore, the discharge of industrial wastewater might be the main input of petrogenic PAHs obtained at this study site. HP4 located in downstream of the Lach Tray River also showed petrogenic PAHs pollution probably because the discharge of wastewater from industrial zones to the river basin or the discharge of wastes including fuel oil from shipping activities, which were seen frequently throughout the year.

Since HN and HCM are well known to have the highest private vehicle density (especially motorcycle) in Vietnam, the leakage of refinery products (such as gasoline, diesel fuel and fuel oil) from urban vehicle traffics and/or small scale vehicle maintenance facilities were considered to be the main contributors to petrogenic PAH inputs in these canals via surface runoff. However, the pyrogenic PAH inputs in the city canals are considered due to vehicle exhaust gases from motorcycles.

Table 5. 8 Molecular ratios of PAHs in 17 sediment samples

Sampling location	Flu/Pyr	Flu/(Flu+Pyr)	MPhens/ Phen
HN 1	1.3	0.56	0.9
HN 2	0.4	0.27	1.6
HN 3	0.8	0.44	2.1
HN 4	0.9	0.47	2.3
HN 5	1.0	0.49	2
HP 1	1.3	0.57	0.4
HP 2	1.3	0.56	0.9
HP 3	1.5	0.61	0.9
HP 4	0.9	0.48	1.8
DN 1	0.7	0.42	–
DN 2	1.6	0.61	0.4
HCM 1	0.7	0.4	–
HCM 2	1.2	0.55	0.6
HCM 3	0.9	0.47	1.6
HCM 4	1.0	0.49	1.4
HCM 5	1.0	0.50	–
HCM 6	1.0	0.50	1.6

Molecular ratio	Petrogenic	Pyrogenic	Reference
Flu/Pyr	<1	>1	Sicre et al. (1987)
Flu/(Flu+Pyr)	<0.5	>0.5*	Budzinski et al.
		(0.4–0.5)**	Yunker et al. (2002)
MPhens/Phen	>2	<1	Garrigues et al. (1995)
LMW/HMW	>1	<1	Tam et al. (2001)
			Yuan et al. (2001)
			Doong and Lin.

Flu/Pyr: fluoranthene/pyrene.

Flu/(Flu+Pyr): fluoranthene/(fluoranthene + pyrene).

MPhens/Phen: sum of 1–, 2–, 3– and 9–methylphenanthrene to phenanthrene.

* Grass, wood or coal combustion.

** liquid fossil fuel (vehicle and crude oil) combustion.

LMW: low molecular weight.

HMW: high molecular weight.

5.4.6 Emerging contaminants

Of the 7 phthalate compounds (PHCs) detected (Table S5.1), two most widely used compounds in industrial production (DEHP, DBP) (Vitali, 1997) were found in almost all of the sediments at significant concentrations ranging from 90–8000 ng g^{-1} dry–wt (median 1600 ng g^{-1} dry–wt) and 2.8–900 ng g^{-1} dry–wt (median 60 ng g^{-1} dry–wt), respectively. Total PHCs (ΣPHCs) concentration ranged from 180 ng g^{-1} dry–wt (DN1) to 11000 ng g^{-1} dry–wt (HN3) with an average value of 3900 ng g^{-1} dry–wt. This latter value is over 4 times higher than alluvial sediment in JiangHan, China (927 ng g^{-1} dry–wt) (Liu et al., 2010). Considering ΣPHCs concentration calculated for each sediment sample, it appears evident that the high concentration of PHCs in urban areas (HN3–5, HCM3–6) is related to the input of urban untreated wastewaters. While ΣPHCs concentrations in suburban and rural areas (DN1–2, HP3–4, HCM2) were less than 800 ng g^{-1} dry–wt, which probably due to the less inputs of wastewaters or the dilution of the streams. In addition, DEHP, an endocrine disrupting chemical (Akingbemi et al., 2004), has a mean concentration (3400 ng g^{-1} dry–wt) over 10 times and 20 times higher than those in JiangHan, China (329 ng g^{-1} dry–wt) (Liu et al., 2010) and in Italy (161 ng g^{-1} dry–wt) (Vitali, 1997), respectively. When compared with the soil cleanup guidelines used in New York, USA, the concentrations of DEHP in 6 out of 17 sediments exceeded the recommended allowable values (4350 ng g^{-1} dry–wt).

Bisphenol A (BPA), 4–tert–octylphenol (OP) and nonylphenol (NP) have confirmed the estrogenic potential even at low concentrations (Jin et al., 2004). The high concentrations of these compounds in sediments are associated with metropolitan areas, while low concentration associated with rural areas (Table S5.1). This pattern suggests that BPA, OP and NP pollution is caused by urban waste discharge possibly due to the increasing population densities and lack of adequate wastewater treatment facilities. The most frequently detected compound was NP (10 of 17 samples), followed by OP and BPA which were detected at four and two samples, respectively. The concentrations of OP and NP were enriched in sediments collected from densely populated urban areas (HN4–5, HCM3–4), which probably due to the wide range of contamination sources (such as untreated domestic wastewaters/ or wastewaters from small enterprises) and heavy use of household products (detergent) near the sites. The detected concentrations of NP varied from 6.8 ng g^{-1} dry–wt to 7800 ng g^{-1} dry–wt, which appeared to be much higher than those in sediments from Jiao Zhou bay, China (3.6– 299 ng g^{-1} dry–wt) (Fu et al., 2007) and Okinawa and Ishigaki Island, Japan (not detected to 44 ng g^{-1} dry–wt) (Kawahata et al., 2004), while comparable to those of Pearl River Delta, China (59–7808 ng g^{-1} dry–wt) (Chen et al., 2006). Concentrations of detected OP were low, ranged from 51 ng g^{-1} dry–wt to 145 ng g^{-1} dry–wt, while BPA was detected at HN2 (7.2 ng g^{-1} dry–wt) and HCM1 (714 ng g^{-1} dry–wt). It should be noted that the sediment taken from HCM1 was contaminated by BPA and NP even though it was located in suburban area of HCM. This probably due to the sample collection site located in downstream of most HCM’s sewage canals, therefore the river is receiving untreated sewage discharge from the city.

Of the 14 PPCPs analyzed, triclosan, L–menthol and squalane were found in the sediment samples (Table S5.1). Elevated concentrations of PPCPs were observed at densely populated urban areas (HN4−5 and HCM6) (Table S5.1), implying the discharge of untreated domestic wastewater to the rivers. Squalene, which has application in numerous vaccine and drug delivery emulsions (Fox, 2009), was the most abundance compound which was observed at 9 out of 17 sediment samples at high concentrations of 1400 ng g^{-1} dry−wt (HN4), followed by 1100 ng g^{-1} dry−wt (HN5) and 900 ng g^{-1} dry−wt (HCM6). Triclosan and L−menthol were only found at HCM4 (211 ng g^{-1} dry−wt) and HCM5 (3.0 ng g^{-1} dry−wt). Caffeine, the most dominant compound, was found at nearly 100% of surface water samples (Duong et al., 2014a), but none of the sediment samples. The high solubility (13.5 g L^{-1}), low octanol–water partition coefficient (log K_{ow} = 0.01) (Ferreira, 2005) and microbial degradation (Nakada et al., 2008) of caffeine may act against the adsorption to sediment layer.

5.4.7 Characteristics of pollution sources

The 17 sampling sites can be divided into four major groups (Fig. 5.3). The first group has one site (HN5) and is remarkably different from other 16 sites. The pollution profile of HN5 demonstrates that the river was seriously polluted by chemical originated from domestic sources, such as insecticides (pyrethroid compounds), PAHs (originated from traffic activities), and other substances of domestic origin. The source of the extremely high concentration of deltamethrin (60000 ng g^{-1} dry−wt) is currently unknown, and requires further detailed research. The second group includes inner city sites (HN1, HN3−4, HCM3−4 and HCM6). The third group includes the sites mainly located in suburban areas (HN2, HP1−3 DN2, and HCM1−2), and the remaining sites were distinguished into the fourth group. A pollution profile was created for a representative river in each group by summing up the concentration of compounds categorized by usage into 13 typical groups (Fig. 5.7). Sterols compounds were excluded in the pollution profile due to their wide spread existence in sediment samples.HN3, a representative site of the second group, was mainly contaminated by insecticides (pyrethroid compounds), antioxidants and PAHs. Chemicals in this group may be regarded as typical of pollution of urban areas, where insecticides are commonly used for vector controls such as mosquitoes and flies. The high density of private vehicles, especially motorcycles, is a source of petrogenic PAH. A representative site of the third group (HCM1) is located in suburban area, and while it has less contamination, is considered to have mixture of industrial and domestic contamination. The pollutants at this site were composed of chemicals used as intermediates for resins, PAHs, PPCPs and other substances of domestic origin. The general characteristics of the fourth group, as represented by DN1 are low concentration of pollutants associated with fewer detected contaminants due to low volatile organic contents in sediment samples (Tables 5.2 and S5.1).

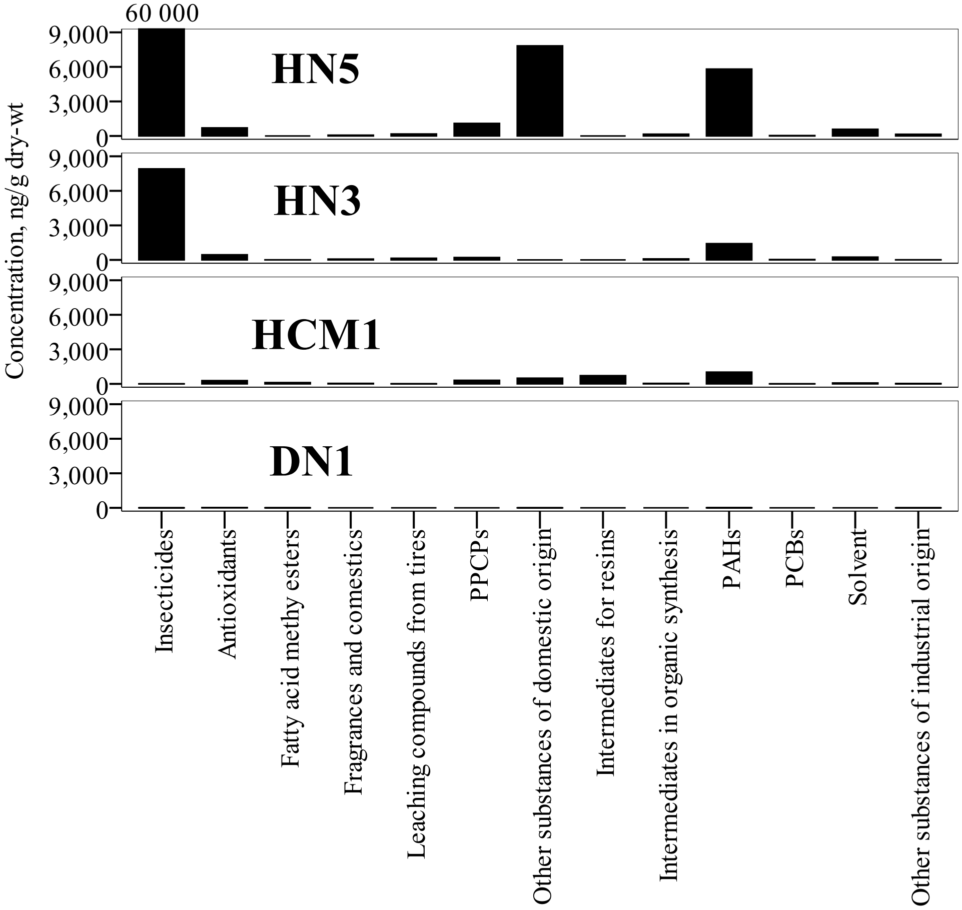


Fig. 5. 7 Typical pollution profile of four rivers. Pollution profile is a graph composed from 13 groups summed up by concentrations of compounds categorized by usage or type. Figure above a column is concentration (ng g^{-1} dry–wt).

5.5 CONCLUSIONS

This study presents the first comprehensive study on a wide spectrum of organic micro–pollutants in river sediments in Vietnam and in doing so provides important baseline data. Important findings derived from our results are as follows: (1) 185 analytes of the detected, or 20% of the substances analyzed, are the same as those found in developed countries; (2) extremely high concentrations of domestic chemicals including fecal sterols were found in the center of big cities, the dominant source being untreated domestic wastewater; (3) high concentrations of pyrethroid insecticides were found in the center of big cities, indicating that these insecticides are widely used in urban areas in Vietnam for hygienic purpose; (4) OCPs and PCBs that were banned several decades ago are still detected, mainly big cities, but their concentrations were low compared with those of previous studies; (5) the levels of PAHs were high in urban areas and low in suburban areas. Contamination source of PAHs in urban areas is mixed from pyrogenic and petrogenic inputs, whilst pyrogenic PAHs was the major source of PAHs in suburban and rural areas.

CHAPTER VI POLLUTION OF PERFLUOROALKYLACIDS IN ENVIRONMENTAL WATERS

6.1 INTRODUCTION

Perfluoroalkyl acids includes perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic and phosphinic acids, which are highly persistent substances that have been directly emitted to the environment or are formed indirectly from the environmental degradation or metabolism of precursor substances, and because they (or their salts) are or have been used in a wide variety of industrial and consumer applications (Buck et al., 2011). Since 2000 long–chain PFCAs($C_nF_{2n+1}COOH$, $n \geq 7$), PFSAs($C_nF_{2n+1}SO_3H$, $n \geq 6$) and their potential precursors (Buck et al., 2011), have attracted attention as global contaminants. Long–chain PFCAs and PFSAs are problematic because they are highly persistent (Parsons et al., 2008; Frömel and Knepper, 2010), bioaccumulative (Conder et al., 2008) and have been detected ubiquitously in the abiotic environment (Rayne and Forest, 2009), biota (Giesy and Kannan, 2001), food items (Clarke and Smith, 2011) and humans (Vestergren and Cousins, 2009).

Of the PFAAs, PFOS and PFOA are the most intensively studied compounds and were the first PFAAs recognized as global pollutants (Giesy and Kannan, 2001). These two compounds have been frequently detected in environmental samples, very often occur at the highest concentrations (So et al., 2007; Post et al., 2013), and can be found in the tissues of aquatic and terrestrial living organisms including humans (Suja et al., 2009). PFOS is the stable end product of the degradation of perfluorooctane sulfonyl fluoride (POSF) and POSF–based polymers (Giesy and Kannan, 2002). The production of PFOA from 8:2 fluorinated telomer alcohols in a biotic system has been first observed by Hagen et al. (1981), and more recently, Dinglasan et al. (2004) reported that the PFOA was also formed from biodegradation of precursor fluorotelomer alcohols. Chronic exposure to PFOA and PFOS causes tumors in experimental animals, but there are no chronic toxicology data for other PFAAs (Lau, 2012). PFOA has been described as a likely human carcinogen by US–EPA Science Advisory Board (URL9) and has been linked to two types of cancer in communities with drinking water exposure (Vieira et al., 2013). PFOA may also increase the risk of prostate cancer (Gilliland and Mandel, 1993).

Concerns about the potential environmental and toxicological impact of long–chain PFSAs and PFCAs have led to the phasing out the production of PFOS, its precursors and POSF by 2003 (URL19). As a result, PFOS and related substances based on POSF were listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009 (URL20). In 2006, eight major fluoropolymer and telomer manufacturers and the

US−EPA jointly launched the 2010/2015 PFOA Stewardship Program with two goals: (1) to commit to achieve, no later than 2010, a 95% reduction, measured from a year 2000 baseline, in both facility emissions to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and product content levels of these chemicals and (2) to commit to working toward the elimination of these chemicals from emissions and products by 2015 (URL21). The five−year agreement (2010–2015) between Environment Canada, Health Canada and four companies from the perfluorinated products industry was signed on March 30, 2010, and is in effect until December 31, 2015. The agreement was negotiated in support of industry's commitment to significantly reduce residual PFCAs and their precursors (URL22). In addition, C11–C14 PFCAs were included in the Candidate List of Substances of Very High Concern under the European chemicals regulation in 2012, REACH (URL23). In 2013, also PFOA and ammonium perfluorooctanoate (APFO) were listed in the Candidate List of Substances of Very High Concern ECHA (2014). US−EPA has promulgated Significant New Use Rules (SNURs) under the Toxic Substances Control Act (TSCA) to limit any future manufacture (including import) of 271 perfluoroalkyl sulfonates (URL24). In addition, on September 30, 2013, EPA published a final SNUR for perfluoroalkyl sulfonate and long−chain perfluoroalkyl carboxylate chemicals that designates manufacturing (including importing) and processing for use as part of carpets or for treating carpet (URL24). A European Union Marketing and Use Directive have been restricted the use of ‘‘perfluorooctane sulfonates’’ in the European Union (URL25). Several water guidelines on PFOS and PFOA have been introduced such as: (1) guidance on the water supply (water quality) regulations 2000/01 specific to PFOS and PFOA concentrations in drinking water (URL26, 27) and (2) guidance for PFOA in drinking water at Pennsgrove Water Supply Company (URL28).

Although the occurrence of PFAAs in various environmental media has been vigorously investigated in other parts of the world, there is only limited information on the number and levels of PFAAs as it is in the Vietnamese environment. To the best of our knowledge, there are only 4 reports of PFAAs in environmental waters in Vietnam (Lien et al., 2006a, 2006b; Isobe et al., 2012; Kim et al., 2013) which were focused on limited study areas, but no extensive study throughout Vietnam. In addition, there is no study on PFAAs in groundwater, even though it is well known that groundwater is easily polluted with PFAAs due to their high water solubility. In order to address this knowledge gap, we undertook a comprehensive survey of 16 PFAAs, which included 11 PFCAs and 5 PFSAs in surface and groundwater of four major cities in Vietnam and the biggest river of northern Vietnam in order: (1) to give an overview on the occurrence of PFAAs in the environmental waters throughout Vietnam; (2) to provide a nationwide profile of the PFAAs concentration; (3) to find potential sources of PFAAs; (4) to compare the determined concentrations of PFAAs pollution with the ones found in other countries; and (5) to assess the potential risk of PFAAs on human and aquatic organisms.

6.2 MATERIALS AND METHODS

6.2.1 Chemicals and standards

Table 6. 1 Target and internal standard compounds

No	Compound	Abbreviation	IS[a]
	Perfluoroalkyl carboxylic acids		
1	Perfluorobutanoic acid	PFBA	IS–1
2	Perfluoropentanoic acid	PFPeA	IS–2
3	Perfluorohexanoic acid	PFHxA	IS–2
4	Perfluoroheptanoic acid	PFHpA	IS–2
5	Perfluorooctanoic acid	PFOA	IS–3
6	Perfluorononanoic acid	PFNA	IS–4
7	Perfluorodecanoic acid	PFDA	IS–5
8	Perfluoroundecanoic acid	PFUdA	IS–6
9	Perfluorododecanoic acid	PFDoA	IS–7
10	Perfluorotridecanoic acid	PFTrDA	IS–7
11	Perfluorotetradecanoic acid	PFTeDA	IS–7
	Perfluoroalkane sulfonic acids		
12	Perfluorobutane sulfonic acid	PFBS	IS–8
13	Perfluorohexane sulfonic acid	PFHxS	IS–8
14	Perfluoroheptane sulfonic acid	PFHpS	IS–8
15	Perfluorooctane sulfonic acid	PFOS	IS–9
16	Perfluorodecane sulfonic acid	PFDS	IS–9

[a] Internal standard group (refer to Table 6.2).

Eleven PFCAs: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA); five PFSAs: perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptane sulfonic acid (PFHpS), PFOS, perfluorodecane sulfonic acid (PFDS) (Table 6.1); eight surrogate compounds: perfluoro–n–[^{13}C5]–pentanoic acid (M5PFPeA), perfluoro–n–[1,2,3,4,6–^{13}C5]–hexanoic acid (M5PFHxA), perfluoro–n–[1,2,3,4–^{13}C4]–heptanoic acid (M4PFHpA), perfluoro–n–[^{13}C8]–octanoic aicd (M8PFOA), perfluoro–n–[^{13}C9]–nonanoic acid (M9PFNA), perfluoro–n–[1,2,3,4,5,6–^{13}C6]–decanoic acid (M6PFDA), perfluoro–n–[1,2,3,4,5,6,7–^{13}C7]–undecanoic acid (M7PFUdA), sodium perfluoro–1–[1,2,3–^{13}C3]–hexanesulfonate (M3PFHxS) (Table 6.2) were obtained from Wellington Laboratories (Guelph, Ontario, Canada).

Table 6. 2 Surrogate compounds

No	Compound	Abbreviation	IS[a]
1	Perfluoro–n–[^{13}C5]pentanoic acid	M5PFPeA	IS–2
2	Perfluoro–n–[1,2,3,4,6–^{13}C5]hexanoic acid	M5PFHxA	IS–2
3	Perfluoro–n–[1,2,3,4–^{13}C4]heptanoic acid	M4PFHpA	IS–2
4	Perfluoro–n–[^{13}C8]–octanoic aicd	M8PFOA	IS–3
5	Perfluoro–n–[^{13}C9]-nonanoic acid	M9PFNA	IS–4
6	Perfluoro–n–[1,2,3,4,5,6–^{13}C6]decanoic acid	M6PFDA	IS–5
7	Perfluoro–n–[1,2,3,4,5,6,7–^{13}C7]undecanoic acid	M7PFUdA	IS–6
8	Sodium perfluoro–1–[1,2,3–^{13}C3]hexane sulfonic acid	M3PFHxS	IS–8

Internal standards

IS–1	Perfluoro–n–[1,2,3,4–^{13}C4]butanoic acid	^{13}C4PFBA
IS–2	Perfluoro–n–[1,2–^{13}C2]hexanoic acid	^{13}C2PFHxA
IS–3	Perfluoro–n–[1,2,3,4,–^{13}C4]octanoic acid	^{13}C4PFOA
IS–4	Perfluoro–n–[1,2,3,4,5–^{13}C5]nonanoic acid	^{13}C5PFNA
IS–5	Perfluoro–n–[1,2–^{13}C2]decanoic acid	^{13}C2PFDA
IS–6	Perfluoro–n–[1,2–^{13}C2]undecanoic acid	^{13}C2-PFUdA
IS–7	Perfluoro–n–[1,2,^{13}C2]dodecanoic acid	^{13}C2PFDoA
IS–8	Sodium perfluoro–1–[^{18}O2]hexane sulfonic acid	^{18}O2–PFHxS
IS–9	Sodium perfluoro–1–[1,2,3,4–^{13}C4]octane sulfonic acid	^{13}C4–PFOS

[a] Internal standard group.

Nine internal standards (ISs): perfluoro–n–[1,2,3,4–^{13}C4]– butanoic acid (^{13}C4PFBA), perfluoro–n–[1,2–^{13}C2]–hexanoic acid (^{13}C2PFHxA), perfluoro–n–[1,2,3,4,–^{13}C4]–octanoic acid (^{13}C4PFOA), perfluoro–n–[1,2,3,4,5–^{13}C5]–nonanoic acid (^{13}C5PFNA), perfluoro–n–[1,2–^{13}C2]– decanoic acid (^{13}C2PFDA), perfluoro–n–[1,2–^{13}C2]–undecanoic acid (^{13}C2–PFUdA), perfluoro–n–[1,2,^{13}C2]–dodecanoic acid (^{13}C2PFDoA), sodium perfluoro–1–hexane–[^{18}O2]–sulfonate (^{18}O2–PFHxS), sodium perfluoro–1–[1,2,3,4–^{13}C4]–octanesulfonate (^{13}C4–PFOS) (Table 6.2) were obtained from Wellington Laboratories

(Guelph, Ontario, Canada). Purities of the standards were >98%. Waters Oasis HLB Plus LP (225 mg, 60 mL) solid–phase extraction cartridges were purchased from Waters (Milford, MA, USA). Grade GF/C glass microfiber filters (0.47 µm) were purchased from Whatman International Ltd (Maidstone, Kent, UK). Other chemicals including methanol (grade, 99.7%), acetonitrile (grade, 99.8%) and HPLC grade formic acid (HLC–SOL, 98%) and 1 mol L^{-1} ammonium formate were purchased from Wako Pure Chemical Industries (Osaka, Japan). Deionized water was used after passing through an Oasis HLB Plus LP cartridge to remove residues of PFCAs and PFSAs.

6.2.2 Sample collection

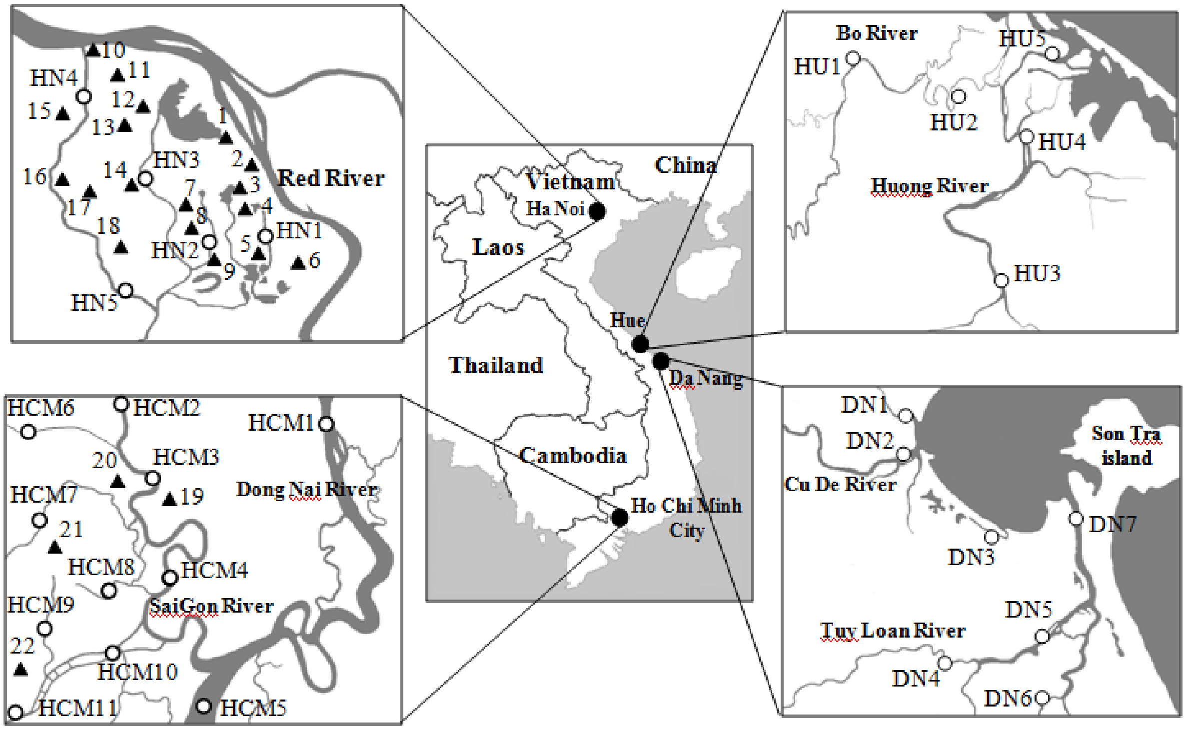


Fig. 6. 1 Surface and groundwater sampling sites in Hanoi, Hue, Da Nang, and Ho Chi Minh City

▲ Groundwater ○ Surface water.

Twenty–eight surface water samples from rivers and canals were collected in four cities: Hanoi (5), Hue (5), Danang (7) and Ho Chi Minh (HCM) (11) (Fig. 6.1) in the dry season (March 2013) and the rainy season (September 2013). River water samples were collected from 14 sites located at nine provinces along the second biggest river of Vietnam, the Red River (March 2013) (Fig. 3.2). Twenty–two groundwater samples were collected from Hanoi (18) and HCM (4) (September 2013) (Fig. 6.1). Detailed information of the sampling locations is given in Tables 3.1.

6.2.3 Sample extraction and analysis

After addition of surrogates (10 ng L^{-1}) to 500 mL of water sample, the pH of each sample was adjusted to 3 by adding of formic acid. The sample was filtered through a glass microfiber filter, previously pre−conditioned by passing through the filter with 10 mL of methanol and 10 mL deionized water, to remove suspended solids. Pre−filtered sample was then loaded onto an Oasis HLB cartridge, previously pre−conditioned with 5 mL of methanol followed by 10 mL of deionized water, using a Sep–Pak concentration system (SPC 10−C, Chratec, Kyoto, Japan) at a flow rate of 10 mL min^{-1}; the eluate from this procedure was discarded. Water remaining in the cartridges was completely removed with a vacuum pump for 30 min. The target PFAAs in the cartridges were then eluted with 5 mL of methanol at a rate of 1 drops s^{-1}, while the targets in the filters were extracted twice with 3 mL of methanol using an ultrasonic cleaner: USK type (AsOne, Osaka, Japan).

Table 6. 3 LC–MS–MS conditions

Agilent 6460 Trip Quadrupole LC–MS					
Column	Agilent ZORBAX Eclipse Plus C18 2.1×150mm 3.5Micron				
Column temperature	40				
Mobile phase	A: 10 mM annmonium formate				
	B: acetonitrile				
Gradient profile	time (min)	0	1.5	16	23
	B(%)	20	40	70	70
Post time	12 min				
Injection volume	5 µL				
Ionization	ESI (–)				
Gas temperature	350				
Gas fow	10 L				
MS1 temperature	100				
MS2 temperature	100				
Nebulizer	50 psi				
Capillary	4000 V				

The final eluate of each fraction was concentrated to approximately 0.5 mL under a gentle nitrogen stream and was spiked with internal standards (2 ng L^{-1}) prior to determination step. The target PFAAs in each fraction were measured LC–MS–MS–SRM and quantified by internal standard method. In case there is a precipitation in a final concentrate, the concentrate was filtered through a membrane filter (Advantec Dismic – 13cp), previously pre–conditioned with 3 mL of methanol and 3 mL of deionized water, prior to analysis. LC–MS/MS–SRM conditions were described in Tables 6.3 and 6.4. The limit of detection (LOD) and limit (level) of quantification (LOQ) of PFAAs were calculated according to standard methods 1030C (Standard methods, 2005), and ranged from 0.05 ng L^{-1} to 0.5 ng L^{-1} and 0.12 ng L^{-1} to 1.2 ng L^{-1}, respectively (Table 6.5).

Table 6. 4 Precursor, product ions and collision energies of SRM of target, surrogate and internal standard compounds

No	Compound	Abbreviation	Precursor ion	Product ion	Collision energy, eV	RT[a]
	Perfluoroalkyl acid compounds					
	Perfluoroalkyl carboxylic acids					
1	Perfluorobutanoic acid	PFBA	213	169	0	3.6
2	Perfluoropentanoic acid	PFPeA	263	219	2	7.1
3	Perfluorohexanoic acid	PFHxA	313	269	5	8.7
4	Perfluoroheptanoic acid	PFHpA	363	319	5	9.9
5	Perfluorooctanoic acid	PFOA	413	369	6	11
6	Perfluorononanoic acid	PFNA	463	419	5	13
7	Perfluorodecanoic acid	PFDA	513	469	5	15
8	Perfluoroundecanoic acid	PFUdA	563	519	5	16
9	Perfluorododecanoic acid	PFDoA	613	569	8	18
10	Perfluorotridecanoic acid	PFTrDA	663	619	6	20
11	Perfluorotetradecanoic acid	PFTeDA	713	669	6	22
	Perfluoroalkane sulfonic acids					
12	Perfluorobutane sulfonic acid	PFBS	299	80	60	8.9
13	Perfluorohexane sulfonic acid	PFHxS	399	80	100	12
14	Perfluoroheptane sulfonic acid	PFHpS	449	80	60	14
15	Perfluorooctane sulfonic acid	PFOS	499	80	60	16
16	Perfluorodecane sulfonic acid	PFDS	599	80	80	19
	Surrogate compounds					
1	Perfluoro–n–[^{13}C5]pentanoic acid	M5PFPeA	268	223	2	7.1
2	Perfluoro–n–[1,2,3,4,6–^{13}C5]hexanoic acid	M5PFHxA	318	273	4	8.7
3	Perfluoro–n–[1,2,3,4–^{13}C4]heptanoic acid	M4PFHpA	367	322	6	9.9
4	Perfluoro–n–[^{13}C8]–octanoic aicd	M8PFOA	421	376	6	11
5	Perfluoro–n–[^{13}C9]-nonanoic acid	M9PFNA	472	427	8	13
6	Perfluoro–n–[1,2,3,4,5,6–^{13}C6]decanoic acid	M6PFDA	519	474	6	15
7	Perfluoro–n–[1,2,3,4,5,6,7–^{13}C7]undecanoic acid	M7PFUdA	570	525	6	16

Table 6. 4 Precursor, product ions and collision energies of SRM of target, surrogate and internal standard compounds (continued)

No	Compound	Abbreviation	Precursor ion	Product ion	Collision energy, eV	RT[a]
8	Sodium perfluoro–1–[1,2,3–^{13}C3]hexane sulfonic acid	M3PFHxS	402	80	100	12
	Internal standards					
IS-1	Perfluoro–n–[1,2,3,4–^{13}C4]butanoic acid	13C4PFBA	217	172	0	3.63
IS-2	Perfluoro–n–[1,2–^{13}C2]hexanoic acid	13C2PFHxA	315	270	0	8.67
IS-3	Perfluoro–n–[1,2,3,4,–^{13}C4]octanoic acid	13C4PFOA	417	372	5	11.3
IS-4	Perfluoro–n–[1,2,3,4,5–^{13}C5]nonanoic acid	13C5PFNA	468	423	5	12.9
IS-5	Perfluoro–n–[1,2–^{13}C2]decanoic acid	13C2PFDA	515	470	5	14.7
IS-6	Perfluoro–n–[1,2–^{13}C2]undecanoic acid	^{13}C2-PFUdA	565	520	5	16.3
IS-7	Perfluoro–n–[1,2,^{13}C2]dodecanoic acid	^{13}C2PFDoA	615	570	5	18.1
IS-8	Sodium perfluoro–1–[^{18}O2]hexane sulfonic acid	^{18}O2–PFHxS	403	103	50	12
IS-9	Sodium perfluoro–1–[1,2,3,4–^{13}C4]octane sulfonic acid	^{13}C4–PFOS	503	80	60	15.6

[a] Retention time.

6.2.4 Quality controls

In order to ensure the precision and accuracy of analytical procedures, procedure blanks and overall recoveries, reproducibility and repeatability tests were conducted for each set of the samples analyzed. Procedural blanks were used to check contamination throughout all procedures. They were prepared following the same procedures as actual samples using deionized water instead of a sample. In this study, procedural blanks (500 mL of deionized water) were run for every 7 samples. In general, most of the PFAAs were not found in blank samples, except for some PFCAs at trace levels lower than the strict, LOD (Table 6.5). Recovery tests were conducted by spiking a mixture of 16 PFAAs (10 ng L^{-1} each) and a mixture of 8 surrogate compounds (10 ng L^{-1} each) into deionized water. Spiked water was treated by the same procedures as actual water samples. Acceptable recoveries were obtained for all the PFAAs and the surrogates (Table 6.5 and Table 6.6, respectively), with the mean recoveries of over 80% except for the long chain PFAAs (PFDS, 58%; M6PFDA, 61%; M7PFUdA, 56%), which were possibly absorbed to extraction apparatus during treatment processes. The relative standard deviations (RSDs) of the recoveries were below 10%. The accuracy of individual sample analysis was checked by examining the recoveries of the surrogates spiked into the environmental water sample before extraction (Table 6.6). Good recoveries (mean, 69–97%) were obtained for six out of eight surrogates except for two PFCAs (M6PFDA, 58% and M7PFUdA, 41%) that were not well recovered even in recovery tests using deionized water. Relative standard deviations of six surrogates were below 15%, confirming that sample analyses were acceptably precise. When reporting data, blank concentrations were subtracted from sample concentrations. The reported concentrations were not corrected using recovery values.

Table 6. 5 Recoveries (%) of PFAAs in spiked deionized water samples and level of procedural blanks (ng L^{-1})

No	Target analyte	LOD[a]	LOQ[b]	Procedural blank (n=10)		Recovery (n=6)		
		ng L^{-1}	ng L^{-1}	Range	Mean	Range[d]	Mean[d]	RSD[e], %
	Perfluoroalkyl carboxylic acids							
1	PFBA	0.05	0.12	N.D.[c] – 0.35	0.01	145 – 152	148	1.8
2	PFPeA	0.05	0.12	N.D.[c]	N.D.[c]	81 – 102	92	8.2
3	PFHxA	0.05	0.12	N.D.[c]	N.D.[c]	125 – 151	139	7.3
4	PFHpA	0.05	0.12	N.D.[c]	N.D.[c]	97 – 119	109	7.4
5	PFOA	0.05	0.12	N.D.[c] – 0.15	0.02	106 – 128	115	7.2
6	PFNA	0.05	0.12	N.D.[c]	N.D.[c]	90 – 113	99	8.6
7	PFDA	0.1	0.25	N.D.[c]	N.D.[c]	117 – 126	122	3.2
8	PFUdA	0.5	1.2	N.D.[c] – 0.06	0.04	109 – 121	113	4.5
9	PFDoA	0.1	0.25	N.D.[c] – 0.22	0.05	130 – 139	135	2.7
10	PFTrDA	0.5	1.2	N.D.[c]	N.D.[c]	136 – 145	139	2.6
11	PFTeDA	0.5	1.2	N.D.[c]	N.D.[c]	154 – 168	159	3.5
	Perfluoroalkane sulfonic acids							
12	PFBS	0.05	0.12	N.D.[c]	N.D.[c]	110 – 132	123	6.6
13	PFHxS	0.05	0.12	N.D.[c]	N.D.[c]	123 – 137	131	4.0
14	PFHpS	0.05	0.12	N.D.[c]	N.D.[c]	116 – 134	124	5.5
15	PFOS	0.05	0.12	N.D.[c]	N.D.[c]	76 – 89	80	6.7
16	PFDS	0.1	0.25	N.D.[c]	N.D.[c]	54 – 67	58	8.9

[a] Limit of detection; [b] limit of quantification; [c] N.D. represents values less than limit of detection; [d] ten nano gram per liter of each target compound was added to the deionized water sample; [e] relative standard deviation.

Table 6. 6 Recoveries (%) of surrogate compounds in spiked deionized and environmental water samples

No	Compound	Spiked deionized water samples (n=6)			Spiked environmental water samples (n=33)		
		Range	Mean[a]	RSD[b], %	Range	Mean[a]	RSD[b], %
1	M5PFPeA	76 – 95	83	8	66 – 110	82	9.3
2	M5PFHxA	85 – 111	94	10	70 – 106	88	9.1
3	M4PFHpA	82 – 103	89	8	68 – 93	97	7.3
4	M8PFOA	88 – 102	93	5	71 – 110	79	9.5
5	M9PFNA	84 – 98	88	6	57 – 99	69	15
6	M6PFDA	57 – 72	61	9	30 – 86	58	30
7	M7PFUdA	53 – 59	56	5	28 – 74	41	25
8	M3PFHxS	93 – 105	96	4	83 – 124	91	8.8

[a] Ten nanogram per liter of each surrogate was added to the sample.

[b] Relative standard deviation.

6.3 RESULTS AND DISCUSSION

All eluates eluted from the filters were found to be free of all studied PFAAs therefore only PFAAs eluted from cartridges can be discussed hereafter.

6.3.1 Occurrence of PFAAs in surface waters

A total 10 PFAAs were observed in one or more of the samples (Table 6.7), although PFBA, PFUdA, PFTrDA, PFTeDA, PFBS and PFDS were not detected at all in any sample and will not, therefore, be discussed hereafter. The most frequently detected compounds were PFOA (98%), PFNA (84%) and PFOS (59%) with concentrations ranging from 0.09 to 18, 0.12 to 0.93, and 0.18 to 5.3 ng L^{-1}, respectively (Table 6.7). Interestingly, this distribution is similar to those in river water in Japan (Murakami et al., 2008), but different to data from coastal water in Hong Kong, South China, Korea (So et al., 2004) and from surface waters in the USA (Simcik and Dorweiler, 2005; Kim and Kannan, 2007), Europe (McLachlan et al., 2007; Loos et al., 2008) and Sri Lanka (Guruge et al., 2007), where PFOS and PFOA were dominant but PFNA was a minor component. The prevalence of PFNA in river water in Japan indicated the shift in PFAA use after the introduction of restrictions (Zushi et al., 2011), since when PFNA has been used in industrial production of PFCA in Japan (Murakami et al., 2008). However, there is only very limited information on the use, production and volumes of

Table 6. 7 Concentrations (ng L^{-1}) of PFAAs in river waters of 4 cities along Vietnam (S1 and S2 represent sample taken in the dry season (March, 2013) and the rainy season (September, 2013), respectively)

Sampling location	**Perfluoroalkyl carboxylic acids**														**Perfluoroalkane sulfonic acids**					
	PFPeA		**PFHxA**		**PFHpA**		**PFOA**		**PFNA**		**PFDA**		**PFDoA**		**PFHxS**		**PFHpS**		**PFOS**	
	S1	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**
LOD[a] (ng L^{-1})	0.05		0.05		0.05		0.05		0.05		0.1		0.1		0.05		0.05		0.05	
DF[c], %	2		30		20		98		84		34		4.5		43		6.8		59	
Hanoi																				
HN1	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.94	1.51	1.5	0.51	0.2	0.43	0.61	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
HN2	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	1.07	0.92	0.38	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
HN3	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.97	0.95	0.39	0.16	0.29	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
HN4	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.91	0.11	0.32	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.22	N.D.[b]
HN5	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	1.4	0.15	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.21	N.D.[b]	N.D.[b]	N.D.[b]
Ho Chi Minh City																				
HCM1	N.D.[b]	N.D.[b]	N.D.[b]	N.D.	N.D.[b]	N.D.[b]	0.21	0.13	0.22	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.19	N.D.[b]
HCM2	N.D.[b]	N.D.[b]	N.D.[b]	N.D.	N.D.[b]	N.D.[b]	0.49	0.16	0.18	N.D.[b]	N.D.[b]	N.D.[b]	0.36	N.D.[b]	0.12	N.D.[b]	N.D.[b]	N.D.[b]	0.25	N.D.[b]
HCM3	N.D.[b]	N.D.[b]	N.D.[b]	0.30	N.D.[b]	N.D.[b]	1.8	1.8	0.25	0.12	0.28	N.D.[b]	N.D.[b]	N.D.[b]	0.88	N.D.[b]	N.D.[b]	N.D.[b]	0.34	0.70
HCM4	N.D.[b]	N.D.[b]	N.D.[b]	0.53	N.D.[b]	N.D.[b]	0.32	2.4	0.14	0.20	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.6	N.D.[b]	N.D.[b]	0.19	1.3
HCM5	N.D.[b]	N.D.[b]	N.D.[b]	N.D.	N.D.[b]	N.D.[b]	0.7	0.78	0.28	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.38	0.14	N.D.[b]	N.D.[b]	0.23	0.60
HCM6	N.D.[b]	N.D.[b]	N.D.[b]	0.48	N.D.[b]	0.55	2.4	1.4	0.33	0.17	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.49	0.10	N.D.[b]	N.D.[b]	0.41	0.47
HCM7	5.8	N.D.[b]	N.D.[b]	5.6	N.D.[b]	9.2	0.33	18	N.D.[b]	0.93	N.D.[b]	1.3	N.D.[b]	N.D.[b]	N.D.[b]	4.4	N.D.[b]	1.3	0.23	5.3
HCM8	N.D.[b]	N.D.[b]	N.D.[b]	N.D.	N.D.[b]	0.59	1.4	2.0	0.28	0.13	0.27	N.D.[b]	N.D.[b]	N.D.[b]	0.88	0.74	N.D.[b]	N.D.[b]	0.35	1.2
HCM9	N.D.[b]	N.D.[b]	N.D.[b]	1.7	N.D.[b]	1.8	5.8	7.1	0.47	0.35	0.36	0.51	N.D.[b]	N.D.[b]	4.6	6.6	N.D.[b]	2.3	N.D.[b]	N.D.[b]
HCM10	N.D.[b]	N.D.[b]	N.D.[b]	0.93	N.D.[b]	0.67	0.28	2.1	0.19	0.23	N.D.[b]	0.33	N.D.[b]	N.D.[b]	N.D.[b]	0.71	N.D.[b]	N.D.[b]	N.D.[b]	2.1
HCM11	N.D.[b]	N.D.[b]	N.D.[b]	1.1	N.D.[b]	1.5	0.22	3.0	0.15	0.28	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.28	0.94	N.D.[b]	N.D.[b]	N.D.[b]	1.4
Hue																				
HU1	N.D.[b]	–	0.29	–	N.D.[b]	–	0.19	–	0.29	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.19	–
HU2	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.21	–	0.40	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.18	–

Table 6.7 Concentrations (ng L^{-1}) of PFAAs in river waters of 4 cities along Vietnam (S1 and S2 represent sample taken in the dry season (March, 2013) and the rainy season (September, 2013), respectively) (continued)

Sampling location	**Perfluoroalkyl carboxylic acids**														**Perfluoroalkane sulfonic acids**					
	PFPeA		**PFHxA**		**PFHpA**		**PFOA**		**PFNA**		**PFDA**		**PFDoA**		**PFHxS**		**PFHpS**		**PFOS**	
	S1	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**
HU3	N.D.[b]	–	0.76	–	0.14	–	0.32	–	0.25	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–
HU4	N.D.[b]	–	3.1	–	N.D.[b]	–	0.09	–	0.28	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.18	–
HU5	N.D.[b]	–	2.1	–	N.D.[b]	–	0.09	–	0.35	–	N.D.[b]	–	0.23	–	N.D.[b]	–	N.D.[b]	–	0.19	–
Da Nang																				
DN1	N.D.[b]	–	0.63	–	N.D.[b]	–	0.41	–	0.30	–	N.D.[b]	–	N.D.[b]	–	0.70	–	N.D.[b]	–	0.28	–
DN2	N.D.[b]	–	0.53	–	N.D.[b]	–	0.21	–	0.27	–	0.33	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.20	–
DN3	N.D.[b]	–	N.D.[b]	–	2.0	–	9.8	–	0.61	–	0.49	–	N.D.[b]	–	3.1	–	N.D.[b]	–	0.84	–
DN4	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.32	–	0.27	–	0.29	–	N.D.[b]	–	0.10	–	N.D.[b]	–	N.D.[b]	–
DN5	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.32	–	0.26	–	0.31	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–
DN6	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.40	–	0.26	–	0.26	–	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.19	–
DN7	N.D.[b]	–	N.D.[b]	–	N.D.[b]	–	0.39	–	0.25	–	0.29	–	N.D.[b]	–	0.30	–	N.D.[b]	–	0.26	–

[a] Limit of detection.

[b] N.D. represents values less than limit of detection.

[c] DF represents "detection frequency".

"–" represents "not quantified".

PFAAs in Vietnam, and so the sources of PFAAs in Vietnamese environmental water still remain to be examined.

In this study, the high detection frequencies of PFOS and PFOA in urban river water demonstrated that these chemicals are ubiquitous in the Vietnamese urban aquatic environment compared to other PFAAs. Among PFCAs, PFDA, PFHxA, PFHpA, PFDoA and PFPeA were observed in the samples at lower frequency than PFOA, with the maximum concentrations as 1.3, 5.6, 9.2, 0.36 and 5.8 ng L^{-1}, respectively (Table 6.7); while PFHxS and PFHpS were the two PFSAs found at lower frequency than PFOS with maximum concentration of 6.6 and 2.3 ng L^{-1}, respectively (Table 6.7).

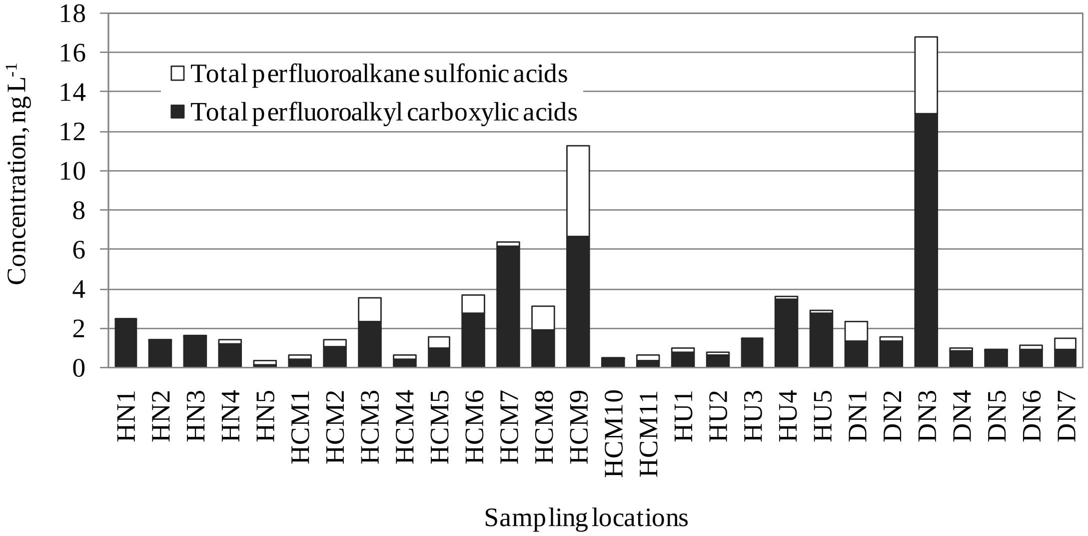


Fig. 6. 2 Sum of concentrations of PFAAs (ng L^{-1}) in surface waters collected in Hanoi, Hue, Da Nang and Ho Chi Minh City in the dry season (March, 2013)

The sum of PFAA concentrations in surface water collected in the dry season from the four cities were relatively low (less than 4 ng L^{-1}; Fig. 6.2), although in some highly populated and industrialized areas such as DN3, HCM9 and HCM7, values were much higher with the concentration of 17 ng L^{-1}, 11ng L^{-1}, and 6.4 ng L^{-1}, respectively. The elevated concentrations of PFAAs at these sites are probably due to the discharge of industrial effluents from nearby highly industrialized areas and untreated domestic sewage from urban activities into rivers. Sites HN5, HCM1, HCM4, HCM10 and HCM11 were shown to be the least contaminated areas; the sampling stations HN5, HCM10 and HCM11 were far away from metropolitan areas, and thus more remote from the perceived pollution sources. The lower contamination levels in HCM1 and HCM4 are probably the result of dilution in the streams. The total concentrations of PFSAs and PFCAs in the surface water samples were also compared among locations (Fig. 6.2). PFCAs were the most abundant, contributing more than 60% of total PFAAs at all the sites (except HN5, 42%). While HN1, HN2, HN3, HCM10, HU3 and DN5 were found to be free of all studied PFSAs. The different contributions of PFSAs and PFCAs to the total PFAAs analyzed in the samples indicate that there are regional differences in the use and emission of PFAAs.

The seasonal differences in the distribution patterns of PFSAs and PFCAs were investigated in two highly urbanized and industrialized cities (Hanoi and HCM) (Fig. 6.3). In general, concentrations were greater in the rainy season than in the dry season at most locations. PFOA and PFNA were the most frequently detected PFCA in the both seasons, which implies the extensive usage of these compounds compared to other PFAAs. These results are consistent with those previously reported by Isobe et al. (2012), who also noted that the amount of products containing PFOA and PFNA imported to Vietnam from Japan increased rapidly, possibly contributing to their prevalence in the Vietnamese environment. However, it should be noted that atmospheric deposition could be a sources of PFCAs to the river during the rainy season (Benskin et al., 2011; Filipovic et al., 2013). PFHxS and PFOS were the most frequently detected PFSAs in both seasons at most sites in HCM, however, the concentrations of PFOS were much lower than PFOA. Although PFOS and PFOA are considered to be the most industrially utilized PFAAs (Zushi et al., 2011), the low levels of PFOS found in the present study might indicate the decrease in use and production of PFOS after the introduction of regulations by the Stockholm Convention (URL20).

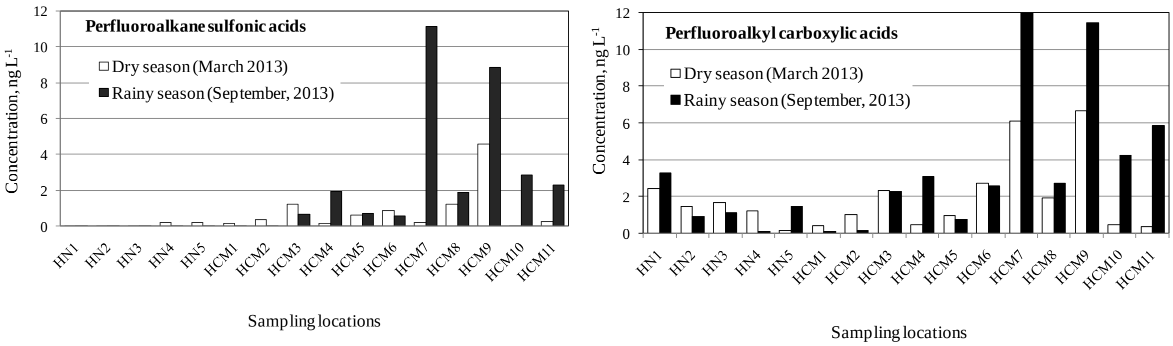


Fig. 6. 3 Concentration of PFSAs and PFCAs in surface waters collected from Hanoi and Ho Chi Minh City in the dry season (March, 2013) and the rainy season (September, 2013)

6.3.2 Occurrence of PFAAs in groundwaters

The 22 groundwater samples collected in Hanoi and HCM were mostly collected from drilled wells with the depth of around 20 m, except for a sample that was collected from digging well (No. 4). Overall, of the total 16 PFAAs analyzed, PFBA, PFHpA, PFOA, PFNA, PFDA, PFHxS and PFOS were the major species detected in groundwater (Table 6.8), which is broadly consistent with the residues observed in surface water in this study (except for PFBA). These results were similar to those in the groundwater samples in European countries, where PFOA and PFOS have been observed at an elevated frequency of detection and as well as at maximum concentrations (Loos et al., 2010). By way in contrast, in Tokyo groundwater, PFOS, PFHpA, PFOA and PFNA were the most prevalent PCFs (Murakami et al., 2009).

Table 6. 8 Concentrations (ng L^{-1}) of PFAAs in groundwaters of Hanoi and Ho Chi Minh City

Sampling location	Perfluoroalkyl carboxylic acids					Perfluoroalkane sulfonic acids		Total concentration
	PFBA	PFHpA	PFOA	PFNA	PFDA	PFHxS	PFOS	
LOD[a] (ng L^{-1})	0.05	0.05	0.05	0.05	0.1	0.05	0.05	
DF[c], %	27	14	36	14	9	9	45	
Hanoi								
No.1	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.2	N.D.[b]	N.D.[b]	0.15	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.15
No.3	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.4	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.5	N.D.[b]	1.3	2.5	0.45	0.42	N.D.	0.64	5.3
No.6	N.D.[b]	N.D.[b]	0.37	0.15	N.D.[b]	N.D.[b]	N.D.[b]	0.53
No.7	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.8	N.D.[b]	N.D.	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.	0
No.9	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.	0
No.10	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.19	0.19
No.11	N.D.[b]	N.D.[b]	0.14	N.D.[b]	N.D.[b]	N.D.[b]	0.22	0.36
No.12	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.19	0.19
No.13	0.07	N.D.[b]	0.30	N.D.[b]	N.D.[b]	N.D.[b]	0.22	0.59
No.14	0.93	0.34	0.93	N.D.[b]	N.D.[b]	N.D.[b]	0.32	2.5
No.15	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.16	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.17	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.20	0.20
No.18	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
Ho Chi Minh City								
No.19	N.D.[b]	N.D.[b]	0.16	N.D.[b]	N.D.[b]	0.11	0.47	0.74
No.20	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0
No.21	1.0	0.58	4.5	0.36	0.43	6.0	8.2	21
No.22	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.42	0.42

[a] Limit of detection; [b] N.D. represents values less than limit of detection; [c] DF represents "detection frequency".

Ten (No. 1, Nos. 3 and 4, Nos. 7–9, No. 15, No. 16, No. 18, No. 20) out of the 22 investigated groundwater samples were free of PFAAs (Table 6.8). PFOS was the most prevalent PFAA detected (45% of the samples), followed by PFOA (36%). These results are not in accordance with those of the surface water where that PFOA were the most prevalent PFAA. PFBA, PFHpA and PFNA were found in only 3 groundwater samples, and PFDA and PFHxS were found in 2 groundwater samples. The source of PFOS detected in the groundwater of this study could be consistent with USGS (2010) (URL29) in which reported that the storm–water runoff contributed to the PFOS levels found in the groundwater of Arizona, USA. The abundance of PFOS and PFOA in groundwater of Hanoi and HCM was also consistent with the surface water data. The origin of these compounds in these cities' groundwater has been unknown although it was strongly suspected that untreated municipal wastewater and storm water that recharges the local aquifer via the adjacent rivers are critical sources (Murakami et al., 2009). However, it should be noted that the other sources of these compounds such as atmospheric deposition, small–scale enterprise, livestock farms and septic systems that are located near the studied areas could be also potential contributing sources to the aquifer. Thus, further investigations of emission sources of PFOS and PFOA in groundwater are necessary.

High levels of total PFAAs were found at a site located in the most densely populated area of HCM (No. 21, 21 ng L^{-1}), followed by two sites located in Hanoi area (No. 5, 5.3 ng L^{-1} and No. 14, 2.5 ng L^{-1}) (Table 6.8) suggesting that the PFAAs were derived from urban activities. The PFAA contributing most to the elevated concentration at No. 21 was PFOS, at a concentration (8.2 ng L^{-1}) higher than in any studied surface water samples (Table 6.7). This is consistent with data from Tokyo, where PFOS was more abundant in groundwater than in rivers (Murakami et al., 2009). Sites Nos. 5 and 14 are located close to the rivers of HN1 and HN3, and the high concentrations of PFAAs were probably related to the leakage of PFAAs contaminated waters from decrepit sewer canals to the aquifers. In addition, it has been hypothesized that the groundwater flow at No. 5 has been also affected by the biggest wastewater reservoir of Hanoi City (Yen So wastewater treatment plant), which receives most of untreated sewage wastewater from the Hanoi metropolitan area. However, this hypothesis remains to be tested.

6.3.3 Occurrence of PFAAs in Red River

The Red River is the biggest river in the northern part of Vietnam, second only to the Mekong River. With length of 1149 km, the river flows from Yunnan Province (China) through nine provinces in the northern Vietnam to the Gulf of Tonkin (Fig. 3.2). We investigated 14 sites on this river, and although only 4 PFAAs (PFOA, PFNA, PFDA and

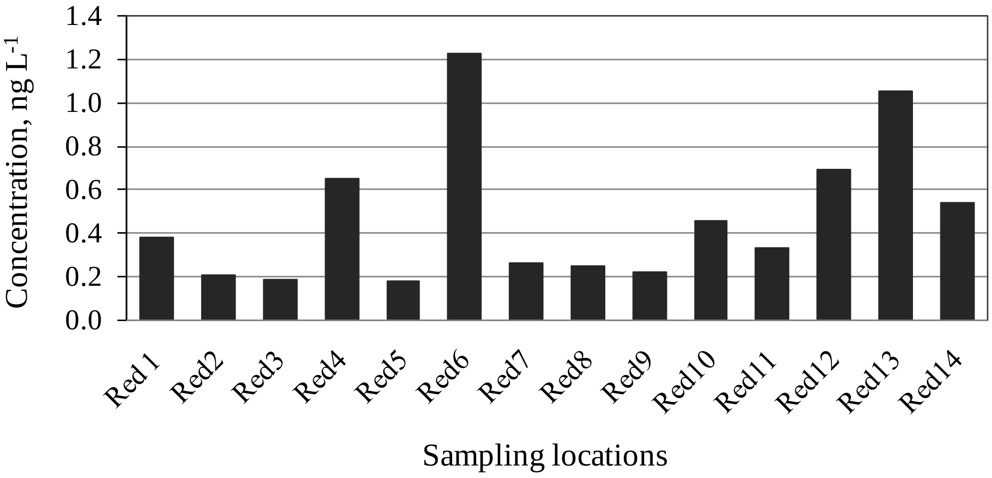


Fig. 6. 4 Sum of concentrations of PFAAs (ng L^{-1}) in surface water of Red River

Table 6. 9Concentrations (ng L^{-1}) of PFAAs in water samples of the Red river

Sampling location	**Perfluoroalkyl carboxylic acids**			**Perfluoroalkane sulfonic acids**
	PFOA	**PFNA**	**PFDA**	**PFOS**
LOD[a] (ng L^{-1})	**0.05**	**0.05**	**0.1**	**0.05**
RED1	**0.18**	**0.20**	**N.D.[b]**	**N.D.[b]**
RED2	**0.21**	**N.D.[b]**	**N.D.[b]**	**N.D.[b]**
RED3	**0.19**	**N.D.[b]**	**N.D.[b]**	**N.D.[b]**
RED4	**0.26**	**0.18**	**0.21**	**N.D.[b]**
RED5	**0.18**	**N.D.[b]**	**N.D.[b]**	**N.D.[b]**
RED6	**0.42**	**0.36**	**0.45**	**N.D.[b]**
RED7	**0.16**	**0.10**	**N.D.[b]**	**N.D.[b]**
RED8	**0.25**	**N.D.[b]**	**N.D.[b]**	**N.D.[b]**
RED9	**0.22**	**N.D.[b]**	**N.D.[b]**	**N.D.[b]**
RED10	**0.25**	**N.D.[b]**	**N.D.[b]**	**0.21**
RED11	**0.17**	**0.16**	**N.D.[b]**	**N.D.[b]**
RED12	**0.28**	**0.20**	**0.21**	**N.D.[b]**
RED13	**0.52**	**0.53**	**N.D.[b]**	**N.D.[b]**
RED14	**0.30**	**0.24**	**N.D.[b]**	**N.D.[b]**

[a] Limit of detection.

[b] N.D. represents values less than limit of detection.

PFOS) were detected, there was no sample free of PFAAs (Table 6.9). PFOA was found in all the samples with the range of 0.16 ng L^{-1} (Red7) to 0.52 ng L^{-1} (Red13), while PFOS was only detected at Red10 (0.21 ng L^{-1}), a site downstream of Hanoi. PFNA were detected 8 out of the 14 samples whereas PFDA were observed in only 3 samples.

Overall, the waters in the Red River have low levels of all four detected PFAAs, however total PFAA concentrations in the downstream of the Red River were slightly higher than upstream (Fig. 6.4). The reason for the increase of the concentrations is probably due to untreated domestic wastewater from Hanoi (Red10) and shipping activities (Red12–13), which were very active throughout the year. The slight increase in total PFAA levels at Red4 (0.65 ng L^{-1}) and Red6 (1.2 ng L^{-1}) was attributed to effluent from a nearby industrial zone and the domestic wastewater of residences near the sites. Concentration of total PFAAs in estuary (Red14) was low due to dilution by seawater.

6.3.4 Correlations among sampling locations

In order to evaluate if there were similarities in pollution sources among sampling locations, principal component analysis (PCA, Fig. 6.5) and cluster analysis (Fig. 6.6) were carried out using the normalized concentration of 10 detected PFAA compounds at 28 surface water sampling sites in the dry season (the values below the LODs were treated as half of LOD values). Two principal components explaining nearly 71% of the total variance were obtained (Fig. 6.5). Component 1 showed significant positive correlations for 20 sites with high loading values (more than 0.71) accounting for 54% of the total variance. The high positive correlation among the studied sites suggested they have similar pollution sources. In addition, component 1 incorporate sites across 4 cities in which total concentrations of PFAAs at these sites were relatively low, suggesting non–point sources of PFAA pollution. Component 2 showed strong positive loading value (more than 0.8) for 5 sites (HU1, HU3–5, DN2) and value of 0.52 for DN1, accounting for nearly 17% of the total variance, also indicates similar pollution sources. On the other hand, PFHxA was only detected at sites belonging to component 2, suggesting point sources. This in turn suggested the need for additional monitoring on PFHxA contamination at these sites. HN5 and HCM7 showed negative correlations, which are remarkably different from other 26 sites involved in above two components. This is probably related to low PFAA levels at HN5 and the existence of PFPeA at high concentration (5.8 ng L^{-1}) in HCM7 (Table 6.7). Therefore, a detailed monitoring of PFPeA in the Vietnamese aquatic environment is required. Similar outcomes were obtained from the cluster analysis (Fig. 6.6). Four groups were clearly distinguished; in which the first group includes 20 sites observed in PCA (component 1). The second group composed of the six sites (component 2 in PCA) and HN5 and HCM7 were distinguished into the third and fourth group.

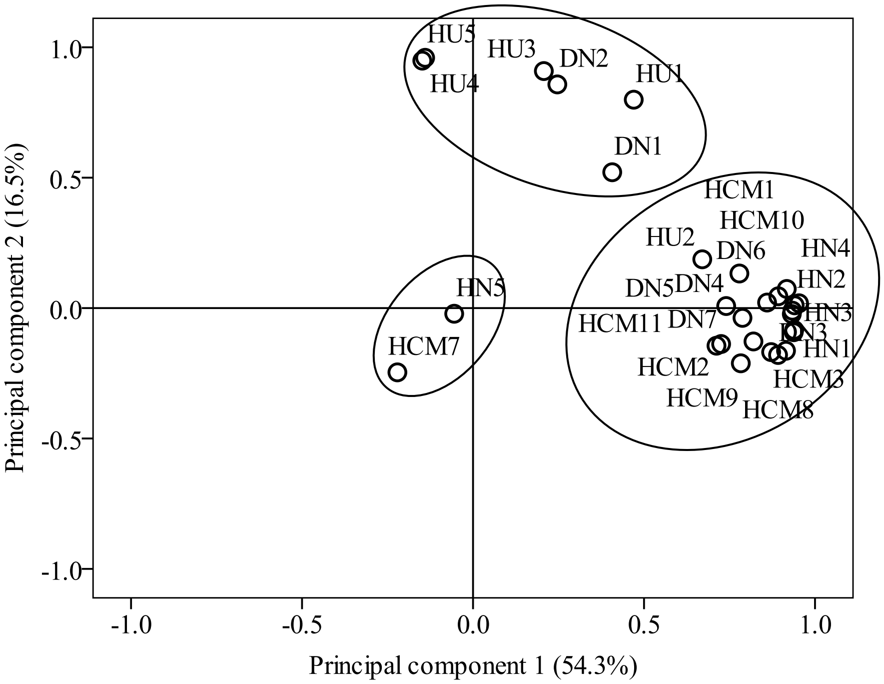


Fig. 6. 5 Principle component analysis of 28 sampling sites using the normalized concentrations of 10 detected PFAA compounds in the dry season (the values below the LODs were treated as half of LOD values)

There is limited research on PFAAs in water environment in Vietnam, and information of usage, production and volumes of PFAAs in Vietnam are currently unknown. Therefore, comparing the pollution profile of PFAAs in Vietnamese surface waters with those in other countries is a good tool to examine the possible sources of contaminants. In this context, a cluster analysis was carried out using the normalized concentrations of six PFAA species (PFOA, PFNA, PFOS, PFDA, PFHxS, PFHpA), which were detected in the surface waters in four cities of this study and those of other Asia countries (Fig. 6.7). As a result, the PFAAs pollution profiles of environmental waters in Vietnam are close to those in China and Japan except for waters from HCM2, HCM4 and HCM7. This result indicates that the potential sources of PFAAs in the environment in Vietnam were quite similar to those in China and Japan. Interestingly, machinery, electronic equipment and components, spare parts, leather products and textile are major imported products (contributed largest proportion of approximately 30% of total imported products in Vietnam in recent years) from China, Japan and Korea (URL30). In addition, these products are considered to contain PFAAs used as surfactants and surface protectors (URL31). Therefore, the similarity of PFAAs profile in Vietnamese water environments with those in China and Japan indicates that the imported products containing PFAAs from China and Japan is one of the major sources of PFAAs in the Vietnamese aquatic environment.

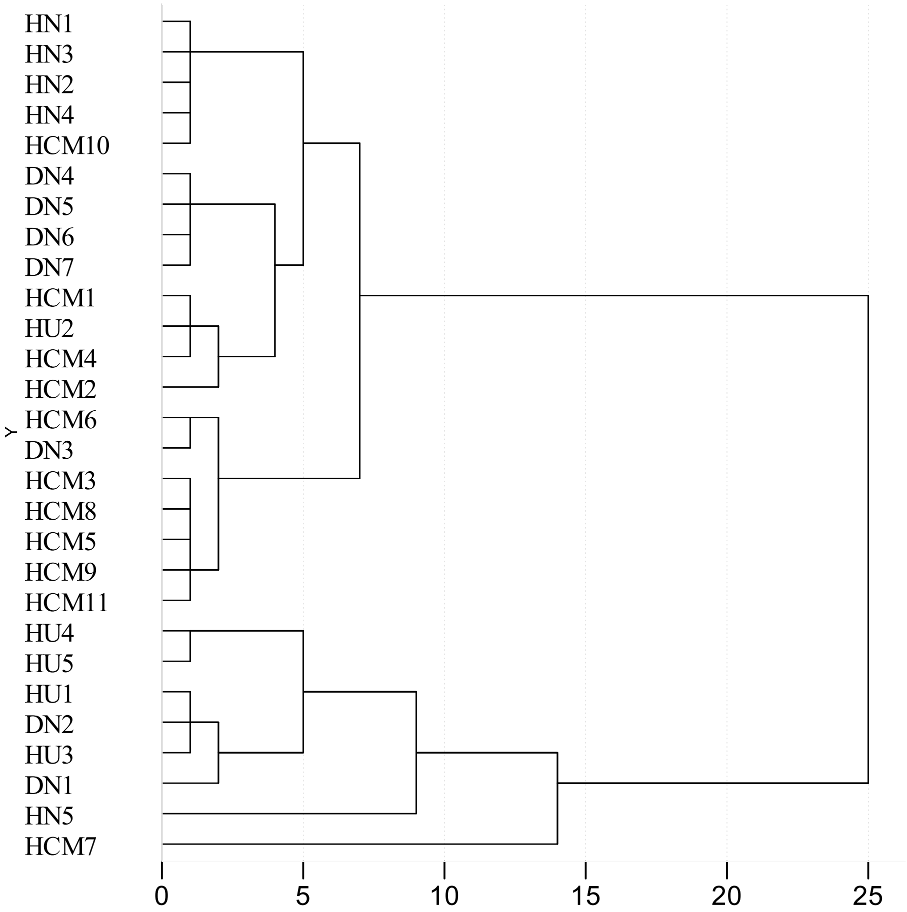


Fig. 6. 6 Hierarchical dendrogram of sampling sites obtained by cluster analysis (Ward's method and squared Euclidean distance) using the normalized concentrations of 10 detected PFAA compounds at 28 sites in the dry season (the values below the LODs were treated as half of LOD values)

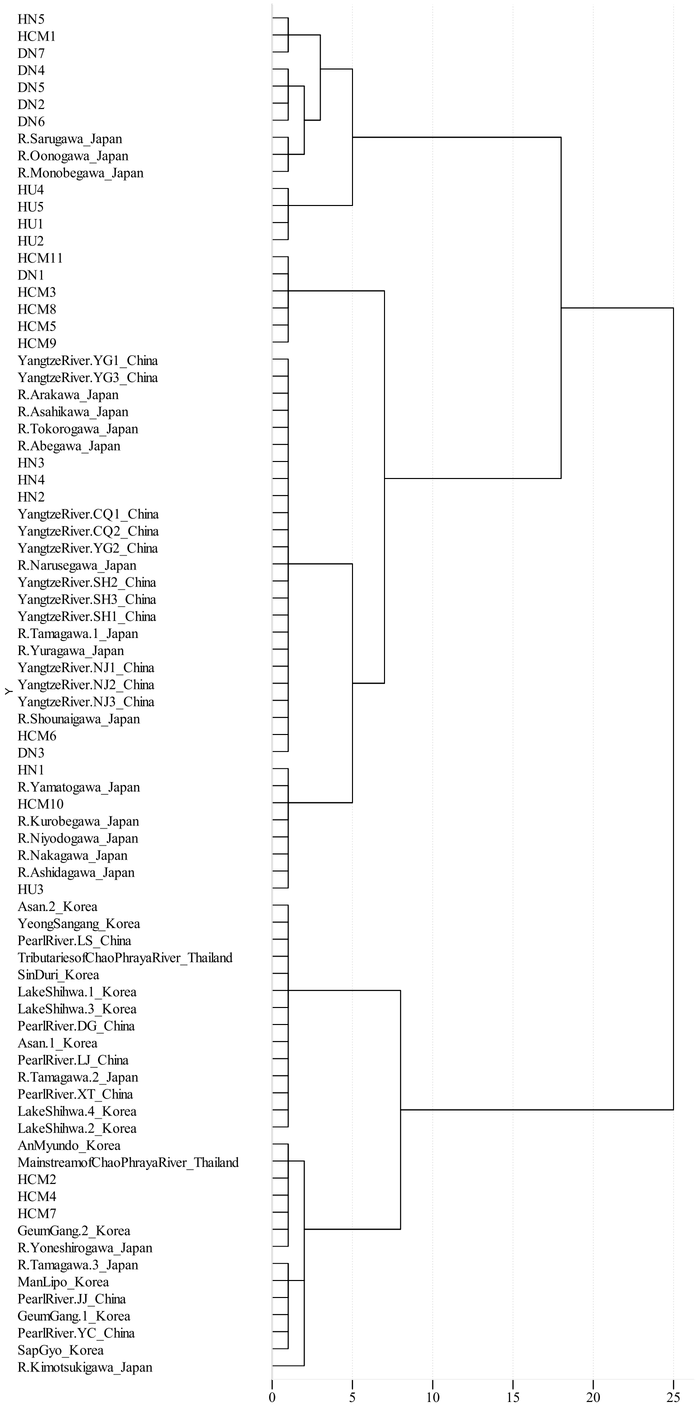


Fig. 6. 7 Hierarchical dendrogram of surface water in this study and those of other Asian countries, obtained by cluster analysis (Ward’s method and squared Euclidean distance) using the normalized concentrations of six PFAA species (PFOA, PFNA, PFOS, PFDA, PFHxS, PFHpA) (the values below the LODs were treated as half of LOD values)

Table 6. 10 Comparison of PFAAs concentrations (ng L^{-1}) in water environment in Vietnam with those from other countries

Location	Sample type	Concentration range (median)			Reference
		PFOS	PFOA	PFNA	
Surface water					
Hanoi, Danang, Hue and Ho Chi Minh	Surface river water	0.18 – 5.3 (0.27)[a]	0.09 – 18 (0.78)[a]	0.12 – 0.93 (0.27)[a]	Present study
Red River, Vietnam	Surface river water	0.21[a]	0.16 – 0.52 (0.22)[a]	0.10 – 0.53 (0.20)[a]	Present study
Hanoi, Vietnam	Surface water	<0.1 – 1.3	<0.2 – 6.6	N.A.	Lien et al. (2006a,b)
Phong River, Thailand	Surface river water	<0.1 – 1.1	<0.2 – 8.8	N.A.	Lien et al. (2006a,b)
Kora Kinabalu, Malaysia	Surface water	<0.1 – 3.4	<0.2 – 3.2	N.A.	Lien et al. (2006a,b)
Rivers in Japan	Surface river water	<0.1 – 191	<0.1 – 1.5	0.25 – 54 (1.9)	Murakami et al. 2008
Estuarine and coastal of Korea	Surface water	4.11 – 450 (28.5)	2.95 – 68.6 (14.7)	1.38 – 14.3 (3.8)	Naile et al. (2010)
Shihwa and Banweol, South Korea	Lake and stream water	2.24 – 651	0.9 – 62	N.A.	Rostkowski et al. (2006)
Guangzhou, China	Surface river water	0.90 – 99	0.85 – 13	N.A.	So et al. (2007)
Yangzte River, China	Surface river water	<0.01 – 14	2.0 – 260	N.A.	So et al. (2007)
Pearl River Delta, China	Surface river water	0.02 – 12	0.24 – 16	N.A.	So et al. (2004)
Liao River, China	Surface river water	n.d. – 6.6 (n.d.)	n.d. – 27.9 (11.5)	N.D.	Yang et al. (2011)
Taihu Lake, China	Lake water	3.6 – 394 (5.8)	10.6 – 36.7 (19.5)	N.D.	Yang et al. (2011)
Rhine, Germany	River water	2.0 – 26	2.0 – 48	N.D.	Skutlarek et al. (2006)
Tennessee River, USA	Surface river water	16.8 – 114	<25 – 598	N.A.	Hansen et al. (2002)
European countries	EU river water	(6)	(3)	(1)	Loos et al. (2009)
Groundwater					
Hanoi and Ho Chi Minh City, Vietnam	Well water	0.19 – 8.2 (0.27)[a]	0.14 – 4.5 (0.34)[a]	0.15 – 0.45 (0.36)[a]	Present study
Tokyo, Japan	Ground water	0.28 – 133 (6.3)	<0.1 – 1.3	0.1 – 94 (1.2)	Murakami et al. (2009)
San Jose, CA, USA	Well water	19 – 87	n.d. – 18	N.D.	Plumlee et al. (2008)

[a] Values of detected concentrations

N.A. represents "not analyzed".

N.D. represents "not detected".

Values in parentheses are median concentrations.

6.3.5 Comparison of PFAAs concentrations in this study to those in other countries

The concentration of PFOS and PFOA in surface water in the four cities sampled in this study were comparable to, or higher than those previously reported in Vietnam, Thailand and Malaysia, while being over 3 times lower than the ones found in South Korea, Yangzte River, China and Rhine River, Germany and over 21 times lower than the ones of Tennessee River, USA (Table 6.10). The levels of PFOS and PFOA in the Red River were over 30 times lower than those in Yangzte River, Pearl River and Liao River in China and over 5 times lower than Phong River in Thailand, implying low usage of these compounds within the catchment of the Red River.

PFNA concentrations detected in surface waters in this study were 0.12–0.93 ng L^{-1}, which were lower compared with the surface water in Japan (0.25–54 ng L^{-1}) and estuarine and coast in Korea (1.38–14.3 ng L^{-1}). The results imply that PFNA amounts used in Vietnam were smaller than in these developed countries.

The concentrations of PFOS, PFOA and PFNA in groundwater in Hanoi and HCM were compared with those in groundwater in Japan, the USA and European countries (Table 6.10). The level of PFOS (0.19–8.2 ng L^{-1}) in groundwater was much lower than those in groundwater in Tokyo, Japan (0.28–133 ng L^{-1}) and San Jose in the USA (19–87 ng L^{-1}). PFOA concentrations in most of the groundwater samples, except for Nos. 5 and 21, fell within the ranges detected in Tokyo (<0.1–1.3 ng L^{-1}). The similar trend was observed in PFNA concentration; PFNA in Tokyo was much higher than in Vietnam, indicating that PFOS, PFOA and PFNA were less used in Vietnam compared with developed countries.

6.3.6 Significance of PFAAs detected in environmental waters in Vietnam

Of the 11 PFAAs detected in the surface and groundwater in this study, PFOS, PFOA, PFNA and PFHxS are known or expected to bioaccumulate in humans (Lau, 2012; Post et al., 2013). Extensive toxicology and epidemiology data is available for PFOS and PFOA, but they are the only two PFAAs with chronic toxicology studies (Lau, 2012). The concentrations of PFOS and PFOA detected in this study were much lower than provisional health−based advisory values for drinking water issued by the US−EPA (200 ng L^{-1} for PFOS and 400 ng L^{-1} for PFOA), that is applicable to short−term exposure (URL32). The maximum concentrations of PFBA in environmental waters were also less than the health−based values and advisory guideline for drinking water 7000 ng L^{-1} (URL17). From these results, it was confirmed that the above individual PFAAs in environmental waters did not pose an immediate health risk to humans. PFNA was prevalent in this study; however, nowadays still there is no health–base drinking water value for PFNA. This information suggests that use of a health–based level for PFOA as preliminary screening benchmark (Post et al., 2013), and in that context none of PFNA concentrations in this study exceeds the PFOA provisional health advisory value for drinking water (400 ng L^{-1}).

An evaluation of the ecological risk to aquatic organisms associated with exposure to PFOS was performed by comparing the measured concentrations of PFOS in water with water quality (guideline) values for protection of aquatic organism. These guideline values were derived following the procedures outlined in US–EPA's Great Lakes Initiative and were based on the results of toxicity testing with freshwater organisms (US–EPA, 1995). The water quality criteria for aquatic animals are represented by the secondary maximum concentration (SMC, 0.78 mg of PFOS L^{-1}) and secondary continuous concentration (SCC, 0.46 mg of PFOS L^{-1}). In this study, the detected concentrations of PFOS were much lower than the value sets for the protection of aquatic plants (8.2 mg L^{-1} of PFOS) and less than the SMC and SCC values (USEPA, 1995). This finding shows that determined concentrations of PFOS in all the sampling locations were unlikely to cause harm to aquatic organisms.

6.4 CONCLUSIONS

This study presents the first comprehensive study on the occurrence of 16 PFAAs in environment waters in Vietnam. The key findings were: (1) PFOS, PFOA and PFNA were the most prevalent of the 11 PFAAs detected, which implies their extensive usage in Vietnam compared to other PFAAs; (2) elevated PFAA concentrations were observed at highly populated and industrialized areas, indicating that the sources of PFAAs were untreated municipal and/or industrial wastewater, while PFAAs concentrations in the Red River were lower than the ones found in other sites of the present study; (3) industrial products containing PFAAs imported from China and Japan might be one of the major sources of PFAAs in the Vietnamese aquatic environment; (4) PFAA concentrations obtained in this study were comparable or higher than those in Southeast Asian countries, but were remarkably lower than in China and developed countries; and (5) none of PFAA exceeded health–based values and advisory guideline for drinking water and guideline values for the protection of aquatic organisms.

PFOS was more abundance in groundwater than in rivers, and its concentration in a site appeared even much higher than that in river water. Routine monitoring on PFAAs in groundwater is necessary to identify possible ‘‘hot spot’’ areas and find the potential emission sources for preventing expansion of pollution.

CHAPTER VII GENERAL CONCLUSIONS AND FURTHER STUDIES

7.1 GENERAL CONCLUSIONS

The objective of this study is to grasp a more complete picture of pollution by anthropogenic chemicals in the aquatic environment in Vietnam. In order to achieve this objective, a comprehensive survey on a wide spectrum of organic micro–pollutants (940) in environmental waters and sediments along with the investigation of 16 PFAAs in environmental waters throughout Vietnam was carried out. The occurrence, contamination levels, pollution characteristic, and the potential sources of contaminants were clarified. In addition, the toxicological effects of detected contaminants on human and aquatic organisms was assessed.

Important findings obtained in this study are as follows:

Pollution of OMPs in aquatic environment:

1. Two hundred and thirty five, 74 and 185 OMPs out of the 940 substances were detected in surface, groundwater, and sediment, respectively.
2. Contamination levels of surface water and sediments, particularly in big cities, were much higher than in Japan because of lack of water treatment facilities.
3. The number of detected contaminants and concentration levels in groundwater were much lower than those of surface water.
4. Chemicals originated from domestic sources are the dominant pollutants in the Vietnamese aquatic environment.
5. OCPs and PCBs, which were banned several decades ago, were still detected in surface water and sediment, but their concentrations were low compared with those of previous studies.
6. Pyrethroids, currently used insecticides, were only detected in surface water and sediment of cities' centre canals at elevated concentrations, implying their wide use in urban areas for hygienic purpose. While some sources of tap water in Hai Phong were contaminated by numerous pesticides, which implies a need for a detailed survey on pesticides in raw water and tap water.
7. PAHs contamination levels were higher in urban areas than in suburban areas. Pyrogenic and petrogenic PAHs polluted urban areas while pyrogenic PAHs were the major source of PAHs in suburban and rural areas.

8. Untreated domestic wastewater heavily polluted surface water and sediment, while non–point sources (eg. leaks from the urban sewer system, underground septic tanks, or recharge by wastewater) polluted groundwater.
9. Endocrine disrupting chemicals (bisphenol A and nonylphenol) were detected at metropolitan surface waters at levels that may pose adverse effect to aquatic organisms.
10. The presence of various OMPs (74) in groundwaters may raise human health concerns even though none of detected chemicals exceeds guideline values.

Pollution of PFAAs in water environment:

1. PFOS, PFOA and PFNA were the most prevalent of the 11 PFAAs detected, which implies their extensive usage in Vietnam.
2. PFAA concentrations in river water were higher in the rainy season than in the dry season, possibly due to storm water runoff, a common phenomenon in Southeast Asian countries
3. PFAAs in the Red River waters were detected at low levels.
4. Elevated PFAA concentrations were observed at highly populated and industrialized areas, indicating that their sources are untreated municipal and/or industrial wastewater.
5. Industrial products containing PFAAs imported from China and Japan might be one of the major sources of PFAAs in the Vietnamese aquatic environment.
6. PFAA concentrations obtained in this study were comparable or higher than those in Southeast Asian countries, but were remarkably lower than in China and developed countries.
7. None of PFAA exceeded health–based values and advisory guideline for drinking water and guideline values, which demonstrated no risks to humans and aquatic organisms.

This is the first comprehensive study on wide variety of OMPs and PFAAs in the aquatic environment in Vietnam. The findings of this study provide valuable information of the occurrence, contamination levels, pollution characteristic, pollution sources, and potential toxicology effects of detected contaminants, for the public and environmental authorities of Vietnam to protect the environment and ecological system by mitigating the discharge of toxic chemicals into the aquatic environment. It is surely concluded that construction of proper wastewater treatment systems is needed to treat entire wastewater discharge, especially in big cities where the treatment capacity of existing wastewater treatment systems covers only 10% of the cities' wastewater discharge. In addition, economic development should take into account environmental protection, which is useful to prevent pollution expansion to rural areas where environmental quality is still good even now.

7.2 FURTHER STUDIES

1. The number of PPCPs detected in the aquatic environment in this study maybe underestimated because there are a limited number of PPCPs registered in the AIQS−DB (14 substances). Consequently, a more detailed survey on PPCPs in the aquatic environment in Vietnam is required after new PPCPs are registered in the database.

2. Sources of drinking water in Hai Phong were contaminated by multiple pesticides at relatively high concentrations, which requires the further monitoring of pesticides in these rivers as well as in of tap water. In addition, elevated concentration of deltamethrin (60000 ng g^{-1} dry−wt) was only detected at a site in Hanoi, which requires further detailed research.

3. A large number of OMPs was detected in environmental waters and sediments and some compounds had values higher than guideline values. This indicated the need of deep study on the detected substances and health risks for human and aquatic environment.

4. Since there is a limited number of sampling events and sampling sites, particularly in HCM, we have only limited information on the occurrence of OMPs in the environmental waters, especially in the groundwater. Therefore, further intensive studies on the occurrence, primary fate, degradation, and transport processes of OMPs in impacted aquifers in groundwater as well as a full evaluation of the potential risks of detected contaminants should be carried out.

5. Routine monitoring on PFAAs in groundwater is necessary to identify possible ‘‘hot spot’’ areas and find the potential emission sources for preventing expansion of pollution.

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APPENDICES

Table S2.1 Chemicals registered in automated identification and quantification system with a database

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
1	Ethylcarbamate	C3H7NO2	51-79-6	89	824	62	IS-1	0.01	reagent	business/household		
2	1-Acetoxy-2-methoxyethane	C5H10O3	110-49-6	118	834	58	IS-1	0.01	solvent	industry		
3	Cyclopentanone, 2-methyl-	C6H10O	1120-72-5	98	838	98	IS-1	0.01	fragrance/synthetic intermediate	industry		
4	3-Methylpyridine	C6H7N	108-99-6	93	857	93	IS-1	0.01	intermediate in organic synthesis/sorvent	industry		
5	N-Ethylmorpholine	C6H13NO	100-74-3	115	876	100	IS-1	0.01	solvent	industry		
6	Cyclohexanol	C6H12O	108-93-0	100	886	82	IS-1	0.01	leaching from tire	business/household		
7	N-Nitrosodiethylamine	C4H10N2O	55-18-5	102	893	102	IS-1	0.01	gasoline & lubricant additive; antioxidant; stabilizer in plastics	business/household		
8	n-Butylacrylate	C7H12O2	141-32-2	128	894	73	IS-1	0.01	intermediate for resin	industry		
9	1,3-Dichloro-2-propanol	C3H6Cl2O	96-23-1	128	898	79	IS-1	0.01	solvent	industry		
10	2-Heptanol	C7H16O	543-49-7	116	900	45	IS-1	0.01	fragrance	business/household		
11	n-C9H20	C9H20	111-84-2	128	900	85	IS-1	0.01	petroleum/plant	business/household		
12	2-Butoxyethanol	C6H14O2	111-76-2	118	902	57	IS-1	0.01	solvent	industry		
13	Propanoic acid, 2-methyl-, 2-methylpropyl ester	C8H16O2	97-85-8	144	914	71	IS-1	0.01	flavoring	business/household		
14	2-Methyl-2,4-pentandiol	C6H14O2	107-41-5	118	922	59	IS-1	0.01	cosmetics/fuel additive/solvent	business/household		
15	Methyl hexanoate	C7H14O2	106-70-7	130	923	87	IS-1	0.01	fatty acid methy ester	business/household		
16	Ethyl methanesulfonate	C3H8O3S	62-50-0	124	927	109	IS-1	0.01	reagent	business/household		
17	Trimethyl phosphate	C3H9O4P	512-56-1	140	928	110	IS-1	0.01	solvent	industry		
18	2-Cyclohexen-1-one	C6H8O	930-68-7	96	929	96	IS-1	0.01	leaching from tire	business/household		
19	Dibutylamine	C8H19N	111-92-2	129	960	86	IS-1	0.01	intermediate in organic synthesis	industry		
20	3-Hexanol, 4-ethyl-	C8H18O	19780-44-0	130	967	59	IS-1	0.01	other	industry		
21	Phenol	C6H6O	108-95-2	94	973	94	IS-1	0.01	intermediate for resin	business/household/traffic		
22	Aniline	C6H7N	62-53-3	93	974	93	IS-1	0.01	intermediate in organic synthesis/leaching from tire	Industry		
23	3-Methoxy-1-butyl acetate	C7H14O3	4435-53-4	146	977	71	IS-2	0.01	intermediate for resin/solvent	industry		
24	1,1,1-Trichloro-2-methyl-2-propanol	C4H7Cl3O	57-15-8	176	979	125	IS-2	0.01	plasticizer	business/household/traffic		
25	Pentachloroethane	C2HCl5	197-61-7	200	979	167	IS-1	0.01	other	industry		
26	2-Chlorophenol	C6H5ClO	95-57-8	128	985	128	IS-2	0.01	by-product of chlorination/intermediate in organic synthesis	industry		
27	Bis(2-chloroethyl)ether	C4H8Cl2O	111-44-4	142	985	93	IS-2	0.01	insecticide	agriculture		
28	Butanoic acid, butyl ester	C8H16O2	109-21-7	136	995	89	IS-2	0.01	cosmetics/fragrance	business/household/traffic		
29	Hymexazol	C4H5NO2	10004-44-1	99	995	99	IS-2	0.01	fungicide	agriculture		
30	*n*-C10H22	C10H22	124-18-5	142	1000	85	IS-2	0.01	petroleum	business/household/traffic		
31	1,3-Dichlorobenzene	C6H4Cl2	541-73-1	146	1006	146	IS-2	0.01	solvent/intermediate in organic synthesis	industry		
32	Nicotinonitrile	C6H4N2	100-54-9	104	1008	104	IS-2	0.01	intermediate for pesticide	industry		
33	Benzyl chloride	C7H7Cl	100-44-7	126	1013	91	IS-2	0.01	intermediate in organic synthesis	industry		
34	1,4-Dichlorobenzene	C6H4Cl2	106-46-7	146	1016	146	IS-2	0.01	insecticidal fumigant	business/household/traffic		
35	4-Cymene	C10H14	99-87-6	134	1025	119	IS-3	0.025	solvent	industry		
36	2-Ethyl-1-hexanol	C8H18O	104-76-7	130	1028	83	IS-2	0.01	plasticizer	business/household/traffic		
37	Dicyclopentadiene	C10H12	77-73-6	132	1028	66	IS-3	0.025	intermediate for resin	industry		
38	1,2-Dichlorobenzene	C6H4Cl2	95-50-1	146	1033	146	IS-2	0.01	solvent	industry		
39	Benzyl alcohol	C7H8O	100-51-6	108	1033	108	IS-2	0.01	cosmetics/fragrance	business/household/traffic		
40	2-Methylphenol	C7H8O	95-48-7	108	1048	108	IS-2	0.01	disinfectant	business/household/traffic		
41	Bis(2-chloroisopropyl)ether (DCIP)	C6H12Cl2O	108-60-1	170	1054	121	IS-2	0.01	insecticide	agriculture		
42	Methomyl oxime	C5H11N3O2S	13749-94-5	105	1059	105	IS-2	0.01	other pesticide	agriculture		
43	trans-Decahydronaphthalene	C10H18	493-02-7	138	1062	138	IS-3	0.025	solvent	industry		
44	*N*-Nitrosopyrrolidine	C4H8N2O	930-55-2	100	1063	100	IS-2	0.01	reagent	business/household/traffic		
45	*N*-Methylaniline	C7H9N	100-61-8	107	1065	106	IS-3	0.025	intermediate in organic synthesis	industry		
46	Acetophenone	C8H8O	98-86-2	120	1066	105	IS-2	0.01	cosmetics/fragrance	business/household/traffic		
47	3-&4-Methylphenol	C7H8O	108-39-4&106-44-5	108	1069	107	IS-2	0.02	intermediate in organic synthesis/leaching from tire	Industry		
48	*N*-Nitrosomorpholine	C4H8N2O2	59-89-2	116	1069	116	IS-2	0.01	solvent/intermediate in organic synthesis	industry		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
49	2-Methylaniline	C7H9N	95-53-4	107	1070	106	IS-2	0.01	intermediate for dyes	industry		
50	Octanol	C8H18O	111-87-5	130	1070	56	IS-2	0.01	cosmetics/fragrance	business/household/traffic		
51	3-Toluidine	C7H9N	108-44-1	107	1077	106	IS-3	0.025	intermediate for dyes	industry		
52	Hexachloroethane	C2Cl6	67-72-1	234	1077	201	IS-2	0.01	intermediate in organic synthesis	industry		
53	2-Chloro-6-methylphenol	C7H7ClO	87-64-9	142	1078	107	IS-2	0.01	other	industry		
54	2-Methoxyphenol	C7H8O2	90-05-1	124	1084	109	IS-3	0.025	leaching from tire	business/household/traffic		
55	Nitrobenzene	C6H5NO2	98-95-3	123	1086	123	IS-2	0.01	intermediate in organic synthesis	industry		
56	*N,N*-Dimethylaniline	C8H11N	121-69-7	121	1089	120	IS-3	0.025	intermediate for dyes	industry		
57	1,2-Dibromo-3-chloropropane	C3H5Br2Cl	96-12-8	234	1090	157	IS-3	0.025	intermediate in organic synthesis	industry		
58	3-Bromochlorobenzene	C6H4BrCl	108-37-2	190	1095	192	IS-3	0.025	other	industry		
59	*n*-C11H24	C11H24	1120-21-4	156	1100	85	IS-2	0.01	petroleum/plant	business/household/traffic		
60	2,6-Dimethylphenol	C8H10O	576-26-1	122	1105	122	IS-2	0.01	intermediate for resin	industry		
61	*N*-Nitrosopiperidine	C5H10N2O	100-75-4	114	1107	114	IS-3	0.01	reagent	business/household/traffic		
62	Phenylethyl alcohol	C8H10O	60-12-8	122	1112	122	IS-2	0.01	cosmetics/fragrance	business/household/traffic		
63	2-Bromochlorobenzene	C6H4BrCl	694-80-4	190	1122	192	IS-3	0.025	other	industry		
64	Isophorone	C9H14O	78-59-1	138	1122	82	IS-3	0.025	solvent/paint	industry		
65	Methyl octanoate	C9H18O2	111-11-5	158	1123	87	IS-3	0.01	fatty acid methy ester	business/household/traffic		
66	2-Chloroaniline	C6H6cLN	95-51-2	127	1127	127	IS-3	0.025	intermediate for dyes	industry		
67	Aldoxycarb (deg)	C7H14N2O4S	1646-88-4	222	1128	68	IS-3	0.01	insecticide	agriculture		
68	*N*-Ethylaniline	C8H11N	103-69-5	121	1129	106	IS-3	0.025	intermediate for dyes	industry		
69	2-Nitrophenol	C6H5NO3	88-75-5	139	1130	139	IS-3	0.01	intermediate in organic synthesis/leaching from tire	Industry		
70	1,3,5-Trichlorobenzene	C6H3Cl3	108-70-3	180	1133	182	IS-3	0.025	intermediate in organic synthesis/solvent	industry		
71	Urea, N,N-diethyl-	C5H12N2O	634-95-7	116	1143	116	IS-3	0.01	leaching from tire	business/household/traffic		
72	2,4-Dimethylphenol	C8H10O	105-67-9	122	1144	107	IS-3	0.01	intermediate in organic synthesis	industry		
73	Bis(2-chloroethoxy)methane	C5H10Cl2O2	111-91-1	172	1160	93	IS-3	0.01	intermediate in organic synthesis	industry		
74	2-Nitrotoluene	C7H7NO2	88-72-2	137	1161	120	IS-3	0.01	intermediate in organic synthesis	industry		
75	2,4-Dichlorophenol	C6H4Cl2O	120-83-2	162	1166	162	IS-3	0.01	reagent, by-product of chlorination	business/household/traffic		
76	2,6-Dimethylaniline	C8H11N	87-62-7	121	1166	121	IS-3	0.01	intermediate in organic synthesis	industry		
77	3,5-Dimethylphenol	C8H10O	108-68-9	122	1166	122	IS-3	0.025	intermediate in organic synthesis	industry		
78	2,5-Dichlorophenol	C6H4Cl2O	583-78-8	162	1168	162	IS-3	0.01	intermediate for pesticides	industry		
79	Clofentezine	C14H8Cl2N4	74115-24-5	302	1168	137	IS-3	0.01	other pesticide	agriculture		
80	1-Nonanol	C9H20O	143-08-8	144	1171	83	IS-3	0.01	cosmetics/fragrance	business/household/traffic		
81	2,5-Dimethylaniline	C8H11N	95-78-3	121	1172	121	IS-3	0.025	intermediates in the synthesis of dyes	industry		
82	2,3-Dichlorophenol	C6H4Cl2O	576-24-9	162	1173	162	IS-3	0.01	reagent	business/household/traffic		
83	2-Anisidine	C7H9NO	90-04-0	123	1174	123	IS-3	0.025	intermediate for dyes	industry		
84	3,5-Dimethylaniline	C8H11N	108-69-0	121	1176	121	IS-3	0.025	intermediate for dyes	industry		
85	1,2,4-Trichlorobenzene	C6H3Cl3	120-82-1	180	1179	180	IS-3	0.01	intermediate in organic synthesis/solvent	industry		
86	L-Menthol	C10H20O	2216-51-5	156	1180	95	IS-3	0.01	PPCPs	business/household/traffic		
87	Naphthalene	C10H8	91-20-3	128	1185	128	IS-3	0.01	PAH	industry	X	
88	3-&4-Chlorophenol	C6H5ClO	108-43-0&106-48-9	128	1190	128	IS-3	0.02	by-product of chlorination/intermediate in organic synthesis	industry		
89	3-Nitrotoluene	C7H7NO2	99-08-1	137	1197	137	IS-3	0.01	intermediate in organic synthesis	industry		
90	alpha-Terpineol	C10H18O	10482-56-1	154	1197	136	IS-3	0.025	cosmetics/fragrance	business/household/traffic		
91	2,3-&3,4-Dimethylaniline	C8H11N	87-59-2&95-64-7	121	1198	121	IS-3	0.05	intermediate in organic synthesis	industry		
92	4-Chloroaniline	C6H6ClN	106-47-8	127	1200	127	IS-3	0.01	intermediate for dyes and pesticides	industry		
93	*n*-C12H26	C12H26	112-40-3	170	1200	85	IS-3	0.01	petroleum	business/household/traffic		
94	2,6-Dichlorophenol	C6H4Cl2O	87-65-0	162	1201	162	IS-3	0.01	by-product of chlorination/intermediate for trichlorophenol	industry		
95	Hexachloropropylene	C3Cl6	1888-71-7	246	1204	213	IS-3	0.01	solvent	industry		
96	2-Acetyl-5-methylthiophene	C7H8OS	13679-74-8	140	1206	125	IS-3	0.01	leaching from tire	business/household/traffic		
97	1,2,3-Trichlorobenzene	C6H3Cl3	87-61-6	180	1211	180	IS-3	0.025	intermediate in organic synthesis/solvent	industry		
98	Hexachlorobutadiene	C4Cl6	87-68-3	258	1213	225	IS-3	0.01	solvent	industry		
99	4-Nitrotoluene	C7H7NO2	99-99-0	137	1217	137	IS-3	0.01	intermediate in organic synthesis	industry		
100	4-Anisidine	C7H9NO	104-94-9	123	1218	108	IS-3	0.025	intermediate for dyes	industry		
101	Ethanol, 2-phenoxy-	C8H10O2	122-99-6	138	1218	94	IS-3	0.01	leaching from tire	business/household/traffic		
102	Methamidophos	C2H8NO2PS	10265-92-6	141	1222	94	IS-3	0.05	insecticide	agriculture		
103	3-Chloronitrobenzene	C6H4ClNO2	121-73-3	157	1229	157	IS-3	0.01	intermediate in organic synthesis	industry		
104	Benzothiazole	C7H5NS	95-16-9	135	1229	135	IS-3	0.01	leaching from tire	business/household/traffic		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
105	3-Anisidine	C7H9NO	536-90-3	123	1238	123	IS-3	0.025	other	industry		
106	Quinoline	C9H7N	91-22-5	129	1241	129	IS-3	0.025	intermediate in organic synthesis	industry		
107	DDVP	C4H7Cl2O4P	62-73-7	220	1243	185	IS-3	0.01	insecticide	agriculture		
108	4-Chloronitrobenzene	C6H4ClNO2	100-00-5	157	1245	157	IS-3	0.01	intermediate in organic synthesis	industry		
109	e-Caprolactam	C6H11NO	105-60-2	113	1252	113	IS-3	0.01	intermediate for fiber	industry		
110	Formamide, N-cyclohexyl-	C7H13NO	766-93-8	127	1257	84	IS-3	0.01	leaching from tire	business/household/traffic		
111	*p*-Phenylenediamine	C6H8N2	106-50-3	108	1260	108	IS-3	0.01	intermediate for dyes/developing fluid	industry		
112	*N*-Nitroso-di-n-butylamine	C8H18N2O	924-16-3	158	1261	84	IS-3	0.01	reagent	business/household/traffic		
113	1,4-Benzenediol	C6H6O2	123-31-9	110	1264	110	IS-3	0.01	developing fluid	business/household/traffic		
114	2-*tert*-Butylphenol	C10H14O	88-18-6	150	1268	135	IS-3	0.01	intermediate in organic synthesis	industry		
115	Novaluron-deg	C17H9ClF8N2O4	116714-46-6	492	1272	335	IS-3	0.01	insecticide	agriculture		
116	2-sec-Butylphenol	C10H14O	89-72-5	150	1273	121	IS-3	0.01	intermediate in organic synthesis	industry		
117	Nereistoxin oxalate deg.	C7H13NO4S2	1631-52-3	239	1274	149	IS-3	0.01	insecticide	agriculture		
118	*m*-Aminophenol	C6H7NO	591-27-5	109	1278	109	IS-3	0.01	intermediate for dyes	industry		
119	4-Bromophenol	C6H5BrO	106-41-2	172	1281	172	IS-3	0.025	natural product	other		
120	Pentamethylbenzene	C11H16	700-12-9	148	1281	133	IS-3	0.025	other	industry		
121	Allidochlor	C8H12ClNO	93-71-0	173	1283	138	IS-3	0.01	herbicide	agriculture		
122	4-Chloro-3-methylphenol	C7H7ClO	59-50-7	142	1285	142	IS-3	0.025	fungicide, paint	agriculture		
123	3- & 4-tert-Butylphenol	C10H14O	585-34-2&98-54-4	150	1289	135	IS-3	0.01	antioxidant	business/household/traffic		
124	Thymol	C10H14O	89-83-8	150	1289	135	IS-3	0.01	PPCPs	business/household/traffic		
125	*m*-Phenylenediamine	C6H8N2	108-45-2	108	1290	108	IS-3	0.01	intermediate for dyes	industry		
126	Safrole	C10H10O2	94-59-7	162	1292	162	IS-3	0.01	intermediate in organic synthesis/preservative	industry		
127	2-Methylbenzothiazole	C8H7NS	120-75-2	149	1298	149	IS-3	0.025	leaching from tire	business/household/traffic		
128	5-Chloro-2-methyl aniline	C7H8ClN	95-79-4	141	1299	106	IS-3	0.025	intermediate for dyes	industry		
129	2-Methylnaphthalene	C11H10	91-57-6	142	1300	142	IS-4	0.01	PAH	industry	X	
130	*n*-C13H28	C13H28	629-50-5	184	1300	85	IS-3	0.01	petroleum/plant	business/household/traffic		
131	1,2,3-Trimethoxybenzene	C9H12O3	634-36-6	168	1306	168	IS-3	0.025	other	industry		
132	4-sec-Butylphenol	C10H14O	99-71-8	150	1309	121	IS-3	0.01	other	business/household/traffic		
133	1-Methylnaphthalene	C11H10	90-12-0	142	1315	142	IS-3	0.01	PAH	industry	X	
134	3-&4-Nitroanisole	C7H7NO3	555-03-3&100-17-4	153	1321	153	IS-3	0.05	intermediate in organic synthesis	industry		
135	Methyl decanoate	C11H22O2	110-42-9	186	1323	87	IS-3	0.01	fatty acid methy ester	business/household/traffic		
136	1,2,4,5-Tetrachlorobenzene	C6H2Cl4	95-94-3	214	1330	216	IS-3	0.01	intermediate in organic synthesis	industry		
137	2,3,5-Trichlorophenol	C6H3Cl3O	933-78-8	196	1330	196	IS-3	0.01	intermediate for pesticides/PRESERVATIVE	industry		
138	2,4-Dichloroaniline	C6H5Cl2N	554-00-7	161	1330	161	IS-4	0.01	reagent/intermediate in organic synthesis	business/household/traffic		
139	Hexachlorocyclopentadiene	C5Cl6	77-47-4	270	1330	237	IS-3	0.01	intermediate in organic synthesis	industry		
140	Dichlobenil	C7H3Cl2N	1194-65-6	171	1338	171	IS-4	0.01	herbicide	agriculture		
141	Tribenuron-methyl	C15H17N5O6S	101200-48-0	395	1342	154	IS-4	0.01	herbicide	agriculture		
142	Chlorimuron-ethyl	C15H15ClN4O6S	99283-00-8	414	1343	159	IS-4	0.01	herbicide	agriculture		
143	2-Nitroanisole	C7H7NO3	91-23-6	153	1346	123	IS-3	0.025	intermediate in organic synthesis	industry		
144	Phenol, 2,6-dimethoxy-	C8H10O3	91-10-1	154	1346	154	IS-3	0.01	leaching from tire	business/household/traffic		
145	Nicotine	C10H14N2	54-11-5	162	1348	84	IS-4	0.01	PPCPs	business/household/traffic		
146	2,3-Dichloroaniline	C6H5Cl2N	608-27-5	161	1350	161	IS-3	0.025	reagent	business/household/traffic		
147	2,4,6-Trichlorophenol	C6H3Cl3O	88-06-2	196	1350	196	IS-4	0.01	by-product of chlorination/intermediate for pesticides	industry		
148	2,4,5-Trichlorophenol	C6H3Cl3O	95-95-4	196	1355	196	IS-4	0.01	intermediate for pesticides/PRESERVATIVE	industry		
149	4-n-Butylphenol	C10H14O	1638-22-8	150	1356	107	IS-4	0.01	intermediate for liquid crystal	industry		
150	EPTC	C9H19NOS	759-94-4	189	1357	128	IS-4	0.01	herbicide	agriculture		
151	2,3,4-Trichlorophenol	C6H3Cl3O	15950-66-0	196	1364	196	IS-4	0.01	intermediate for pesticides/PRESERVATIVE	industry		
152	2,5-Dichloronitrobenzene	C6H3Cl2NO2	89-61-2	191	1364	191	IS-4	0.01	intermediate in organic synthesis	industry		
153	Acetamide, N-phenyl-	C8H9NO	103-84-4	135	1372	135	IS-4	0.01	leaching from tire	business/household/traffic		
154	2,4-Dichloronitrobenzene	C6H3Cl2NO2	611-06-3	191	1373	191	IS-4	0.01	intermediate in organic synthesis	industry		
155	Isosafrole	C10H10O2	120-58-1	162	1381	162	IS-4	0.01	cosmetics/fragrance	business/household/traffic		
156	1-Chloronaphthalene	C10H7Cl	90-13-1	162	1382	162	IS-4	0.01	PCN	industry		
157	2,3,6-Trichlorophenol	C6H3Cl3O	933-75-5	196	1382	196	IS-4	0.01	intermediates in the synthesis of dyes, pigments, and phenolic resins	industry		
158	2-Chloronaphthalene	C10H7Cl	91-58-7	162	1383	162	IS-4	0.01	PCN	industry		
159	2,6-Diaminotoluene	C7H10N2	823-40-5	122	1384	122	IS-4	0.01	intermediate in organic synthesis	industry		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
160	3,5-Dichlorophenol	C6H4Cl2O	591-35-5	162	1384	162	IS-4	0.01	reagent	business/household/traffic		
161	Biphenyl	C12H10	92-52-4	154	1385	154	IS-3	0.025	intermediate in organic synthesis	industry		
162	Propamocarb	C9H20N2O2	25606-41-1	188	1393	58	IS-4	0.01	fungicide	agriculture		
163	2,3-Dichloronitrobenzene	C6H3Cl2NO2	3209-22-1	191	1394	191	IS-3	0.025	intermediate in organic synthesis	industry		
164	*n* -C14H30	C14H30	629-59-4	198	1400	85	IS-4	0.01	petroleum	business/household/traffic		
165	2-Nitroaniline	C6H6N2O2	88-74-4	138	1404	138	IS-4	0.01	intermediate in organic synthesis	industry		
166	Diphenyl ether	C12H10O	101-84-8	170	1405	170	IS-3	0.025	cosmetics/fragrance	business/household/traffic		
167	2,4,6-Trichloroaniline	C6H4Cl3N	634-93-5	195	1408	195	IS-3	0.025	reagent/intermediate in organic synthesis	business/household/traffic		
168	3,4-Dichlorophenol	C6H4Cl2O	95-77-2	162	1408	162	IS-4	0.01	intermediate in organic synthesis	industry		
169	2,6-Dimethylnaphthalene	C12H12	581-42-0	156	1410	156	IS-3	0.025	PAH	industry		
170	Longifolene	C15H24	475-20-7	204	1418	161	IS-3	0.025	other	industry		
171	Mevinphos 1	C7H13O6P	7786-34-7	224	1421	127	IS-4	0.01	insecticide	agriculture		
172	Cyclohexanamine, N-cyclohexyl-	C12H23N	101-83-7	181	1422	138	IS-4	0.01	leaching from tire	business/household/traffic		
173	Methyl undecanoate	C12H24O2	1731-86-8	200	1423	87	IS-4	0.005	fatty acid methy ester	business/household/traffic		
174	1,3-Dimethylnaphthalene	C12H12	575-41-7	156	1425	156	IS-3	0.025	PAH	industry		
175	Mevinphos 2	C7H13O6P	7786-34-7	224	1425	127	IS-4	0.01	insecticide	agriculture		
176	Quinoline, 2,7-dimethyl-	C11H11N	93-37-8	287	1426	157	IS-4	0.01	other	industry		
177	3,4-Dichloroaniline	C6H5Cl2N	95-76-1	161	1428	161	IS-3	0.025	intermediate for dyes and pesticides	industry		
178	Acephate	C4H10NO3PS	30560-19-1	183	1429	136	IS-4	0.05	insecticide	agriculture		
179	Butylate	C11H23NOS	2008-41-5	217	1429	146	IS-4	0.01	herbicide	agriculture		
180	1,4-Dinitrobenzene	C6H4N2O4	100-25-4	168	1434	168	IS-4	0.01	intermediate in organic synthesis	industry		
181	Diphenylmethane	C13H12	101-81-5	168	1436	167	IS-3	0.025	PAH	industry		
182	Chlormephos	C5H12ClO2PS2	24934-91-6	235	1438	234	IS-4	0.01	insecticide	agriculture		
183	1,4-&2,3-Dimethylnaphthalene	C12H12	571-58-4&581-40-8	156	1445	156	IS-3	0.05	PAH	industry		
184	1,3-Dinitrobenzene	C6H4N2O4	99-65-0	168	1447	168	IS-4	0.01	intermediate in organic synthesis	industry		
185	Etridiazole (Echlomezol)	C5H5Cl3N2OS	2593-15-9	246	1448	211	IS-3	0.025	fungicide	agriculture		
186	Dimethyl phthalate	C10H10O4	131-11-3	194	1449	163	IS-4	0.01	plasticizer	business/household/traffic		
187	3-Hydroxycarbofuran 1	C12H15NO4	16655-82-6	237	1452	137	IS-4	0.01	insecticide	agriculture		
188	2,6-Dinitrotoluene	C7H6N2O4	606-20-2	182	1455	165	IS-4	0.01	intermediate in organic synthesis	industry		
189	Acenaphthylene	C12H8	208-96-8	152	1456	152	IS-4	0.01	PAH	industry	X	
190	Trichlorfon	C4H8Cl3O4P	52-68-6	256	1456	109	IS-4	0.01	insecticide	agriculture		
191	4-*n* -Pentylphenol	C11H16O	14938-35-3	164	1457	107	IS-4	0.01	dyes tuff intermediates/ rubber chemicals/ surfactants	business/household/traffic		
192	Propham	C10H13NO2	122-42-9	179	1459	179	IS-4	0.01	herbicide	agriculture		
193	1,2-Dimethylnaphthalene	C12H12	573-98-8	156	1460	141	IS-3	0.025	PAH	industry		
194	2-Isopropylnaphthalene	C13H14	2027-17-0	170	1461	155	IS-3	0.025	PAH	industry		
195	Pebulate	C10H21NOS	1114-71-2	203	1462	128	IS-4	0.01	herbicide	agriculture		
196	2,6-Di-*tert* -butyl-4-benzoquinone	C14H20O2	719-22-2	220	1464	177	IS-3	0.025	antioxidant	business/household/traffic		
197	Phthalimide	C8H5NO2	85-41-6	147	1469	147	IS-4	0.01	leaching from tire	business/household/traffic		
198	1,8-Dimethylnaphthalene	C12H12	569-41-5	156	1481	156	IS-3	0.025	PAH	industry		
199	3-Nitroaniline	C6H6N2O2	99-09-2	138	1481	138	IS-4	0.01	intermediate in organic synthesis	industry		
200	2-*tert* -Butyl-4-methoxyphenol	C11H16O2	121-00-6	180	1484	165	IS-4	0.01	antioxidant	business/household/traffic		
201	Acenaphthene	C12H10	83-32-9	154	1489	153	IS-4	0.01	PAH	industry	X	
202	Methacrifos	C7H13O5PS	30864-28-9	240	1497	208	IS-4	0.01	insecticide	agriculture		
203	Dimethylterephthalate	C10H10O4	120-61-6	194	1498	163	IS-5	0.025	intermediate for resin	industry		
204	Thiocyclam	C5H11NS3	31895-21-3	181	1499	135	IS-4	0.01	insecticide	agriculture		
205	*n* -C15H32	C15H32	629-62-9	212	1500	85	IS-4	0.02	petroleum/plant	business/household/traffic		
206	2,4-Dinitrophenol	C6H4N2O5	51-28-5	184	1501	184	IS-4	0.01	intermediate in organic synthesis	industry		
207	2-Bromo-4,6-dichloroaniline	C6H4BrCl2N	697-86-9	239	1502	241	IS-5	0.025	reagent	business/household/traffic		
208	PCB #1	2-	2051-60-7	188	1503	188	IS-4	0.01	PCB	industry	X	X
209	4-Methyl-2,6-di-t-butylphenol	C15H24O	128-37-0	220	1504	220	IS-5	0.025	antioxidant	business/household/traffic		
210	Acetamide, N-(2-phenylethyl)-	C10H13NO	877-95-2	163	1505	104	IS-4	0.01	leaching from tire	business/household/traffic		
211	Chloroneb	C8H8Cl2O2	2675-77-6	206	1505	191	IS-4	0.01	fungicide	agriculture		
212	Crimidine	C7H10ClN3	535-89-7	172	1505	156	IS-4	0.01	insecticide	agriculture		
213	4-Bromo-2,6-dichloroaniline	C6H4BrCl2N	697-86-9	239	1509	241	IS-5	0.025	reagent	business/household/traffic		
214	1-Naphthol	C10H8O	90-15-3	144	1510	144	IS-4	0.01	intermediate for dyes	industry		
215	2-Amino-6-nitrotoluene	C7H8N2O2	603-83-8	152	1516	152	IS-4	0.01	other	industry		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
216	Pentachlorobenzene	C6HCl5	608-93-5	248	1516	250	IS-4	0.01	by-product	industry	X	X
217	2-Phenylphenol (OPP)	C12H10O	90-43-7	170	1518	170	IS-4	0.01	intermediate in organic synthesis	industry		
218	2-Naphthol	C10H8O	135-19-3	144	1521	144	IS-4	0.01	intermediate in organic synthesis	industry		
219	4-Nitrophenol	C6H5NO3	100-02-7	139	1521	139	IS-4	0.01	intermediate in organic synthesis/fungcide	industry		
220	Methyl dodecanoate	C13H26O2	111-82-0	214	1523	87	IS-4	0.01	fatty acid methy ester	business/household/traffic		
221	Dibenzofuran	C12H8O	132-64-9	168	1524	168	IS-4	0.01	intermediate in organic synthesis	industry		
222	4-Methyl-3-nitrophenol	C7H7NO3	2042-14-0	153	1528	136	IS-4	0.01	other	industry		
223	2,4-Dinitrotoluene	C7H6N2O4	121-14-2	182	1529	165	IS-4	0.01	intermediate in organic synthesis	industry		
224	Metribuzin DADK	C8H14N4OS	21087-64-9	214	1533	154	IS-4	0.01	herbicide	agriculture		
225	Isoprocarb	C11H15NO2	2631-40-5	193	1536	121	IS-4	0.01	insecticide	agriculture		
226	1-Naphthylamine	C10H9N	134-32-7	143	1539	143	IS-4	0.01	reagent	business/household/traffic		
227	2,3,5,6-&2,3,4,5-Tetrachlorophenol	C6H2Cl4O	935-95-5&4901-51-3	230	1542	232	IS-4	0.02	other	industry		
228	4-Amino-2-nitrotoluene	C7H8N2O2	119-32-4	152	1542	152	IS-4	0.01	other	industry		
229	Molinate	C9H17NOS	2212-67-1	187	1543	126	IS-4	0.01	herbicide	agriculture		
230	Amitraz (deg)	C19H23N3	33089-61-1	293	1545	162	IS-4	0.01	other pesticide	agriculture		
231	2,3,4,6-Tetrachlorophenol	C6H2Cl4O	58-90-2	230	1550	232	IS-4	0.01	fungicide	agriculture		
232	2,6-Di-t-butyl-4-ethylphenol	C16H26O	4130-42-1	234	1555	219	IS-5	0.025	antioxidant	business/household/traffic		
233	2-Naphthylamine	C10H9N	91-59-8	143	1556	143	IS-4	0.01	reagent	business/household/traffic		
234	Aspirin	C9H8O4	50-78-2	180	1557	120	IS-4	0.01	PPCPs	business/household/traffic		
235	4-n-Hexylphenol	C12H18O	2446-69-7	178	1559	107	IS-4	0.01	intermediate in organic synthesis	industry		
236	1,4-&1,6-Dichloronaphthalene	C10H6Cl2	1825-31-6&2050-72-8	196	1560	196	IS-4	0.01	PCN	industry		
237	XMC	C10H13NO2	2655-14-3	179	1561	122	IS-4	0.01	insecticide	agriculture		
238	1,5-Dichloronaphthalene	C10H6Cl2	1825-30-5	196	1563	196	IS-4	0.01	PCN	industry		
239	2,6-&1,7-Dichloronaphthalene	C10H6Cl2	2065-70-5&2050-73-9	196	1571	196	IS-4	0.01	PCN	industry		
240	Diethyltoluamide	C12H17NO	134-62-3	191	1575	119	IS-4	0.01	PPCPs	business/household/traffic		
241	Omethoate	C5H12NO4PS	1113-02-6	213	1586	156	IS-4	0.01	insecticide	agriculture		
242	PCB #3	4-	2051-62-9	188	1586	188	IS-4	0.01	PCB	industry	X	X
243	Tecnazene	C6HCl4NO2	117-18-0	259	1587	261	IS-4	0.01	fungicide	agriculture		
244	Diethyl phthalate	C14H14O4	84-66-2	246	1588	149	IS-4	0.01	plasticizer	business/household/traffic		
245	2,4,6-Tri-tert-butylphenol	C18H30O	732-26-3	262	1590	247	IS-4	0.01	other	industry		
246	Fluorene	C13H10	86-73-7	166	1591	166	IS-4	0.01	PAH	industry	X	
247	Crotamiton	C13H17NO	483-63-6	203	1593	69	IS-4	0.01	PPCPs	business/household/traffic		
248	Xylylcarb	C10H13NO2	2425-10-7	179	1596	122	IS-4	0.01	insecticide	agriculture		
249	5-Nitro-o-toluidine	C7H8N2O2	99-55-8	152	1597	152	IS-4	0.01	intermediate for dyes	industry		
250	4-Chloro-2-nitroaniline	C6H5ClN2O2	89-63-4	172	1598	172	IS-5	0.025	intermediate in organic synthesis	industry		
251	4-Nitroaniline	C6H6N2O2	100-01-6	138	1599	138	IS-4	0.01	intermediate in organic synthesis	industry		
252	2,6-Dibromo-4-chloroaniline	C6H4Br2ClN	874-17-9	283	1600	285	IS-5	0.025	reagent	business/household/traffic		
253	Ethenzamide	C9H11NO2	738-73-8	165	1600	120	IS-4	0.01	PPCPs	business/household/traffic		
254	*n* -C16H34	C16H34	544-76-3	226	1600	85	IS-4	0.01	petroleum	business/household/traffic		
255	4-Chlorophenylphenyl ether	C12H9ClO	7005-72-3	204	1601	204	IS-4	0.01	dielectric fluid	industry		
256	4-tert-Octylphenol	C14H22O	140-66-9	206	1602	135	IS-4	0.01	nonionic detergent metabolite	business/household/traffic		
257	Fenobucarb	C12H17NO2	3766-81-2	207	1605	150	IS-4	0.01	insecticide	agriculture		
258	Propachlor	C11H14ClNO	1918-16-7	211	1605	120	IS-4	0.01	herbicide	agriculture		
259	2-Methyl-4,6-dinitrophenol	C7H6N2O5	534-52-1	198	1606	198	IS-5	0.01	intermediate for dyes/pesticide/	industry		
260	Propoxur	C11H15NO3	114-26-1	209	1607	110	IS-4	0.01	insecticide	agriculture		
261	Tris(2-chloroethyl)phosphite	C6H12Cl3O3P	140-08-9	268	1607	233	IS-4	0.01	fire retardant	business/household/traffic		
262	2-(Methylthio)-benzothiazol	C8H7NS2	615-22-5	181	1609	181	IS-5	0.025	leaching from tire	business/household/traffic		
263	2-Nitronaphthalene	C10H7NO2	581-89-5	173	1609	173	IS-4	0.01	PAH	industry		
264	Chlorethoxyfos	C6H11Cl4O3PS	54593-83-8	334	1615	153	IS-4	0.02	insecticide	agriculture		
265	Ibuprofen	C13H18O2	15687-27-1	206	1615	161	IS-4	0.01	PPCPs	business/household/traffic		
266	3,4,5-Trichlorophenol	C6H3Cl3O	609-19-8	196	1616	196	IS-5	0.01	intermediates in the synthesis of dyes, pigments, and phenolic resins	industry		
267	Demeton-S-methyl	C6H15O3PS2	919-86-8	230	1620	142	IS-4	0.01	insecticide	agriculture		
268	PCB #4&10	22'-&26-	13029-08-8&33146-45-1	222	1621	222	IS-4	0.02	PCB	industry	X	X

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
269	Methyl tridecanoate	C14H28O2	1731-88-0	228	1623	87	IS-4	0.005	fatty acid methy ester	business/household/traffic		
270	Diphenylamine	C12H11N	122-39-4	169	1626	169	IS-4	0.01	intermediate in organic synthesis	industry		
271	Ethoprophos	C8H19O2PS2	13194-48-4	242	1635	158	IS-4	0.01	insecticide	agriculture		
272	Cycloate	C11H21NOS	1134-23-2	215	1637	154	IS-5	0.01	herbicide	agriculture		
273	2,4,6-Tribromophenol	C6H3Br3O	118-79-6	328	1640	332	IS-5	0.025	intermediate for resin	industry		
274	Tributyl phosphate	C12H27O4P	126-73-8	266	1641	99	IS-4	0.01	fire retardant	business/household/traffic		
275	Phenmedipham deg.	C16H16N2O4	13684-63-4	300	1643	167	IS-5	0.25	herbicide	agriculture		
276	5-Bromoindole	C8H6BrN	10075-50-0	195	1647	195	IS-5	0.01	other	industry		
277	Ethalfluralin	C13H14F3N3O4	55283-68-6	333	1648	316	IS-5	0.01	herbicide	agriculture		
278	Naled	C4H7Br2Cl2O4P	300-76-5	378	1652	109	IS-5	0.01	insecticide	agriculture		
279	1-Nitronaphthalene	C10H7NO2	86-57-7	173	1653	173	IS-5	0.01	PAH	industry		
280	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	C9H10O4	134-96-3	182	1653	182	IS-4	0.01	leaching from tire	business/household/traffic		
281	Dibenzylether	C14H14O	103-50-4	198	1655	91	IS-5	0.025	solvent	industry		
282	Dichlofluanid metabolite	C9H11Cl2FN2O2S2	1085-98-9	333	1655	200	IS-5	0.01	fungicide	agriculture		
283	Chlorpropham	C10H12ClNO2	101-21-3	213	1657	213	IS-5	0.01	herbicide	agriculture		
284	2,6-Dichlorobenzamid	C7H5Cl2NO	2008-58-4	190	1660	173	IS-5	0.01	herbicide	agriculture		
285	Dicrotophos	C8H16NO5P	141-66-2	237	1661	127	IS-5	0.01	insecticide	agriculture		
286	Flusilazole metabolite	C16H15 F2 N3Si	85509-19-9	315	1661	235	IS-5	0.01	fungicide	agriculture		
287	4-n-Heptylphenol	C13H20O	1987-50-4	192	1663	107	IS-5	0.01	PPCP	business/household/traffic		
288	Trifluralin	C13H16F3N3O4	1582-09-8	335	1665	306	IS-5	0.01	herbicide	agriculture		
289	Dioxabenzofos(Salithion)	C8H9O3PS	3811-49-2	216	1668	216	IS-5	0.01	insecticide	agriculture		
290	Benfluralin	C13H16F3N3O4	1861-40-1	335	1670	292	IS-5	0.025	herbicide	agriculture		
291	Bendiocarb	C11H13NO4	22781-23-3	223	1671	151	IS-5	0.01	insecticide	agriculture		
292	2(3H)-Benzothiazolone	C7H5NOS	934-34-9	151	1673	151	IS-5	0.01	leaching from tire	business/household/traffic		
293	Sulfotep	C8H20O5P2S2	3689-24-5	322	1673	322	IS-5	0.01	insecticide	agriculture		
294	Metribuzin DK	C8H14N4OS	21087-64-9	214	1678	168	IS-5	0.01	herbicide	agriculture		
295	Monocrotophos	C7H14NO5P	6923-22-4	223	1679	127	IS-5	0.01	insecticide	agriculture		
296	1,3,5-Trinitrobenzene	C6H3N3O6	99-35-4	213	1685	213	IS-5	0.01	vulcanization/reagent	business/household/traffic		
297	Cadusafos	C10H23O2PS2	95465-99-9	270	1686	159	IS-5	0.01	insecticide	agriculture		
298	Pencycron	C19H21ClN2O	66063-05-6	328	1686	125	IS-5	0.01	fungicide	agriculture		
299	2,4,6-Trinitrotoluene	C7H5N3O6	118-96-7	227	1691	210	IS-5	0.01	explosive	industry		
300	Phorate	C7H17O2PS3	298-02-2	260	1693	260	IS-5	0.01	insecticide	agriculture		
301	Phenacetin	C10H13NO2	62-44-2	179	1696	179	IS-5	0.01	PPCP	business/household/traffic		
302	α-HCH	C6H6Cl6	319-84-6	288	1698	219	IS-5	0.01	insecticide	agriculture	X	X
303	4-Bromophenylphenyl ether	C12H9BrO	101-55-3	248	1700	248	IS-5	0.01	reagent	business/household/traffic		
304	*n* -C17H36	C17H36	629-78-7	240	1700	85	IS-5	0.01	petroleum/plant	business/household/traffic		
305	Hexachlorobenzene	C6Cl6	118-74-1	282	1703	284	IS-5	0.01	by-product	industry	X	X
306	PCB #8	24'-	34883-43-7	222	1705	222	IS-5	0.01	PCB	industry	X	X
307	2,4,6-Tribromoaniline	C6H4Br3N	147-82-0	327	1707	331	IS-5	0.025	reagent	business/household/traffic		
308	4-Phenylphenol	C12H10O	92-69-3	170	1714	170	IS-5	0.01	intermediate in organic synthesis	industry		
309	Thiometon	C6H15O2PS3	640-15-3	246	1715	88	IS-5	0.01	insecticide	agriculture		
310	Desmedipham	C16H16N2O4	13684-56-5	300	1719	181	IS-5	0.5	herbicide	agriculture		
311	2,6-Dichloro-4-nitroaniline	C6H4Cl2N2O2	99-30-9	206	1721	206	IS-5	0.025	intermediate in organic synthesis	industry		
312	Dicloran	C6H4Cl2N2O2	99-30-9	206	1723	206	IS-5	0.01	fungicide	agriculture		
313	Methyl myristate	C15H30O2	124-10-7	242	1723	87	IS-5	0.01	fatty acid methy ester	business/household/traffic		
314	Dimethoate	C5H12NO3PS2	60-51-5	229	1724	125	IS-5	0.01	insecticide	agriculture		
315	2,6-Diisopropylnaphthalene	C16H20	24157-81-1	212	1730	197	IS-5	0.025	PAH	industry		
316	1,3,7-&1,4,6-Trichloronaphthalene	C10H5Cl3	55720-37-1&2737-54-9	230	1731	230	IS-4	0.01	PCN	industry		
317	Ethoxyquin	C14H19NO	91-53-2	217	1733	202	IS-5	0.01	fungicide	agriculture		
318	Furilazole	C11H13Cl2NO3	121776-33-8	277	1736	220	IS-5	0.01	herbicide	agriculture		
319	Carbofuran	C12H15NO3	1563-66-2	221	1738	164	IS-5	0.01	insecticide	agriculture		
320	Simazine (CAT)	C7H12ClN5	122-34-9	201	1739	201	IS-5	0.01	herbicide	agriculture		
321	PCB #19	22'6-	38444-73-4	256	1740	256	IS-5	0.01	PCB	industry	X	X
322	1,2,4,5-Tetrabromobenzene	C6H2Br4	636-28-2	390	1742	394	IS-5	0.01	other	industry		
323	β-HCH	C6H6Cl6	319-85-7	288	1746	219	IS-5	0.01	insecticide	agriculture	X	X
324	Phenazine	C12H8N2	92-82-0	180	1747	180	IS-5	0.01	other	industry		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
325	Dimethipin	C6H10O4S2	55290-64-7	210	1748	54	IS-5	0.01	herbicide	agriculture		
326	Nonylphenol	C15H24O	25154-52-3	220	1748	135	IS-5	0.01	nonionic detergent metabolite	business/household/traffic		
327	Swep	C8H7Cl2NO2	1918-18-9	219	1748	187	IS-5	0.01	herbicide	agriculture		
328	Atrazine	C8H14cLN5	1912-24-9	215	1749	200	IS-5	0.01	herbicide	agriculture		
329	Pentachlorophenol	C6HCl5O	87-86-5	264	1749	266	IS-5	0.01	herbicide	agriculture		
330	Pentachloronitrobenzene (Quintozene)	C6Cl5NO2	82-68-8	293	1751	237	IS-5	0.01	fungicide	agriculture		
331	Cyromazine	C6H10N6	66215-27-8	166	1754	151	IS-5	0.01	insecticide	agriculture		
332	4-Aminobiphenyl	C12H11N	92-67-1	169	1755	169	IS-5	0.01	reagent	business/household/traffic		
333	Clomazone	C12H14ClNO2	81777-89-1	239	1755	204	IS-5	0.01	herbicide	agriculture		
334	Propazine	C9H16ClN5	139-40-2	229	1757	214	IS-5	0.01	herbicide	agriculture		
335	Tris(2-chloroethyl) phosphate	C6H12Cl3O4P	115-96-8	284	1757	249	IS-5	0.01	fire retardant	business/household/traffic		
336	3,5-di-*tert* -Butyl-4-hydroxybenzaldehyde	C15H22O2	1620-98-0	234	1759	219	IS-5	0.01	antioxidant/leaching from tire	business/household/traffic		
337	Tolylfluanid metabolite	C10H13Cl2FN2O2S2	731-27-1	347	1762	214	IS-5	0.05	fungicide	agriculture		
338	Diazinon oxon	C12H21N2O4P	962-58-3	288	1763	273	IS-5	0.01	insecticide	agriculture		
339	γ-HCH	C6H6Cl6	58-89-9	288	1763	219	IS-5	0.01	insecticide	agriculture	X	X
340	Dibenzothiophene	C12H8S	132-65-0	184	1764	184	IS-5	0.025	petroleum	business/household/traffic		
341	4-n-Octylphenol	C14H22O	1806-26-4	206	1766	107	IS-5	0.01	nonionic detergent metabolite	business/household/traffic		
342	Dipropyl phthalate	C14H18O4	131-16-8	250	1767	149	IS-5	0.01	plasticizer	business/household/traffic		
343	Cyanophos, CYAP	C9H10NO3PS	2636-26-2	243	1775	243	IS-5	0.01	insecticide	agriculture		
344	Propetamphos	C10H20NO4PS	31218-83-4	281	1775	138	IS-5	0.01	insecticide	agriculture		
345	Terbufos	C9H21O2PS3	13071-79-9	288	1775	231	IS-5	0.01	insecticide	agriculture		
346	1,2,3-Trichloronaphthalene	C10H5Cl3	50402-52-3	230	1778	230	IS-6	0.01	PCN	industry		
347	Fonofos	C10H15OPS2	994-22-9	246	1781	246	IS-5	0.01	insecticide	agriculture		
348	Phenoxathiin	C12H8OS	262-20-4	200	1781	200	IS-5	0.01	other	industry		
349	Propyzamide	C12H11Cl2NO	23950-58-5	255	1781	173	IS-5	0.01	herbicide	agriculture		
350	2,2'-Dibromobiphenyl (BB-4)	C12H8Br2	59080-37-4	310	1784	312	IS-5	0.01	fire retardant	business/household/traffic		
351	Pyroquilon	C11H11NO	57369-32-1	173	1784	130	IS-5	0.01	fungicide	agriculture		
352	PCB #18	22'5-	37680-65-2	256	1785	256	IS-5	0.01	PCB	industry	X	X
353	Diazinon	C12H21N2O3PS	333-41-5	304	1789	137	IS-5	0.01	insecticide	agriculture		
354	Phenanthrene	C14H10	85-01-8	178	1791	178	IS-5	0.01	PAH	industry	X	
355	Chlorothalonil (TPN)	C8Cl4N2	1897-45-6	264	1792	266	IS-5	0.01	fungicide	agriculture		
356	Pyrimethanil	C12H13N3	53112-28-0	199	1795	198	IS-5	0.01	fungicide	agriculture		
357	PCB #15	44'-	2050-68-2	222	1797	222	IS-5	0.01	PCB	industry	X	X
358	Dichlone	C10H4Cl2O2	117-80-6	226	1800	226	IS-5	0.01	fungicide	agriculture		
359	*n* -C18H38	C18H38	593-45-3	254	1800	85	IS-5	0.01	petroleum	business/household/traffic		
360	Dinoseb	C10H12N2O5	88-85-7	240	1801	211	IS-5	0.01	insecticide	agriculture		
361	Anthracene	C14H10	120-12-7	178	1802	178	IS-5	0.01	PAH	industry	X	
362	Flufenoxuron dec2	C21H11ClF6N2O3	101463-69-8	488	1802	331	IS-5	0.01	insecticide	agriculture		
363	1,4,5-Trichloronaphthalene	C10H5Cl3	2437-55-0	230	1806	230	IS-4	0.01	PCN	industry		
364	Terbacil	C9H13ClN2O2	5902-51-2	216	1808	161	IS-5	0.01	herbicide	agriculture		
365	Disulfoton	C8H19O2PS3	298-04-4	274	1809	88	IS-5	0.01	insecticide	agriculture		
366	Prohydrojasmon	C15H26O3	158474-72-7	254	1810	153	IS-5	0.01	other pesticide	agriculture		
367	Isazofos	C9H17ClN3O3PS	42509-80-8	313	1811	161	IS-5	0.01	insecticide	agriculture		
368	Tefluthrin	C17H14ClF7O2	79538-32-2	418	1818	177	IS-5	0.01	insecticide	agriculture		
369	δ-HCH	C6H6Cl6	319-86-8	288	1819	219	IS-5	0.01	insecticide	agriculture	X	X
370	Etrimfos	C10H17N2O4PS	38260-54-7	292	1820	292	IS-5	0.01	insecticide	agriculture		
371	Tri-allate	C10H16Cl3NOS	2303-17-5	303	1823	268	IS-5	0.01	herbicide	agriculture		
372	Methyl pentadecanoate	C16H32O2	7132-64-1	256	1824	87	IS-5	0.005	fatty acid methy ester	business/household/traffic		
373	MCPA-thioethyl (Phenothiol)	C11H13ClO2S	25319-90-8	244	1826	244	IS-5	0.01	herbicide	agriculture		
374	Flufenoxuron dec3	C21H11ClF6N2O3	101463-69-8	488	1833	305	IS-5	0.01	insecticide	agriculture		
375	Pirimicarb	C11H18N4O2	23103-98-2	238	1835	166	IS-5	0.01	insecticide	agriculture		
376	Tebupirimfos	C13H23N2O3PS	96182-53-5	318	1835	318	IS-5	0.01	insecticide	agriculture		
377	Iprobenfos (IBP)	C13H21O3PS	26087-47-8	288	1838	204	IS-5	0.01	fungicide	agriculture		
378	Oxabetrinil	C12H12N2O3	74782-23-3	232	1839	73	IS-5	0.01	herbicide	agriculture		
379	Tridemorph	C19H39NO	81412-43-3	297	1840	153	IS-5	0.01	fungicide	agriculture		
380	Diphenyldisulfide	C12H10S2	882-33-7	218	1841	218	IS-5	0.025	other	industry		
381	Caffeine	C8H10N4O2	58-08-2	194	1843	194	IS-5	0.01	PPCPs	business/household/traffic		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
382	Benoxacor	C11H11Cl2NO2	98730-04-2	259	1844	120	IS-5	0.01	herbicide	agriculture		
383	Carbazole	C12H9N	86-74-8	167	1847	167	IS-5	0.025	intermediate in organic synthesis	industry		
384	PCB #54	22'66'-	15968-05-5	290	1847	292	IS-5	0.01	PCB	industry	X	X
385	Metribuzin DA	C8H13N3OS	35045-02-4	199	1848	199	IS-5	0.01	herbicide	agriculture		
386	Ethiofencarb	C11H15NO2S	29973-13-5	225	1850	107	IS-5	0.01	insecticide	agriculture		
387	MCPB-ethyl	C13H17ClO3	10443-70-6	256	1853	115	IS-5	0.01	herbicide	agriculture		
388	Diisobutyl phthalate	C16H22O4	84-69-5	278	1859	149	IS-5	0.025	plasticizer	business/household/traffic		
389	Phosphamidon	C10H19ClNO5P	13171-21-6	299	1862	127	IS-5	0.01	insecticide	agriculture		
390	Phenoxazine	C12H9NO	135-67-1	183	1864	183	IS-5	0.01	other	industry		
391	1-Phenylnaphthalene	C16H12	605-02-7	204	1865	204	IS-5	0.025	PAH	industry		
392	Benfuresate	C12H16O4S	68505-69-1	256	1865	163	IS-5	0.01	herbicide	agriculture		
393	Fenitrothion oxon	C9H12NO6P	2255-17-6	261	1866	244	IS-5	0.01	insecticide	agriculture		
394	Dichlofenthion, ECP	C10H13Cl2O3PS	97-17-6	314	1867	279	IS-5	0.01	insecticide	agriculture		
395	Dimethenamid	C12H18ClNO2S	87674-68-8	275	1868	154	IS-5	0.01	herbicide	agriculture		
396	Propanil	C9H9Cl2NO	709-98-8	217	1869	161	IS-5	0.01	herbicide	agriculture		
397	4-n-Nonylphenol	C15H24O	104-40-5	220	1871	107	IS-5	0.01	co-stabilizer	industry		
398	Terbcarb (MBPMC)	C17H27NO2	1918-11-2	277	1872	205	IS-5	0.01	herbicide	agriculture		
399	Acetochlor	C14H20ClNO2	34256-82-1	269	1875	223	IS-5	0.01	herbicide	agriculture		
400	Chlorpyrifos-methyl	C7H7Cl3NO3PS	5598-13-0	321	1878	286	IS-5	0.01	insecticide	agriculture		
401	Bromobutide	C15H22BrNO	74712-19-9	311	1879	119	IS-5	0.01	herbicide	agriculture		
402	Metribuzin	C8H14N4OS	21087-64-9	214	1879	198	IS-5	0.01	herbicide	agriculture		
403	PCB #28	244'-	7012-37-5	256	1880	256	IS-5	0.01	PCB	industry	X	X
404	Oxpoconazole-formyl	C17H23ClN2O3	154-02371	338	1884	114	IS-5	0.01	fungicide	agriculture		
405	Vinclozolin	C12H9Cl2NO3	50471-44-8	285	1885	285	IS-5	0.01	fungicide	agriculture		
406	3-Hydroxycarbofuran 2	C12H15NO4	16655-82-6	237	1888	137	IS-5	0.01	insecticide	agriculture		
407	Methyl parathion	C8H10NO5PS	298-00-0	263	1890	263	IS-5	0.01	insecticide	agriculture		
408	*o* -Terphenyl	C18H14	84-15-1	230	1890	230	IS-5	0.01	storage and transfer agents/intermediate for resin	industry		
409	Tolclofos-methyl	C9H11Cl2O3PS	57018-04-9	301	1892	265	IS-5	0.01	fungicide	agriculture		
410	Alachlor	C14H20ClNO2	15972-60-8	269	1893	188	IS-5	0.01	herbicide	agriculture		
411	Simeconazole	C14H20FN3OSi	149508-90-7	293	1893	121	IS-5	0.01	fungicide	agriculture		
412	Spiroxamine 1	C18H35NO2	118134-30-8	297	1893	100	IS-5	0.01	fungicide	agriculture		
413	1,2,5,7-&1,2,4,6-&1,2,4,7-Tetrachloronaphthalene	C10H4Cl4	67922-23-0&51570-45-7&67922-21-8	264	1896	266	IS-4	0.01	PCN	industry		
414	PCB #33	2'34-	38444-86-9	256	1896	256	IS-5	0.01	PCB	industry	X	X
415	2,4-Diamino-6-nitrotoluene	C7H9N3O2	6629-29-4	167	1897	167	IS-5	0.1	explosive	industry		
416	*n* -C19H40	C19H40	629-92-5	268	1900	85	IS-5	0.01	petroleum/plant	business/household/traffic		
417	Simetryn	C8H15N5S	1014-70-6	213	1901	213	IS-5	0.01	herbicide	agriculture		
418	Carbaryl	C12H11NO2	63-25-2	201	1902	144	IS-5	0.01	insecticide	agriculture		
419	Methyl palmitoleate	C17H32O2	1120-25-8	268	1903	236	IS-5	0.005	fatty acid methy ester	business/household/traffic		
420	Heptachlor	C10H5Cl7	76-44-8	370	1905	272	IS-5	0.01	insecticide	agriculture	X	X
421	3-Methylphenanthrene	C15H12	832-71-3	192	1905	192	IS-5	0.01	PAH	industry	X	
422	Mefenoxam (Metalaxyl-M)	C15H21NO4	70630-17-0	279	1907	206	IS-5	0.01	fungicide	agriculture		
423	Metalaxyl	C15H21NO4	57837-19-1	279	1908	206	IS-5	0.01	fungicide	agriculture		
424	Ametryn	C9H17N5S	834-12-8	227	1909	227	IS-5	0.01	herbicide	agriculture		
425	Fenchlorphos	C8H8Cl3O3PS	299-84-3	320	1911	285	IS-5	0.01	insecticide	agriculture		
426	PCB #22	234'-	38444-85-8	256	1912	256	IS-5	0.01	PCB	industry	X	X
427	2-Methylphenanthrene	C15H12	2531-84-2	192	1913	192	IS-5	0.01	PAH	industry	X	
428	Cinmethylin	C18H26O2	87818-31-3	274	1915	105	IS-5	0.01	herbicide	agriculture		
429	Diethyl-p-nitrophenyl phosphate	C10H14NO6P	311-45-5	275	1916	109	IS-5	0.025	insecticide, metabolite of parathion	agriculture		
430	Prometryn	C10H19N5S	7287-19-6	241	1916	241	IS-5	0.01	herbicide	agriculture		
431	4-Amino-2,6-dinitrotoluene	C7H7N3O4	19406-51-0	197	1918	180	IS-5	0.01	explosive	industry		
432	1,4,6,7-Tetrachloronaphthalene	C10H4Cl4	55720-43-9	264	1920	266	IS-4	0.01	PCN	industry		
433	Dithiopyr	C15H16F5NO2S2	97886-45-8	401	1920	286	IS-5	0.01	herbicide	agriculture		
434	Bensulide	C14H24NO4PS3	741-58-2	397	1921	77	IS-5	0.01	herbicide	agriculture		
435	Methyl palmitate	C17H34O2	112-39-0	270	1924	270	IS-6	0.015	fatty acid methy ester	business/household/traffic		
436	Demeton-S-methylsulphon	C6H15O5PS2	17040-19-6	262	1926	169	IS-5	0.01	insecticide	agriculture		
437	4,5-Methylene-phenanthrene	C15H10	203-64-5	190	1927	189	IS-5	0.025	PAH	industry		
438	Phenol, 4-(phenylamino)-	C12H11NO	122-37-2	185	1930	185	IS-5	0.01	leaching from tire	business/household/traffic		
439	9-Methylphenanthrene	C15H12	883-20-5	192	1930	192	IS-6	0.01	PAH	industry	X	

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
440	1-Methylphenanthrene	C15H12	832-69-9	192	1937	192	IS-5	0.01	PAH	industry		
441	Pirimiphos-methyl	C11H20N3O3PS	29232-93-7	305	1937	290	IS-6	0.01	insecticide	agriculture		
442	2,4-Dibromodiphenyl ether (BDE-7)	C12H8Br2O	147217-71-8	327	1941	328	IS-6	0.01	fire retardant	business/household/traffic		
443	Fenitrothion (MEP)	C9H12NO5PS	122-14-5	261	1941	277	IS-6	0.01	insecticide	agriculture		
444	Terbutryn	C10H19N5S	886-50-0	241	1941	226	IS-6	0.01	herbicide	agriculture		
445	1,2,3,5-Tetrachloronaphthalene	C10H4Cl4	53555-63-8	264	1942	266	IS-6	0.01	PCN	industry		
446	2,4-Dinitroaniline	C6H5N3O4	97-02-9	183	1943	183	IS-6	0.01	intermediate for dyes	industry		
447	Methiocarb	C11H15NO2S	2032-65-7	225	1944	168	IS-6	0.01	insecticide	agriculture		
448	Spiroxamine 2	C18H35NO2	118134-30-8	297	1946	100	IS-6	0.01	fungicide	agriculture		
449	Ethofumesate	C13H18O5S	26225-79-6	286	1947	286	IS-6	0.01	herbicide	agriculture		
450	Probenazole	C10H9NO3S	27605-76-1	223	1947	130	IS-6	0.01	other pesticide	agriculture		
451	Bromacil	C9H13BrN2O2	314-40-9	260	1948	205	IS-6	0.01	herbicide	agriculture		
452	PCB #52	22'55'-	35693-99-3	290	1948	292	IS-6	0.01	PCB	industry	X	X
453	Dimetylvinphos 1	C10H10Cl3O4P	2274-67-1	330	1950	295	IS-6	0.01	insecticide	agriculture		
454	Di-n-butyl phthalate	C16H22O4	84-74-2	278	1954	149	IS-5	0.01	plasticizer	business/household/traffic		
455	Dichlofluanid	C9H11Cl2FN2O2S2	1085-98-9	332	1955	224	IS-6	0.01	fungicide	agriculture		
456	PCB #49	22'45'-	41464-40-8	290	1955	292	IS-6	0.01	PCB	industry	X	X
457	Propyphenazone	C14H18N2O	479-92-5	230	1957	215	IS-6	0.01	PPCPs	business/household/traffic		
458	Esprocarb	C15H23NOS	85785-20-2	265	1959	222	IS-6	0.01	herbicide	agriculture		
459	Malathion	C10H19O6PS2	121-75-5	330	1961	173	IS-6	0.01	insecticide	agriculture		
460	Quinoclamine	C10H6ClNO2	2797-51-5	207	1961	172	IS-6	0.01	herbicide	agriculture		
461	Benzamide, N-phenyl-	C13H11NO	93-98-1	197	1962	197	IS-5	0.01	leaching from tire	business/household/traffic		
462	2-Mercaptobenzothiazole	C7H5NS2	149-30-4	167	1965	167	IS-6	0.01	leaching from tire	business/household/traffic		
463	Metolachlor	C15H22ClNO2	51218-45-2	283	1969	162	IS-6	0.01	herbicide	agriculture		
464	2-Amino-4,6-dinitrotoluene	C7H7N3O4	35572-78-2	197	1970	180	IS-6	0.01	explosive	industry		
465	Chlorpyrifos	C9H11Cl3NO3PS	2921-88-2	349	1973	314	IS-6	0.01	insecticide	agriculture		
466	PCB #104	22'466'-	56558-16-8	324	1975	326	IS-6	0.01	PCB	industry	X	X
467	*N* -Nitroquinoline-N-oxide	C9H6N2O3	56-57-5	190	1976	190	IS-6	0.01	reagent	business/household/traffic		
468	Thiobencarb	C12H16ClNOS	28249-77-6	257	1976	100	IS-6	0.01	herbicide	agriculture		
469	Aldrin	C12H8Cl6	309-00-2	362	1977	263	IS-6	0.01	insecticide	agriculture	X	X
470	Dimetylvinphos 2	C10H10Cl3O4P	2274-67-1	330	1977	295	IS-6	0.01	insecticide	agriculture		
471	2,6-Diamino-4-nitrotoluene	C7H9N3O2	59229-75-3	167	1978	167	IS-6	0.1	explosive	industry		
472	Diethofencarb	C14H21NO4	87130-20-9	267	1979	225	IS-6	0.01	fungicide	agriculture		
473	2,3,6,7-&1,2,4,8-Tetrachloronaphthalene	C10H4Cl4	34588-40-4 & 6529-87-9	264	1981	266	IS-4	0.01	PCN	industry		
474	Anthraquinone	C14H8O2	84-65-1	208	1981	208	IS-5	0.025	cosmetics/fragrance	business/household/traffic		
475	2-Phenylnaphthalene	C16H12	612-94-2	204	1982	204	IS-5	0.025	PAH	industry		
476	Chlorthal-dimethyl	C10H6Cl4O4	1861-32-1	330	1982	301	IS-6	0.01	herbicide	agriculture		
477	Fenthion	C10H15O3PS2	55-38-9	278	1982	278	IS-6	0.01	insecticide	agriculture		
478	Cyanazine	C9H13ClN6	21725-46-2	240	1983	225	IS-5	0.01	herbicide	agriculture		
479	PCB #44	22'35'-	41464-39-5	290	1986	292	IS-6	0.01	PCB	industry	X	X
480	Parathion	C10H14NO5PS	56-38-2	291	1989	291	IS-6	0.01	insecticide	agriculture		
481	Fenpropimorph	C20H33NO	67306-03-0	303	1990	128	IS-6	0.01	fungicide	agriculture		
482	Isofenphos oxon	C15H24NO5P	31120-85-1	329	1993	229	IS-6	0.01	insecticide	agriculture		
483	Tetraconazole	C13H11Cl2F4N3O	112281-77-3	371	1995	336	IS-6	0.01	fungicide	agriculture		
484	Triadimefon	C14H16ClN3O2	43121-43-3	293	1995	208	IS-6	0.01	fungicide	agriculture		
485	Isocarbophos	C11H16NO4PS	24353-61-5	289	1996	136	IS-6	0.01	insecticide	agriculture		
486	1,2,5,8-&1,2,6,8-Tetrachloronaphthalene	C10H4Cl4	&67922-24-1	264	1998	266	IS-4	0.01	PCN	industry		
487	Carbetamide	C12H16N2O3	16118-49-3	236	1998	119	IS-6	0.05	herbicide	agriculture		
488	PCB #37	344'-	38444-90-5	256	1998	258	IS-6	0.01	PCB	industry	X	X
489	Fenoprofen	C15H14O3	31879-05-7	242	2000	197	IS-6	0.01	PPCPs	business/household/traffic		
490	*n* -C20H42	C20H42	112-95-8	282	2000	85	IS-6	0.01	petroleum	business/household/traffic		
491	cis-10-Heptadecenoic acid methyl ester	C18H32O2	75190-82-8	282	2003	250	IS-6	0.005	fatty acid methy ester	business/household/traffic		
492	Dicofol-deg	C14H9Cl5O	115-32-2	368	2003	139	IS-6	0.01	other pesticide	agriculture		
493	Fthalide	C8H2Cl4O2	27355-22-2	270	2005	243	IS-6	0.01	fungicide	agriculture		
494	Nitrothal-isopropyl	C14H17NO6	10552-74-6	295	2005	236	IS-6	0.01	fungicide	agriculture		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
495	Triphenylmethane	C19H16	519-73-3	244	2006	244	IS-6	0.01	intermediate for dyes	industry		
496	Bentazone	C10H12N2O3S	25057-89-0	240	2011	198	IS-6	0.01	herbicide	agriculture		
497	Methapyrilene	C14H19N3S	91-80-5	297	2012	97	IS-6	0.01	PPCP	business/household/traffic		
498	Bromophos	C8H8BrCl2O3PS	2104-96-3	364	2017	331	IS-6	0.01	insecticide	agriculture		
499	3,6-Dimethylphenanthrene	C16H14	1576-67-6	206	2018	206	IS-5	0.025	PAH	industry		
500	Diphenamid	C16H17NO	957-51-7	239	2019	167	IS-6	0.01	herbicide	agriculture		
501	Fosthiazate 1	C9H18NO3PS2	98886-44-3	283	2020	195	IS-6	0.01	other pesticide	agriculture		
502	Fosthiazate 2	C9H18NO3PS2	98886-44-3	283	2025	195	IS-6	0.01	other pesticide	agriculture		
503	Methyl heptadecanoate	C18H36O2	1731-92-6	284	2025	284	IS-6	0.005	fatty acid methy ester	business/household/traffic		
504	Isopropalin	C15H23N3O4	33820-53-0	309	2028	280	IS-6	0.01	herbicide	agriculture		
505	Thiamethoxam deg.	C8H10ClN5O3S	153719-23-4	291	2030	212	IS-6	0.1	insecticide	agriculture		
506	Fluazinam	C13H4Cl2F6N4O4	79622-59-6	464	2034	372	IS-6	0.01	fungicide	agriculture		
507	1,4,5,8-Tetrachloronaphthalene	C10H4Cl4	3432-57-3	264	2035	266	IS-4	0.01	PCN	industry		
508	Chlorfenvinphos E	C12H14Cl3O4P	18708-86-6	358	2040	267	IS-6	0.01	insecticide	agriculture		
509	Pendimethalin	C13H19N3O4	40487-42-1	281	2040	252	IS-6	0.01	herbicide	agriculture		
510	Cyprodinil	C14H15N3	121552-61-2	225	2042	224	IS-6	0.01	fungicide	agriculture		
511	Fipronil	C12H4Cl2F6N4OS	120068-37-3	436	2050	367	IS-6	0.01	insecticide	agriculture		
512	Penconazole	C13H15Cl2N3	66246-88-6	283	2053	248	IS-6	0.01	fungicide	agriculture		
513	Dimethametryn	C11H21N5S	22936-75-0	255	2055	212	IS-6	0.01	herbicide	agriculture		
514	Heptachlor epoxide (B)	C10H5Cl7O	1024-57-3	386	2057	353	IS-6	0.01	insecticide	agriculture	X	X
515	Tolylfluanid	C10H13Cl2FN2O2S2	731-27-1	346	2058	238	IS-6	0.01	fungicide	agriculture		
516	Oxychlordane	C10H4Cl8O	27304-13-8	420	2059	387	IS-6	0.02	insecticide	agriculture	X	X
517	Isofenphos	C15H24NO4PS	25311-71-1	345	2060	213	IS-6	0.01	insecticide	agriculture		
518	Phenothiazine	C12H9NS	92-84-2	199	2060	199	IS-6	0.01	intermediate in organic synthesis	industry		
519	Pyrifenox Z	C14H12Cl2N2O	88283-41-4	294	2060	262	IS-6	0.01	fungicide	agriculture		
520	Ethychlozate	C11H11ClN2O2	27512-72-7	238	2061	165	IS-6	0.1	other pesticide	agriculture		
521	PCB #74	244'5-	32690-93-0	290	2061	292	IS-6	0.01	PCB	industry	X	X
522	1,3-Dicyclohexylurea	C13H24N2O	2387-23-7	224	2062	224	IS-6	0.01	leaching from tire	business/household/traffic		
523	Allethrin 1	C19H26O3	584-79-2	302	2062	123	IS-6	0.01	insecticide	agriculture		
524	Chlorfenvinphos Z	C12H14Cl3O4P	18708-87-7	358	2062	267	IS-6	0.01	insecticide	agriculture		
525	Methyl dymron	C17H20N2O	42609-73-4	268	2062	107	IS-6	0.01	herbicide	agriculture		
526	Tetryl	C7H5N5O8	479-45-8	287	2063	194	IS-6	0.01	explosive	industry		
527	Mecarbam	C10H20NO5PS2	2595-54-2	329	2067	131	IS-6	0.01	insecticide	agriculture		
528	PCB #70	23'4'5-	32598-11-1	290	2070	292	IS-6	0.01	PCB	industry	X	X
529	Allethrin 2 & Bioallethrin 1	C19H26O3	584-79-2	302	2073	123	IS-6	0.01	insecticide	agriculture		
530	Diclocymet 1	C15H18Cl2N2O	139920-32-4	312	2073	277	IS-6	0.01	fungicide	agriculture		
531	PCB #95	22'35'6-	38379-99-6	324	2073	326	IS-6	0.01	PCB	industry	X	X
532	Phenthoate	C12H17O4PS2	2597-03-7	320	2073	274	IS-6	0.01	insecticide	agriculture		
533	Fluoranthene	C16H10	206-44-0	202	2074	202	IS-6	0.01	PAH	industry	X	
534	Thiabendazole	C10H7N3S	148-79-8	201	2074	201	IS-6	0.01	fungicide	agriculture		
535	gamma-Linolenic acid methyl ester	C19H32O2	301-00-8	292	2075	292	IS-6	0.005	fatty acid methy ester	business/household/traffic		
536	Quinalphos	C12H15N2O3PS	13593-03-8	298	2075	146	IS-6	0.01	insecticide	agriculture		
537	Captan	C9H8Cl3NO2S	133-06-2	299	2077	79	IS-6	0.01	fungicide	agriculture		
538	1,2,3,5,7-Pentachloronaphthalene	C10H3Cl5	53555-65-0	298	2078	300	IS-6	0.01	PCN	industry		
539	Procymidone	C13H11Cl2NO2	32809-16-8	283	2079	283	IS-6	0.01	fungicide	agriculture		
540	Triadimenol 1	C14H18ClN3O2	89482-17-7	295	2081	168	IS-6	0.01	fungicide	agriculture		
541	Dimepiperate	C15H21NOS	61432-55-1	263	2084	119	IS-6	0.01	herbicide	agriculture		
542	Triflumizole	C15H15ClF3N3O	99387-89-0	345	2084	278	IS-6	0.01	fungicide	agriculture		
543	Folpet	C9H4Cl3NO2S	133-07-3	295	2087	260	IS-6	0.02	fungicide	agriculture		
544	4-Chloro-o-terphenyl	C18H13Cl	21711-54-6	264	2089	229	IS-6	0.01	other	industry		
545	Linolelaidic acid methyl ester	C19H34O2	2566-97-4	294	2092	294	IS-6	0.005	fatty acid methy ester	business/household/traffic		
546	Ferimzone	C15H18N4	89269-64-7	254	2094	239	IS-6	0.01	fungicide	agriculture		
547	Methoprene	C19H34O3	40596-69-8	310	2095	73	IS-6	0.02	insecticide	agriculture		
548	Naproxen	C14H14O3	22204-53-1	230	2095	185	IS-6	0.01	PPCPs	business/household/traffic		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
549	Triadimenol 2	C14H18ClN3O2	82200-72-4	295	2097	168	IS-6	0.01	fungicide	agriculture		
550	Linolenic acid methyl ester	C19H32O2	7361-80-0	292	2098	292	IS-6	0.005	fatty acid methy ester	business/household/traffic		
551	PCB #155	22'44'66'-	33979-03-2	358	2098	360	IS-6	0.01	PCB	industry	X	X
552	Oleic acid methyl ester	C19H36O2	112-62-9	296	2099	264	IS-6	0.005	fatty acid methy ester	business/household/traffic		
553	Linoleic acid methyl ester	C19H34O2	112-63-0	294	2100	294	IS-6	0.005	fatty acid methy ester	business/household/traffic		
554	*n* -C21H44	C21H44	629-94-7	296	2100	85	IS-6	0.01	petroleum/plant	business/household/traffic		
555	Methidathion	C6H11N2O4PS3	950-37-8	302	2103	145	IS-6	0.01	insecticide	agriculture		
556	Elaidic acid methyl ester	C19H36O2	1937-62-8	296	2105	264	IS-6	0.01	fatty acid methy ester	business/household/traffic		
557	Diclocymet 2	C15H18Cl2N2O	139920-32-4	312	2107	277	IS-6	0.01	fungicide	agriculture		
558	*trans* -Chlordane	C10H6Cl8	5103-74-2	406	2107	373	IS-6	0.01	insecticide	agriculture	X	X
559	Hexythiazox	C17H21ClN2O2S	78587-05-0	352	2108	227	IS-6	0.01	other pesticide	agriculture		
560	Triclosan	C12H7Cl3O2	3380-34-5	288	2108	290	IS-6	0.01	PPCPs	business/household/traffic		
561	Chinomethionat	C10H6N2OS2	2439-01-2	234	2109	206	IS-6	0.01	fungicide	agriculture		
562	1,2,4,6,8-Pentachloronaphthalene	C10H3Cl5	150224-22-9	298	2111	300	IS-6	0.01	PCN	industry		
563	Propaphos	C13H21O4PS	7292-16-2	304	2111	220	IS-6	0.01	insecticide	agriculture		
564	*o,p'* -DDE	C14H8Cl4	3424-82-6	316	2113	246	IS-6	0.01	insecticide	agriculture	X	X
565	Pyrifenox E	C14H12Cl2N2O	88283-41-4	294	2113	262	IS-6	0.01	fungicide	agriculture		
566	Tetrachlorvinphos	C10H9Cl4O4P	22248-79-9	364	2116	329	IS-6	0.01	insecticide	agriculture		
567	Trichlamid	C13H16Cl3NO3	70193-21-4	339	2119	148	IS-6	0.01	fungicide	agriculture		
568	Paclobutrazol	C15H20ClN3O	76738-62-0	293	2120	236	IS-6	0.01	other pesticide	agriculture		
569	PCB #101	22'455'-	37680-73-2	324	2122	326	IS-6	0.01	PCB	industry	X	X
570	Butachlor	C17H26ClNO2	23184-66-9	311	2123	176	IS-6	0.01	herbicide	agriculture		
571	Benzidine	C12H12N2	92-87-5	184	2124	184	IS-6	0.01	intermediate for dyes	industry		
572	Stearic acid methyl ester	C19H38O2	112-61-8	298	2125	298	IS-6	0.01	fatty acid methy ester	business/household/traffic		
573	Fenothiocarb	C13H19NO2S	62850-32-2	253	2128	160	IS-6	0.01	other pesticide	agriculture		
574	Pyrene	C16H10	129-00-0	202	2129	202	IS-6	0.01	PAH	industry	X	
575	PCB #99	22'44'5-	38380-01-7	324	2131	326	IS-6	0.01	PCB	industry	X	X
576	*cis* -Chlordane	C10H6Cl8	5103-71-9	406	2134	373	IS-6	0.01	insecticide	agriculture	X	X
577	Endosulfan I	C9H6Cl6O3S	959-98-8	404	2134	241	IS-6	0.01	insecticide	agriculture		
578	Ditalimfos	C12H14NO4PS	5131-24-8	299	2138	130	IS-6	0.01	fungicide	agriculture		
579	Mepanipyrim	C14H13N3	110235-47-7	223	2138	222	IS-6	0.01	fungicide	agriculture		
580	9-Nitrophenanthrene	C14H9NO2	954-46-1	223	2139	165	IS-6	0.01	PAH	industry		
581	Butamifos	C13H21N2O4PS	36335-67-8	332	2140	286	IS-6	0.01	herbicide	agriculture		
582	*trans* -Nonachlor	C10H5Cl9	5103-73-1	440	2140	409	IS-5	0.1	insecticide	agriculture	X	X
583	2,5-Dichloro-o-terphenyl	C18H12Cl2	61577-02-4	299	2141	228	IS-6	0.01	other	industry		
584	PCB #119	23'44'6-	56558-17-9	324	2143	326	IS-6	0.01	PCB	industry	X	X
585	9-Nitroanthracene	C14H9NO2	602-60-8	223	2144	223	IS-6	0.01	PAH	industry		
586	Dipentyl phthalate	C18H26O4	131-18-0	306	2144	149	IS-6	0.01	plasticizer	business/household/traffic		
587	Flutriafol	C16H13F2N3O	76674-21-0	301	2145	219	IS-6	0.01	fungicide	agriculture		
588	Fenamiphos	C13H22NO3PS	22224-92-6	303	2149	303	IS-6	0.01	other pesticide	agriculture		
589	Napropamide	C17H21NO2	15299-99-7	271	2151	128	IS-6	0.01	fungicide	agriculture		
590	Mefenamic Acid	C15H15NO2	61-68-7	241	2152	223	IS-6	0.01	PPCPs	business/household/traffic		
591	*N* -Phenyl-1-naphthylamine	C16H13N	90-30-2	219	2152	219	IS-5	0.025	antioxidant	business/household/traffic		
592	TCMTB	C9H6N2S3	21564-17-0	238	2154	180	IS-6	0.02	fungicide	agriculture		
593	Flutolanil	C17H16F3NO2	66332-96-5	323	2156	173	IS-6	0.01	fungicide	agriculture		
594	Chlorfenson	C12H8Cl2O3S	80-33-1	302	2159	175	IS-6	0.01	insecticide	agriculture		
595	Imazalil	C14H14Cl2N2O	35554-44-0	296	2159	215	IS-6	0.01	fungicide	agriculture		
596	Fludioxonil	C12H6F2N2O2	131341-86-1	248	2160	248	IS-6	0.01	fungicide	agriculture		
597	*m* -Terphenyl	C18H14	92-06-8	230	2160	230	IS-6	0.01	storage and transfer agents/intermediate for resin	industry		
598	1,2,4,5,6-Pentachloronaphthalene	C10H3Cl5	150224-20-7	298	2161	300	IS-6	0.01	PCN	industry		
599	Hexaconazole	C14H17Cl2N3O	79983-71-4	313	2161	214	IS-6	0.01	fungicide	agriculture		
600	Metominostrobin E	C16H16N2O3	133408-50-1	284	2161	191	IS-6	0.01	fungicide	agriculture		
601	Prothiofos	C11H15Cl2O2PS2	34643-46-4	344	2164	309	IS-6	0.01	insecticide	agriculture		
602	2-Hydroxy-4-methoxy-4'-methyl-benzophenone	C15H14O3	1641-17-4	242	2166	241	IS-6	0.01	other	industry		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
603	Pretilachlor	C17H26ClNO2	51218-49-6	311	2166	162	IS-6	0.01	herbicide	agriculture		
604	Isoprothiolane	C12H18O4S2	50512-35-1	290	2167	118	IS-6	0.01	fungicide	agriculture		
605	Tricyclazole	C9H7N3S	41814-78-2	189	2167	189	IS-6	0.01	fungicide	agriculture		
606	Isoxathion oxon	C13H16NO5P	32306-29-9	297	2168	161	IS-6	0.01	insecticide	agriculture		
607	Bisphenol A	C15H16O2	80-05-7	228	2170	213	IS-6	0.01	intermediate for resin	business/household/traffic		
608	1,2,4,7,8-Pentachloronaphthalene	C10H3Cl5	150224-21-8	298	2171	300	IS-6	0.01	PCN	industry		
609	Profenofos	C11H15BrClO3PS	41198-08-7	372	2174	337	IS-6	0.01	insecticide	agriculture		
610	PCB #87	22'345'-	38380-02-8	324	2176	326	IS-6	0.01	PCB	industry	X	X
611	1,2,3,5,8-&1,2,3,6,8-Pentachloronaphthalene	C10H3Cl5	150224-24-1 & 150224-23-0	298	2178	300	IS-6	0.01	PCN	industry		
612	PCB #81	344'5-	70362-50-4	290	2179	292	IS-6	0.01	PCB	industry	X	X
613	*p,p'* -DDE	C14H8Cl4	72-55-9	316	2181	246	IS-6	0.01	insecticide	agriculture	X	X
614	Uniconazole P	C15H18ClN3O	83657-17-4	291	2182	234	IS-6	0.01	other pesticide	agriculture		
615	Oxadiazon	C15H18Cl2N2O3	19666-30-9	344	2183	258	IS-6	0.01	herbicide	agriculture		
616	Thifluzamide	C13H6Br2F6N2O2S	130000-40-7	526	2184	194	IS-6	0.01	fungicide	agriculture		
617	Flamprop-methyl	C17H15ClFNO3	52756-25-9	335	2187	105	IS-6	0.01	herbicide	agriculture		
618	Tribufos	C12H27OSP3	78-48-8	314	2188	169	IS-6	0.01	other pesticide	agriculture		
619	Myclobutanil	C15H17ClN4	88671-89-0	288	2190	179	IS-6	0.01	fungicide	agriculture		
620	Dieldrin	C12H8Cl6O	60-57-1	378	2191	79	IS-6	0.01	insecticide	agriculture	X	X
621	Oxyfluorfen	C15H11ClF3NO4	42874-03-3	361	2193	252	IS-6	0.01	herbicide	agriculture		
622	Flusilazole	C16H15F2N3Si	85509-19-9	315	2194	233	IS-6	0.01	fungicide	agriculture		
623	*o,p'* -DDD	C14H10Cl4	53-19-0	318	2195	235	IS-6	0.01	insecticide	agriculture	X	
624	PCB #110	233'4'6-	38380-03-9	324	2195	326	IS-6	0.01	PCB	industry	X	X
625	Bupirimate	C13H24N4O3S	41483-43-6	316	2196	273	IS-6	0.01	fungicide	agriculture		
626	1,2,4,5,8-Pentachloronaphthalene	C10H3Cl5	26063-13-8	298	2198	300	IS-7	0.01	PCN	industry		
627	Buprofezin	C16H23N3OS	69327-76-0	305	2198	105	IS-6	0.01	insecticide	agriculture		
628	Difenzoquat metilsulfate	C18H20N2O4S	43222-48-6	360	2198	234	IS-6	0.02	herbicide	agriculture		
629	*p* -Terphenyl	C18H14	92-94-4	230	2198	230	IS-6	0.01	storage and transfer agents	industry		
630	Amino-chlornitrofen	C12H8Cl3NO	26306-61-6	287	2199	289	IS-6	0.01	herbicide	agriculture		
631	Kresoxim methyl	C18H19NO4	143390-89-0	313	2199	116	IS-6	0.01	fungicide	agriculture		
632	Imazamethabenz-methyl	C16H20N2O3	81405-85-8	288	2200	256	IS-6	0.01	herbicide	agriculture		
633	*n* -C22H46	C22H46	629-97-0	310	2200	85	IS-6	0.01	petroleum	business/household/traffic		
634	Carboxin	C12H13NO2S	5234-68-4	235	2201	235	IS-6	0.01	fungicide	agriculture		
635	PCB #77	33'44'-	32598-13-3	290	2201	292	IS-6	0.01	PCB	industry	X	X
636	Azaconazole	C12H11Cl2N3O2	60207-31-0	299	2203	217	IS-6	0.01	fungicide	agriculture		
637	Diclobutrazol	C15H19Cl2N3O	75736-33-3	327	2203	270	IS-6	0.05	fungicide	agriculture		
638	Metominostrobin Z	C16H16N2O3	133408-50-1	284	2203	191	IS-6	0.01	fungicide	agriculture		
639	Pyrethrin 1	C21H28O3	121-21-1	328	2205	123	IS-6	0.01	insecticide	agriculture		
640	Triclopyr	C7H4Cl3NO3	55335-06-3	255	2205	212	IS-6	0.01	herbicide	agriculture		
641	Chlorfenapyr	C15H11BrClF3N2O	122453-73-0	406	2216	59	IS-6	0.01	insecticide	agriculture		
642	PCB #151	22'355'6-	52663-63-5	358	2218	360	IS-6	0.01	PCB	industry	X	X
643	Cyflufenamid	C20H17F5N2O2	180409-60-3	412	2219	91	IS-6	0.01	fungicide	agriculture		
644	4-Nitrophenanthrene	C14H9NO2	82064-15-1	223	2221	223	IS-6	0.01	PAH	industry		
645	Isoxathion	C13H16NO4PS	18854-01-8	313	2223	177	IS-6	0.01	insecticide	agriculture		
646	Cyproconazole	C15H18ClN3O	113096-99-4	291	2227	222	IS-6	0.01	fungicide	agriculture		
647	4-Dimethylaminoazobenzene	C14H15N3	60-11-7	225	2231	225	IS-2	0.01	reagent	business/household/traffic		
648	Fenoxanil	C15H18Cl2N2O2	115852-48-7	328	2232	293	IS-7	0.01	fungicide	agriculture		
649	Nitrofen (NIP)	C12H7Cl2NO3	1836-75-5	283	2233	283	IS-5	0.025	herbicide	agriculture		
650	Endrin	C12H8Cl6O	72-20-8	378	2236	263	IS-6	0.01	insecticide	agriculture	X	X
651	2,3-Benzofluorene	C17H12	243-17-4	216	2244	216	IS-5	0.025	PAH	industry		
652	*N* -Phenyl-2-naphthylamine	C16H13N	135-88-6	219	2244	219	IS-5	0.025	antioxidant	business/household/traffic		
653	PCB #149	22'34'5'6-	38380-04-0	358	2244	360	IS-6	0.01	PCB	industry	X	X
654	PCB #123	2'344'5-	65510-44-3	324	2245	326	IS-6	0.01	PCB	industry	X	X
655	Pyriminobac-methyl Z	C17H19N3O6	136191-64-5	361	2251	302	IS-6	0.01	herbicide	agriculture		
656	Chlorobenzilate	C16H14Cl2O3	510-15-6	324	2253	251	IS-6	0.01	other pesticide	agriculture		
657	Chlorpropylate	C17H16Cl2O3	5836-10-2	338	2253	251	IS-6	0.01	insecticide	agriculture		
658	PCB #118	23'44'5-	31508-00-6	324	2253	326	IS-6	0.01	PCB	industry	X	X

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
659	Arachidonic acid methyl ester	C21H34O2	2566-89-4	318	2256	150	IS-6	0.005	fatty acid methy ester	business/household/traffic		
660	Fensulfothion	C11H17O4PS2	115-90-2	308	2256	293	IS-6	0.01	other pesticide	agriculture		
661	Endosulfan II	C9H6Cl6O3S	33213-65-9	404	2260	195	IS-6	0.01	insecticide	agriculture		
662	cis-5,8,11,14,17-Eicosapentaenoic acid, methyl ester	C21H32O2	2734-47-6	316	2262	119	IS-7	0.005	fatty acid methy ester	business/household/traffic		
663	Diniconazole	C15H17Cl2N3O2	83657-24-3	325	2262	268	IS-7	0.01	fungicide	agriculture		
664	Oxadixyl	C14H18N2O4	77732-09-3	278	2267	163	IS-7	0.01	fungicide	agriculture		
665	cis-Nonachlor	C10H5Cl9	5103-73-1	444	2270	406.8	IS-7	0.01	insecticide	agriculture	X	X
666	3-Nitrophenanthrene	C14H9NO2	17024-19-0	223	2271	223	IS-7	0.01	PAH	industry		
667	*p,p'*-DDD	C14H10Cl4	72-54-8	318	2272	235	IS-6	0.01	insecticide	agriculture	X	X
668	Ethion	C9H22O4P2S4	563-12-2	384	2273	231	IS-7	0.01	insecticide	agriculture		
669	*cis*-8,11,14-Eicosatrienoic acid methyl ester	C21H36O2	21061-10-9	320	2275	150	IS-7	0.005	fatty acid methy ester	business/household/traffic		
670	PCB #114	2344'5-	74472-37-0	324	2275	326	IS-7	0.01	PCB	industry	X	X
671	*o,p'*-DDT	C14H9Cl5	789-02-6	352	2276	235	IS-7	0.01	insecticide	agriculture	X	X
672	PCB #188	22'34'566'-	74487-85-7	392	2279	394	IS-7	0.01	PCB	industry	X	X
673	Pyrethrin 2	C22H28O5	121-29-9	372	2284	123	IS-7	0.01	insecticide	agriculture		
674	Fluacrypyrim	C20H21F3N2O5	229977-93-9	426	2289	204	IS-7	0.01	other pesticide	agriculture		
675	Endrin aldehyde	C12H8Cl6O	7421-93-4	378	2291	345	IS-7	0.01	insecticide	agriculture		
676	*cis*-11,14-Eicosadienoic acid methyl ester	C21H38O2	2463-02-7	322	2295	322	IS-7	0.005	fatty acid methy ester	business/household/traffic		
677	PCB #153&168	22'44'55'-&23'44'5'6-	35065-27-1&41411-63-6	358	2299	360	IS-7	0.02	PCB	industry	X	X
678	*cis*-11-Eicosenoic acid methyl ester	C21H40O2	2390-09-2	324	2300	292	IS-7	0.005	fatty acid methy ester	business/household/traffic		
679	n-C23H48	C23H48	638-67-5	324	2300	85	IS-7	0.01	petroleum/plant	business/household/traffic		
680	*cis*-11,14,17-Eicosatrienoic acid methyl ester	C21H36O2	55682-88-7	320	2301	95	IS-7	0.005	fatty acid methy ester	business/household/traffic		
681	Mepronil	C17H19NO2	55814-41-0	269	2302	119	IS-7	0.01	fungicide	agriculture		
682	1,2,3,4,6,7-Hexachloronaphthalene	C10H2Cl6	103426-96-6	332	2303	334	IS-7	0.01	PCN	industry		
683	Triazophos	C12H16N3O3PS	24017-47-8	313	2304	161	IS-7	0.01	insecticide	agriculture		
684	PCB #105	233'44'-	32598-14-4	324	2307	326	IS-7	0.01	PCB	industry	X	X
685	Sulprofos	C12H19O3PS2	38527-90-1	306	2307	322	IS-7	0.1	insecticide	agriculture		
686	Pyrethrin 3				2313	123	IS-7	0.01	insecticide	agriculture		
687	Tris(1,3-dichloro-2-propyl) phosphate	C9H15Cl6O4P	13674-87-8	428	2316	381	IS-8	0.025	fire retardant	business/household/traffic		
688	Azamethiphos	C9H10ClN2O5PS	35575-96-3	324	2317	215	IS-7	0.01	insecticide	agriculture		
689	Famphur	C10H16NO5PS2	52-85-7	325	2319	218	IS-7	0.01	insecticide	agriculture		
690	Isoxadifen-ethyl	C18H17NO3	163520-33-0	295	2321	182	IS-7	0.02	herbicide	agriculture		
691	Carfentrazone-ethyl	C15H14Cl2F3N3O3	128639-02-1	411	2323	312	IS-7	0.01	herbicide	agriculture		
692	Benalaxyl	C20H23NO3	71626-11-4	325	2324	148	IS-7	0.01	fungicide	agriculture		
693	Chlornitrofen (CNP)	C12H6Cl3NO3	1836-77-7	317	2325	317	IS-8	0.025	herbicide	agriculture		
694	Arachidic acid methyl ester	C21H42O2	1120-28-1	326	2327	326	IS-7	0.01	fatty acid methy ester	business/household/traffic		
695	Carbophenothion	C11H16ClO2PS3	786-19-6	342	2331	121	IS-7	0.01	insecticide	agriculture		
696	Norflurazon	C12H9ClF3N3O	27314-13-2	303	2331	303	IS-7	0.01	herbicide	agriculture		
697	2,2',5,5'-Tetrabromobiphenyl (BB-52)	C12H6Br4	59080-37-4	469	2333	310	IS-7	0.01	fire retardant	business/household/traffic		
698	Cyanofenphos	C15H14NO2PS	13067-93-1	303	2334	169	IS-7	0.05	insecticide	agriculture		
699	Trifloxystrobin	C20H19F3N2O4	141517-21-7	408	2335	116	IS-7	0.01	fungicide	agriculture		
700	Edifenphos	C14H15O2PS2	17109-49-8	310	2337	173	IS-7	0.01	fungicide	agriculture		
701	Propiconazole 1	C15H17Cl2N3O2	60207-90-1	341	2339	259	IS-7	0.01	fungicide	agriculture		
702	Diofenolan 1	C18H20O4	63837-33-2	300	2341	300	IS-7	0.01	insecticide	agriculture		
703	Quinoxyfen	C15H8Cl2FNO	124495-18-7	307	2341	237	IS-7	0.01	fungicide	agriculture		
704	1,2,3,5,7,8-Hexachloronaphthalene	C10H2Cl6	103426-94-4	332	2343	334	IS-7	0.01	PCN	industry		
705	Endosulfan sulfate	C9H6Cl6O4S	1031-07-8	420	2343	272	IS-7	0.01	insecticide	agriculture		
706	Butyl benzyl phtalate	C19H20O4	85-68-7	312	2345	149	IS-7	0.01	plasticizer	business/household/traffic		
707	Pyriminobac-methyl E	C17H19N3O6	136191-64-5	361	2345	302	IS-7	0.01	herbicide	agriculture		
708	Lenacil	C13H18N2O2	2164-08-1	234	2346	153	IS-7	0.01	herbicide	agriculture		
709	Chloridazon	C10H8ClN3O	1698-60-8	221	2349	221	IS-7	0.1	herbicide	agriculture		
710	Pyraflufen ethyl	C15H13Cl2F3N2O4	129630-17-7	412	2350	412	IS-7	0.01	herbicide	agriculture		
711	Propiconazole 2	C15H17Cl2N3O2	60207-90-1	341	2352	259	IS-7	0.01	fungicide	agriculture		
712	Carbamazepine	C15H12N2O	298-46-4	236	2354	193	IS-7	0.01	PPCPs	business/household/traffic		
713	*p,p'*-DDT	C14H9Cl5	50-29-3	352	2355	235	IS-7	0.01	insecticide	agriculture	X	X

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
714	1,2,4,5,6,8-&1,2,4,5,7,8-Hexachloronaphthalene	C10H2Cl6	90948-28-0 & 103426-92-2	332	2356	334	IS-7	0.01	PCN	industry		
715	Diofenolan 2	C18H20O4	63837-33-2	300	2356	300	IS-7	0.01	insecticide	agriculture		
716	PCB #138&158	22'344'5'-&233'44'6-	35065-28-2&74472-42-7	358	2359	360	IS-7	0.02	PCB	industry	X	X
717	EPN oxon	C14H14NO5P	2012-00-2	307	2365	141	IS-7	0.01	insecticide	agriculture		
718	Hexazinone	C12H20N4O2	51235-04-2	252	2365	171	IS-7	0.01	herbicide	agriculture		
719	PCB #178	22'33'55'6-	52663-67-9	392	2369	394	IS-7	0.01	PCB	industry	X	X
720	Thenylchlor	C16H18ClNO2S	96491-05-3	323	2375	127	IS-7	0.01	herbicide	agriculture		
721	PCB #126	33'44'5-	57465-28-8	324	2381	326	IS-7	0.01	PCB	industry	X	X
722	Di(2-ethylhexyl)adipate	C22H42O4	103-23-1	370	2386	129	IS-7	0.01	plasticizer	business/household/traffic		
723	Tebuconazole	C16H22ClN3O	107534-96-3	307	2386	250	IS-7	0.01	fungicide	agriculture		
724	Diclofop-methyl	C16H14Cl2O4	51338-27-3	340	2389	340	IS-7	0.01	herbicide	agriculture		
725	PCB #187	22'34'55'6-	52663-68-0	392	2389	394	IS-7	0.01	PCB	industry	X	X
726	2-Acetylaminofluorene	C15H13NO	53-96-3	223	2391	181	IS-7	0.01	reagent	business/household/traffic		
727	Propargite 1	C19H26O4S	2312-35-8	350	2391	135	IS-7	0.01	other pesticide	agriculture		
728	Diflufenican	C19H11F5N2O2	83164-33-4	394	2392	266	IS-7	0.01	herbicide	agriculture		
729	Propargite 2	C19H26O4S	2312-35-8	350	2394	135	IS-7	0.01	other pesticide	agriculture		
730	Diclomezine	C11H8Cl2N2O	62865-36-5	254	2398	254	IS-7	0.01	fungicide	agriculture		
731	*n* -C24H50	C24H50	646-31-1	338	2400	85	IS-7	0.01	petroleum	business/household/traffic		
732	PCB #183	22'344'5'6-	52663-69-1	392	2401	394	IS-7	0.01	PCB	industry	X	X
733	Nitralin	C13H19N3O6S	4726-14-1	345	2403	316	IS-7	0.25	herbicide	agriculture		
734	Captafol	C10H9Cl4NO2S	2425-06-1	347	2405	79	IS-7	0.01	fungicide	agriculture		
735	Piperonyl butoxide	C19H30O5	51-03-6	338	2405	176	IS-7	0.01	insecticide	agriculture		
736	Benzo(*c*)phenenthrene	C18H12	195-19-7	228	2406	228	IS-7	0.01	PAH	industry		
737	Bioresmethrin	C22H26O3	28434-01-7	338	2412	123	IS-7	0.01	insecticide	agriculture		
738	PCB #128	2,2',3,3',4,4'-	38380-07-3	358	2415	360	IS-7	0.01	PCB	industry	X	X
739	Zoxamide	C14H16Cl3NO2	156052-68-5	335	2418	187	IS-7	0.01	fungicide	agriculture		
740	Mefenpyr-diethyl	C16H18Cl2N2O4	135590-91-9	372	2421	253	IS-7	0.01	herbicide	agriculture		
741	PCB #167	23'44'55'-	52663-72-6	358	2421	360	IS-7	0.01	PCB	industry	X	X
742	4-Chloro-p-terphenyl	C18H13Cl	1762-83-0	264	2422	264	IS-7	0.01	other	industry		
743	1,2,3,4,5,8-Hexachloronaphthalene	C10H2Cl6	103426-93-3	332	2424	334	IS-7	0.01	PCN	industry		
744	Heneicosanoic acid methyl ester	C22H44O2	6064-90-0	340	2427	340	IS-7	0.005	fatty acid methy ester	business/household/traffic		
745	Pyributicarb	C18H22N2O2S	88678-67-5	330	2430	165	IS-7	0.01	herbicide	agriculture		
746	Acetamiprid	C10H11ClN4	135410-20-7	222	2440	152	IS-7	0.01	insecticide	agriculture		
747	Pyridaphenthion	C14H17N2O4PS	119-12-0	340	2442	340	IS-7	0.01	insecticide	agriculture		
748	Iprodione	C13H13Cl2N3O3	36734-19-7	329	2443	314	IS-7	0.01	fungicide	agriculture		
749	*cis* -4,7,10,13,16,19-Docosahexaenoic acid methyl ester	C23H34O2	301-01-9	342	2448	119	IS-7	0.005	fatty acid methy ester	business/household/traffic		
750	Tris(2-ethylhexyl) phosphate	C24H51O4P	78-42-2	434	2449	99	IS-8	0.025	fire retardant	business/household/traffic		
751	Endrin ketone	C12H8Cl6O	53494-70-5	378	2450	317	IS-7	0.01	insecticide	agriculture		
752	PCB #177	22'33'4'56-	52663-70-4	392	2453	324	IS-7	0.01	PCB	industry	X	X
753	Tetramethrin-1	C19H25NO4	7696-12-0	331	2453	164	IS-7	0.05	insecticide	agriculture		
754	Bromuconazole-1	C13H12BrCl2N3O	116255-48-2	375	2454	173	IS-7	0.05	fungicide	agriculture		
755	PCB #202	22'33'55'66'-	2136-99-4	426	2458	430	IS-7	0.01	PCB	industry	X	X
756	Phosmet	C11H12NO4PS2	732-11-6	317	2459	160	IS-7	0.01	insecticide	agriculture		
757	PCB #171	22'33'44'6-	52663-71-5	392	2463	394	IS-7	0.01	PCB	industry	X	X
758	Bifenthrin	C23H22ClF3O2	82657-04-3	422	2466	181	IS-7	0.01	insecticide	agriculture		
759	EPN	C14H14NO4PS	2104-64-5	323	2466	157	IS-7	0.01	insecticide	agriculture		
760	Benzo(*a*)anthracene	C18H12	56-55-3	228	2467	228	IS-7	0.01	PAH	industry	X	
761	Bromopropylate	C17H16Br2O3	18181-80-1	426	2469	341	IS-7	0.01	other pesticide	agriculture		
762	PCB #156	233'44'5-	38380-08-4	358	2470	360	IS-7	0.01	PCB	industry	X	X
763	Picolinafen	C19H12F4N2O2	137641-05-5	376	2471	376	IS-7	0.01	herbicide	agriculture		
764	Piperophos	C14H28NO3PS2	24151-93-7	353	2473	320	IS-7	0.01	herbicide	agriculture		
765	Sulfentrazone	C11H10Cl2F2N4O3S	122836-35-5	386	2473	307	IS-7	0.01	herbicide	agriculture		
766	Tetramethrin-2				2473	164	IS-7	0.01	insecticide	agriculture		
767	Fenoxycarb	C17H19NO4	72490-01-8	301	2476	116	IS-7	0.01	insecticide	agriculture		
768	PCB #201	22'33'45'66'-	40186-71-8	426	2476	430	IS-7	0.01	PCB	industry	X	X

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
769	3,3'-Dichlorobenzidine	C12H10Cl2N2	91-94-1	252	2477	252	IS-8	0.025	intermediate for dyes	industry		
770	Bifenazate	C17H20N2O3	149877-41-8	300	2477	258	IS-7	0.1	insecticide	agriculture		
771	Chrysene & Triphenylene	C18H12	218-01-9&217-59-4	228	2477	228	IS-7	0.01	PAH	industry	X	
772	Flusulfamide	C13H7Cl2F3N2O4S	106917-52-6	414	2480	179	IS-7	0.02	fungicide	agriculture		
773	Methoxychlor	C16H15Cl3O2	72-43-5	344	2480	227	IS-7	0.01	insecticide	agriculture		
774	PCB #157	233'44'5'-	69782-90-7	358	2481	360	IS-7	0.01	PCB	industry	X	X
775	4,4'-Methylene-bis(2-chloroaniline)	C13H12Cl2N2	101-14-4	266	2483	266	IS-8	0.025	intermediate for resin	industry		
776	Etoxazole	C21H23F2NO2	153233-91-1	359	2484	204	IS-7	0.01	other pesticide	agriculture		
777	Fenpropathrin	C22H23NO3	39515-41-8	349	2488	181	IS-7	0.01	other pesticide	agriculture		
778	Fenamidone	C17H17N3OS	161326-34-7	311	2489	238	IS-7	0.01	fungicide	agriculture		
779	Dicofol	C14H9Cl5O	115-32-2	368	2492	139	IS-7	0.01	other pesticide	agriculture		
780	6-Benzylaminopurine	C12H11N5	1214-39-7	225	2496	225	IS-7	0.01	other pesticide	agriculture		
781	*cis* -13,16-Docosadienoic acid methyl ester	C23H42O2	61012-47-3	350	2498	350	IS-7	0.005	fatty acid methy ester	business/household/traffic		
782	2,4-&2,5-Dichloro-p-terphenyl	C18H12Cl2	61576-83-8	299	2499	298	IS-7	0.02	other	industry		
783	*n* -C25H52	C25H52	629-99-2	352	2500	85	IS-7	0.01	petroleum/plant	business/household/traffic		
784	Indanofan	C20H17ClO3	133220-30-1	340	2501	174	IS-7	0.01	herbicide	agriculture		
785	Tebufenpyrad	C18H24ClN3O	119168-77-3	333	2501	171	IS-7	0.01	other pesticide	agriculture		
786	Anilofos	C13H19ClNO3PS2	64249-01-0	367	2502	226	IS-7	0.01	herbicide	agriculture		
787	Erucic acid methyl ester	C23H44O2	1120-34-9	352	2502	320	IS-7	0.005	fatty acid methy ester	business/household/traffic		
788	Bifenox	C14H9Cl2NO5	42576-02-3	340	2504	341	IS-7	0.01	herbicide	agriculture		
789	Bromuconazole-2	C13H12BrCl2N3O	116255-48-2	375	2506	173	IS-7	0.05	fungicide	agriculture		
790	PCB #180	22'344'55'-	35065-29-3	392	2506	324	IS-7	0.01	PCB	industry	X	X
791	Etoxazole metabolite	C21H23F2NO2	153233-91-1	359	2508	246	IS-7	0.05	insecticide	agriculture		
792	Benzanthrone	C17H10O	82-05-3	230	2511	230	IS-8	0.025	intermediate in organic synthesi	industry		
793	Dicyclohexyl phthalate	C20H26O4	84-61-7	330	2515	149	IS-7	0.01	plasticizer	business/household/traffic		
794	Clomeprop	C16H15Cl2NO2	84496-56-0	324	2516	288	IS-7	0.01	herbicide	agriculture		
795	Furametpyr	C17H20ClN3O2	123572-88-3	333	2516	157	IS-7	0.01	fungicide	agriculture		
796	PCB #191	233'44'5'6-	74472-50-7	392	2516	394	IS-7	0.01	PCB	industry	X	X
797	Phenothrin 1	C23H26O3	26002-80-2	350	2522	183	IS-7	0.01	insecticide	agriculture		
798	2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	C12H6Br4O	5436-43-1	485	2523	326	IS-7	0.01	fire retardant	business/household/traffic		
799	Iprodione metabolite	C13H13Cl2N3O3	36734-19-7	330	2526	142	IS-7	0.05	fungicide	agriculture		
800	Behenic acid methyl ester	C23H46O2	929-77-1	354	2528	354	IS-7	0.01	fatty acid methy ester	business/household/traffic		
801	Tetradifon	C12H6Cl4O2S	116-29-0	354	2530	356	IS-7	0.01	other pesticide	agriculture		
802	Di(2-ethylhexyl)phthalate	C24H38O4	117-81-7	390	2531	149	IS-5	0.01	plasticizer	business/household/traffic		
803	Phenothrin 2	C23H26O3	26002-80-2	350	2537	183	IS-7	0.01	insecticide	agriculture		
804	Pentoxazone	C17H17ClFNO4	110956-75-7	353	2542	285	IS-7	0.01	herbicide	agriculture		
805	Phosalone	C12H15ClNO4PS2	2310-17-0	367	2545	182	IS-7	0.01	insecticide	agriculture		
806	Pyrethrin 4		8003-34-7		2546	107	IS-7	0.01	insecticide	agriculture		
807	Leptophos	C13H10BrCl2O2PS	21609-90-5	412	2547	377	IS-7	0.01	insecticide	agriculture		
808	Azinphos-methyl	C10H12N3O3PS2	86-50-0	317	2555	160	IS-7	0.01	insecticide	agriculture		
809	PCB #169	33'44'55'-	32774-16-6	358	2556	360	IS-7	0.01	PCB	industry	X	X
810	3-Nitrofluoranthene	C16H9NO2	892-21-7	247	2563	247	IS-7	0.01	PAH	industry		
811	Cyhalothrin 1	C23H19ClF3NO3	68085-85-8	449	2568	181	IS-7	0.01	insecticide	agriculture		
812	Pyriproxyfen	C20H19NO3	95737-68-1	321	2569	136	IS-7	0.01	insecticide	agriculture		
813	1,2,3,4,5,6,7-Heptachloronaphthalene	C10HCl7	58863-14-2	366	2570	368	IS-7	0.01	PCN	industry		
814	PCB #170	22'33'44'5-	35065-30-6	392	2570	324	IS-7	0.01	PCB	industry	X	X
815	2,4,6-Trichloro-p-terphenyl	C18H11Cl3	57346-61-9	333	2573	332	IS-7	0.01	other	industry		
816	Cyhalofop Butyl	C20H20FNO4	122008-85-9	357	2574	256	IS-7	0.01	herbicide	agriculture		
817	Mefenacet	C16H14N2O2S	73250-68-7	298	2575	192	IS-7	0.01	herbicide	agriculture		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
818	Furametpyr metabolite	C17H20ClN3O2	123572-88-3	333	2577	296	IS-7	0.05	fungicide	agriculture		
819	1,2,3,4,5,6,8-Heptachloronaphthalene	C10HCl7	58863-15-3	366	2586	368	IS-7	0.01	PCN	industry		
820	Amitraz	C19H23N3	33089-61-1	293	2586	293	IS-7	0.01	other pesticide	agriculture		
821	PCB #199	22'33'455'6'-	52663-75-9	426	2586	358	IS-7	0.01	PCB	industry	X	X
822	Cyhalothrin 2	C23H19ClF3NO3	68085-85-8	449	2591	181	IS-7	0.01	insecticide	agriculture		
823	*n* -C26H54	C26H54	630-01-3	366	2600	85	IS-7	0.01	petroleum	business/household/traffic		
824	Pyrazophos	C14H20N3O5PS	13457-18-6	373	2613	221	IS-7	0.01	fungicide	agriculture		
825	Acrinathrin	C26H21F6NO5	101007-06-1	541	2614	181	IS-7	0.01	other pesticide	agriculture		
826	Fenarimol	C17H12Cl2N2O	60168-88-9	330	2614	219	IS-7	0.01	fungicide	agriculture		
827	1-Nitropyrene	C16H9NO2	5522-43-0	247	2621	247	IS-7	0.01	PAH	industry		
828	Tricosanoic acid methyl ester	C24H48O2	2433-97-8	368	2629	368	IS-7	0.005	fatty acid methy ester	business/household/traffic		
829	Azinphos-ethyl	C12H16N3O3PS2	2642-71-9	345	2632	132	IS-7	0.05	insecticide	agriculture		
830	PCB #189	233'44'55'-	36935-31-9	392	2639	394	IS-7	0.01	PCB	industry	X	X
831	Dialifos	C14H17cLNO4PS2	10311-84-9	394	2640	208	IS-7	0.25	insecticide	agriculture		
832	Pyraclofos	C14H18ClN2O3PS	77458-01-6	360	2650	360	IS-7	0.01	insecticide	agriculture		
833	Squalane	C30H62	111-01-3	422	2650	85	IS-8	0.025	PPCPs	business/household/traffic		
834	Oryzalin	C12H18N4O6S	19044-88-3	346	2657	317	IS-7	0.01	herbicide	agriculture		
835	Fenoxaprop-ethyl	C18H16ClNO5	66441-23-4	361	2661	288	IS-7	0.01	herbicide	agriculture		
836	PCB #208	22'33'455'66'-	52663-77-1	460	2663	392	IS-7	0.01	PCB	industry	X	X
837	Tricresyl phosphate	C21H21O4P	1330-78-5	368	2674	368	IS-8	0.025	fire retardant	business/household/traffic		
838	Tris(4-chlorophenyl)methane	C19H13Cl3	27575-78-6	348	2676	311	IS-7	0.01	other	industry		
839	Spirodiclofen	C21H24Cl2O4	148477-71-8	410	2677	71	IS-8	0.01	other pesticide	agriculture		
840	Bitertanol	C20H23N3O2	55179-31-2	337	2687	170	IS-8	0.01	fungicide	agriculture		
841	Permethrin 1	C21H20Cl2O3	52645-53-1	390	2697	183	IS-8	0.01	insecticide	agriculture		
842	*n* -C27H56	C27H56	593-49-7	380	2700	85	IS-8	0.01	petroleum/plant	business/household/traffic		
843	Nervonic acid methyl ester	C25H48O2	2733-88-2	380	2705	348	IS-8	0.005	fatty acid methy ester	business/household/traffic		
844	Coumaphos	C14H16ClO5PS	56-72-4	362	2711	362	IS-8	0.01	insecticide	agriculture		
845	Fluquinconazole	C16H8Cl2FN5O	136426-54-5	375	2712	340	IS-8	0.01	fungicide	agriculture		
846	Permethrin 2	C21H20Cl2O3	52645-53-1	390	2715	183	IS-8	0.01	insecticide	agriculture		
847	PCB #194	22'33'44'55'-	35694-08-7	426	2718	358	IS-8	0.01	PCB	industry	X	X
848	Prochloraz	C15H16Cl3N3O2	67747-09-5	375	2719	180	IS-8	0.01	fungicide	agriculture		
849	Pyridaben	C19H25ClN2OS	96489-71-3	364	2719	147	IS-8	0.01	insecticide	agriculture		
850	Oxpoconazole-fumalate	C23H28ClN3O6	174212-12-5	478	2724	294	IS-8	0.5	fungicide	agriculture		
851	PCB #205	233'44'55'6-	74472-53-0	426	2727	358	IS-8	0.01	PCB	industry	X	X
852	Di-n-octyl phthalate	C24H38O4	117-84-0	390	2728	149	IS-8	0.01	plasticizer	business/household/traffic		
853	Lignoceric acid, methyl ester	C25H50O2	2442-49-1	382	2729	382	IS-8	0.01	fatty acid methy ester	business/household/traffic		
854	Butafenacil	C20H18ClF3N2O6	134605-64-4	475	2737	331	IS-8	0.05	herbicide	agriculture		
855	Cafenstrole	C16H22N4O3S	125306-83-4	350	2756	100	IS-8	0.01	herbicide	agriculture		
856	Etobenzanid	C16H15Cl2NO3	79540-50-4	339	2756	179	IS-8	0.01	herbicide	agriculture		
857	Fenbuconazole	C19H17ClN4	114369-43-6	336	2766	198	IS-8	0.01	fungicide	agriculture		
858	Cyfluthrin 1	C22H18Cl2FNO3	68359-37-5	433	2771	163	IS-8	0.01	insecticide	agriculture		
859	Benzo(*j&b*)fluoranthene	C20H12	205-82-3&205-99-2	252	2785	252	IS-8	0.02	PAH	industry	X	
860	Cyfluthrin 2	C22H18Cl2FNO3	68359-37-5	433	2785	163	IS-8	0.01	insecticide	agriculture		
861	7,12-Dimethylbenz(*a*)anthracene	C20H16	57-97-6	256	2786	256	IS-8	0.01	PAH	industry		
862	Benzo(*k*)fluoranthene	C20H12	207-08-9	252	2792	252	IS-8	0.01	PAH	industry	X	
863	Cyfluthrin 3	C22H18Cl2FNO3	68359-37-5	433	2793	163	IS-8	0.01	insecticide	agriculture		
864	Bis(2-ethylhexyl) sebacate	C26H50O4	122-62-3	426	2795	185	IS-8	0.01	plasticizer	business/household/traffic		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
865	Cyfluthrin 4	C22H18Cl2FNO3	68359-37-5	433	2799	163	IS-8	0.01	insecticide	agriculture		
866	Octachloronaphthalene	C10Cl8	2234-13-1	400	2799	404	IS-8	0.01	PCN	industry		
867	2,3,5,6-Tetrachloro-p-terphenyl	C18H10Cl4	61576-99-6	366	2800	368	IS-8	0.01	other	industry		
868	*n*-C28H58	C28H58	630-02-4	394	2800	85	IS-8	0.01	petroleum	business/household/traffic		
869	PCB #206	22'33'44'55'6-	40186-72-9	460	2801	392	IS-8	0.01	PCB	industry	X	X
870	2,4,4',6-Tetrachloro-p-terphenyl	C18H10Cl4		366	2812	368	IS-8	0.01	other	industry		
871	7-Nitrobenz(*a*)anthracene	C18H11NO2	20268-51-3	273	2816	273	IS-8	0.01	PAH	industry		
872	Cypermethrin 1	C22H19Cl2NO3	52315-07-8	415	2817	163	IS-8	0.01	insecticide	agriculture		
873	Tris(4-chlorophenyl)methanol	C19H13Cl3O	3010-80-8	364	2818	251	IS-8	0.01	other	industry		
874	Halfenprox	C24H23BrF2O3	111872-58-3	476	2827	263	IS-8	0.01	other pesticide	agriculture		
875	Cypermethrin 2	C22H19Cl2NO3	52315-07-8	415	2832	163	IS-8	0.01	insecticide	agriculture		
876	Cypermethrin 3	C22H19Cl2NO3	52315-07-8	415	2839	163	IS-8	0.01	insecticide	agriculture		
877	Flucythrinate 1	C26H23F2NO4	70124-77-5	451	2841	199	IS-8	0.01	insecticide	agriculture		
878	Quizalofop-ethyl	C19H17ClN2O4	76578-14-8	372	2842	299	IS-8	0.01	herbicide	agriculture		
879	Cypermethrin 4	C22H19Cl2NO3	52315-07-8	415	2845	163	IS-8	0.01	insecticide	agriculture		
880	Fenbuconazole lactone B	C19H17ClN4	114369-43-6	337	2847	256	IS-8	0.005	fungicide	agriculture		
881	Cholestane	C27H48	481-21-0	372	2858	217	IS-8	0.1	animal sterol	sterol	X	
882	Benzo(*e*)pylene	C20H12	192-97-2	252	2860	252	IS-8	0.025	PAH	industry		
883	Etofenprox	C25H28O3	80844-07-1	376	2862	163	IS-8	0.01	insecticide	agriculture		
884	Flucythrinate 2	C26H23F2NO4	70124-77-5	451	2868	199	IS-8	0.01	insecticide	agriculture		
885	Benzo(a)pyrene	C20H12	50-32-8	252	2875	252	IS-8	0.01	PAH	industry	X	
886	PCB #209	22'33'44'55'66'-	2051-24-3	494	2875	498	IS-8	0.01	PCB	industry	X	X
887	Silafluofen	C25H29FO2Si	105024-66-6	408	2884	179	IS-8	0.01	insecticide	agriculture		
888	Fluridone	C19H14F3NO	59756-60-4	329	2887	328	IS-8	0.01	herbicide	agriculture		
889	Fenbuconazole lactone A	C19H17ClN4	114369-43-6	337	2892	145	IS-8	0.005	fungicide	agriculture		
890	Perylene	C20H12	198-55-0	252	2899	252	IS-8	0.025	PAH	industry		
891	*n*-C29H60	C29H60	630-03-5	408	2900	85	IS-8	0.01	petroleum/plant	business/household/traffic		
892	6-Nitrochrysene	C18H11NO2	7496-02-8	273	2907	273	IS-8	0.01	PAH	industry		
893	Pyrimidifen	C20H28ClN3O2	105779-78-0	377	2919	184	IS-8	0.01	other pesticide	agriculture		
894	Pyridate	C19H23ClN2O2S	55512-33-9	378	2932	207	IS-8	0.02	herbicide	agriculture		
895	Flumioxazin	C19H15FN2O4	103361-09-7	354	2938	354	IS-8	0.01	herbicide	agriculture		
896	Esfenvalerate 1	C25H22ClNO3	66230-04-4	419	2944	225	IS-8	0.01	insecticide	agriculture		
897	Fenvalerate 1	C25H22ClNO3	51630-58-1	419	2945	167	IS-8	0.01	insecticide	agriculture		
898	Pyraclostrobin	C19H18ClN3O4	175013-18-0	388	2957	132	IS-8	0.05	fungicide	agriculture		
899	Fluvalinate 1	C26H22ClF3N2O3	69409-94-5	502	2962	250	IS-8	0.01	insecticide	agriculture		
900	2,2',4,4',5,5'-Hexabromobiphenyl (BB-153)	C12H4Br6	59080-40-9	622	2964	308	IS-8	0.01	fire retardant	business/household/traffic		
901	Fluvalinate 2	C26H22ClF3N2O3	69409-94-5	502	2971	250	IS-8	0.01	insecticide	agriculture		
902	Esfenvalerate 2	C25H22ClNO3	66230-04-4	419	2974	225	IS-8	0.01	insecticide	agriculture		
903	Fenvalerate 2	C25H22ClNO3	51630-58-1	419	2974	167	IS-8	0.01	insecticide	agriculture		
904	3-Methylcholanthrene	C21H16	56-49-5	268	2983	268	IS-8	0.01	PAH	industry		
905	*n*-C30H62	C30H62	638-68-6	422	3000	85	IS-8	0.02	petroleum	business/household/traffic		
906	Difenoconazole 1	C19H17Cl2N3O3	119446-68-3	405	3009	265	IS-8	0.01	fungicide	agriculture		
907	Difenoconazole 2	C19H17Cl2N3O3	119446-68-3	405	3019	265	IS-8	0.01	fungicide	agriculture		
908	Pyrazoxyfen	C20H16Cl2N2O3	71561-11-0	402	3021	105	IS-8	0.01	herbicide	agriculture		
909	Indoxacarb	C22H17ClF3N3O7	144171-61-9	528	3031	150	IS-8	0.25	insecticide	agriculture		
910	2,3,4,5,6-Pentachloro-p-terphenyl	C18H9Cl5	61577-01-3	400	3034	402	IS-8	0.01	other	industry		
911	2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	C12H4Br6O	68631-49-2	638	3054	484	IS-8	0.01	fire retardant	business/household/traffic		
912	Deltamethrin	C22H19Br2NO3	52918-63-5	503	3054	181	IS-8	0.01	insecticide	agriculture		

Table S2.1 Chemicals registered in automated identification and quantification system with a database (continued)

No.	Compound	Formula	CAS number	MW	PTRIs[a]	m/z	IS[b]	IDL[c], ng	Use/Origin	Class	SIM[d]	SRM[e]
913	Diclosulam	C13H10Cl2FN5O3S	145701-21-9	405	3054	342	IS-8	0.01	herbicide	agriculture		
914	Tralomethrin-deg	C22H19Br4NO3	66841-25-6	661	3054	253	IS-8	0.01	insecticide	agriculture		
915	Flumiclorac-pentyl	C21H23ClFNO5	87546-18-7	423	3074	423	IS-8	0.01	herbicide	agriculture		
916	Azoxystrobin	C22H17N3O5	131860-33-8	403	3077	344	IS-8	0.01	fungicide	agriculture		
917	Coprostanol	C27H48O	360-68-9	388	3089	233	IS-8	0.01	facal sterol	sterol	X	
918	Epicoprostanol	C27H46O	516-92-7	388	3092	370	IS-8	0.01	facal sterol	sterol	X	
919	Dimethomorph E	C21H22ClNO4	110488-70-5	387	3095	301	IS-8	0.01	fungicide	agriculture		
920	Tecloftalam	C14H5Cl6NO3	76280-91-6	473	3098	394	IS-8	0.02	other pesticide	agriculture		
921	*n* -C31H64	C31H64	630-04-6	437	3100	85	IS-8	0.02	petroleum/plant	business/household/traffic		
922	Famoxadone	C22H18N2O4	131807-57-3	374	3105	330	IS-8	1	fungicide	agriculture		
923	Tolfenpyrad	C21H22ClN3O2	129558-76-5	383	3118	383	IS-8	0.01	insecticide	agriculture		
924	Cholesterol	C27H46O	57-88-5	386	3124	386	IS-8	0.1	animal sterol	sterol	X	
925	Coprostanone	C27H46O	360-68-9	388	3128	316	IS-8	0.01	animal sterol	sterol	X	
926	1,2,5,6,9,10-Hexabromocyclododecane	C12H18Br6	3194-55-6	636	3135	239	IS-8	0.01	fire retardant	business/household/traffic		
927	Cholestanol	C27H48O	80-97-7	388	3136	233	IS-8	0.1	animal sterol	sterol	X	
928	Dimethomorph Z	C21H22ClNO4	110488-70-5	387	3140	301	IS-8	0.01	fungicide	agriculture		
929	Imibenconazole	C17H13Cl3N4S	86598-92-7	410	3183	125	IS-8	0.01	fungicide	agriculture		
930	Indeno(1,2,3-*cd*)pyrene	C22H12	193-39-5	276	3190	276	IS-8	0.01	PAH	industry	X	
931	n-C32H66	C32H66	4981-99-1	451	3200	85	IS-8	0.02	petroleum	business/household/traffic		
932	Dibenzo(*a,h*)anthracene	C22H14	53-70-3	278	3201	278	IS-8	0.01	PAH	industry	X	
933	Ergosterol	C28H44O	57-87-4	396	3212	363	IS-8	0.1	phytosterol	sterol	X	
934	Fluthiacet-methyl	C15H15ClFN3O3S2	117337-19-6	403	3223	403	IS-8	0.01	herbicide	agriculture		
935	Campesterol	C28H48O	474-62-4	400	3234	400	IS-8	0.01	phytosterol	sterol	X	
936	Benzo(*ghi*)perylene	C22H12	191-24-2	276	3256	276	IS-8	0.01	PAH	industry	X	
937	Stigmasterol	C29H48O	83-48-7	412	3258	412	IS-8	0.1	phytosterol	sterol	X	
938	*n* -C33H68	C33H68	630-05-7	465	3300	85	IS-8	0.02	petroleum/plant	business/household/traffic		
939	Temephos	C16H20O6P2S3	3383-96-8	466	3304	466	IS-8	0.01	insecticide	agriculture		
940	β-Sitosterol	C29H50O	83-46-5	414	3324	414	IS-8	0.1	phytosterol	sterol	X	

Internal standard

IS-1	4-Chlorotoluene-d4	130	956	130
IS-2	1,4-Dichlorobenzene-d4	150	1013	150
IS-3	Naphthalene-d8	136	1185	136
IS-4	Acenaphthene-d10	164	1484	164
IS-5	Phenanthrene-d10	188	1787	188
IS-6	Fluoranthene-d10	212	2070	212
IS-7	Chrysene-d12	240	2470	240
IS-8	Perylene-d12	264	2893	264

[a] Programmed-temperature retention indices.

[b] Internal standard group.

[c] Instrument detection limit.

[d] Compounds measured by GC-MS using selected ion monitoring mode.

[e] Compounds measured by GC-MS-MS using selected reaction monitoring mode .

Table S2.2 Quantification and confirmation ions of SIM

No.	Compound	Quantification ion	Confirmation ion	IS^a
1	Naphthalene	128	-	IS-3
2	2-Methylnaphthalene	142	-	IS-3
3	1-Methylnaphthalene	142	-	IS-3
4	Acenaphthylene	152	-	IS-4
5	Acenaphthene	153	-	IS-4
6	PCB #1	188.05	190.05	IS-4
7	Pentachlorobenzene	249.9	251.9	IS-4
8	PCB #3	188.05	190.05	IS-4
9	Fluorene	166	165	IS-4
10	PCB #4&10	222	224	IS-4
11	α-HCH	218.9	216.9	IS-5
12	Hexachlorobenzene	283.8	285.8	IS-5
13	PCB #8	222	224	IS-5
14	PCB #19	255.95	257.95	IS-5
15	β-HCH	218.9	216.9	IS-5
16	γ-HCH	218.9	216.9	IS-5
17	PCB #18	255.95	257.95	IS-5
18	Phenanthrene	178	-	IS-5
19	PCB #15	222	224	IS-5
20	Anthracene	178	-	IS-5
21	δ-HCH	218.9	216.9	IS-5
22	PCB #54	291.9	289.9	IS-5
23	PCB #28	255.95	257.95	IS-5
24	PCB #33	255.95	257.95	IS-5
25	Heptachlor	271.8	273.8	IS-5
26	3-Methylphenanthrene	192	-	IS-5
27	PCB #22	255.95	257.95	IS-5
28	2-Methylphenanthrene	192	-	IS-5
29	9-Methylphenanthrene	192	-	IS-6
30	PCB #52	291.9	289.9	IS-6
31	PCB #49	291.9	289.9	IS-6
32	PCB #104	325.9	323.9	IS-6
33	Aldrin	262.85	264.85	IS-6
34	PCB #44	291.9	289.9	IS-6
35	PCB #37	257.95	255.95	IS-6
36	Heptachlor epoxide (B)	352.85	354.85	IS-6
37	Oxychlordane	386.8	388.8	IS-6
38	PCB #74	291.9	289.9	IS-6
39	PCB #70	291.9	289.9	IS-6
40	PCB #95	325.9	323.9	IS-6
41	Fluoranthene	202	-	IS-6
42	PCB #155	359.85	361.85	IS-6
43	*trans*-Chlordane	372.85	374.8	IS-6
44	o,p'-DDE	246	248	IS-6
45	PCB #101	325.9	323.9	IS-6
46	Pyrene	202	-	IS-6
47	PCB #99	325.9	323.9	IS-6
48	*cis*-Chlordane	372.85	374.8	IS-6
49	*trans*-Nonachlor	408.8	406.8	IS-6
50	PCB #119	325.9	323.9	IS-6
51	PCB #87	325.9	323.9	IS-6
52	PCB #81	291.9	289.9	IS-6
53	*p,p'*-DDE	246	248	IS-6
54	Dieldrin	262.85	264.85	IS-6
55	PCB #110	325.9	323.9	IS-6
56	*o,p'*-DDD	235	237	IS-6
57	PCB #77	291.9	289.9	IS-6
58	PCB #151	359.85	361.85	IS-6
59	Endrin	262.85	264.85	IS-6
60	PCB #149	359.85	361.85	IS-6
61	PCB #123	325.9	323.9	IS-6
62	PCB #118	325.9	323.9	IS-6
63	*cis*-Nonachlor	406.8	408.8	IS-7
64	*p,p'*-DDD	235	237	IS-7
65	PCB #114	325.9	323.9	IS-7
66	*o,p'*-DDT	235	237	IS-7
67	PCB #188	393.8	395.8	IS-7
68	PCB #153&168	359.85	361.85	IS-7
69	PCB #105	325.9	323.9	IS-7
70	*p,p'*-DDT	235	237	IS-7
71	PCB #138&158	359.85	361.85	IS-7
72	PCB #178	393.8	395.8	IS-7
73	PCB #126	325.9	323.9	IS-7
74	PCB #187	393.8	395.8	IS-7
75	PCB #183	393.8	395.8	IS-7
76	PCB #128	359.85	361.85	IS-7
77	PCB #167	359.85	361.85	IS-7
78	PCB #177	393.8	395.8	IS-7
79	PCB #202	429.75	427.75	IS-7
80	PCB #171	393.8	395.8	IS-7
81	Benzo(*a*)anthracene	228	-	IS-7
82	PCB #156	359.85	361.85	IS-7
83	PCB #201	429.75	427.75	IS-7
84	Chrysene & Triphenylene	228	-	IS-7
85	PCB #157	359.85	361.85	IS-7
86	PCB #180	323.9	325.9	IS-7
87	PCB #191	393.8	395.8	IS-7
88	PCB #169	359.85	361.85	IS-7
89	PCB #170	323.9	325.9	IS-7
90	PCB #199	429.75	427.75	IS-7
91	PCB #189	393.8	395.8	IS-7
92	PCB #208	463.7	461.7	IS-7
93	PCB #194	429.75	427.75	IS-8
94	PCB #205	429.75	427.75	IS-8
95	Benzo(*j&b*)fluoranthene	252.1	-	IS-8
96	Benzo(*k*)fluoranthene	252.1	-	IS-8
97	PCB #206	463.7	461.7	IS-8
98	Cholestane	217	372	IS-8
99	PCB #209	497.7	499.7	IS-8
100	Benzo(*a*)pyrene	252.1	-	IS-8
101	Coprostanol	373	331	IS-8
102	Epicoprostanol	370	316	IS-8
103	Cholesterol	301	368	IS-8
104	Coprostanone	316	231	IS-8
105	Cholestanol	215	388	IS-8
106	Indeno(1,2,3-*cd*)pyrene	276	-	IS-8
107	Dibenzo(*a,h*)anthracene	278	-	IS-8
108	Ergosterol	363	396	IS-8

Table S2.2 Quantification and confirmation ions of SIM (continued)

No.	Compound	Quantification ion	Confirmation ion	IS[a]
109	Campesterol	400	315	IS-8
110	Benzo(*ghi*)perylene	276	-	IS-8
111	Stigmasterol	215	416	IS-8
112	β-Sitosterol	414	329	IS-8

[a] Internal standard group

Internal standard			
IS-3	Naphthalene-d8	136	-
IS-4	Acenaphthene-d10	164	-
IS-5	Phenanthrene-d10	188	-
IS-6	Fluoranthene-d10	212	-
IS-7	Chrysene-d12	240	-
IS-8	Perylene-d12	264	-

Table S2.3 Precursor and product ions of SRM

No	Compound	IS[a]	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
1	PCB #1	IS-4	188.04	153.03	20	17.48	18.48
			190.04	153.03	20	17.48	18.48
2	Pentachlorobenzene	IS-4	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	IS-4	188.04	153.03	20	18.75	19.75
			190.04	153.03	20	18.75	19.75
4	PCB #4&10	IS-4	222	152	20	19.26	20.26
			224	152	20	19.26	20.26
5	α-HCH	IS-5	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	IS-5	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	IS-5	222	152	20	20.47	21.47
			224	152	20	20.47	21.47
8	PCB #19	IS-5	255.96	185.97	20	20.95	21.95
			257.96	185.97	20	20.95	21.95
9	β-HCH	IS-5	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	IS-5	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	IS-5	255.96	185.97	20	21.58	22.58
			257.96	185.97	20	21.58	22.58
12	PCB #15	IS-5	222	152	20	21.73	22.73
			224	152	20	21.73	22.73
13	δ-HCH	IS-5	180.91	108.95	25	22.04	23.04
			180.91	144.93	10	22.04	23.04

Table S2.3 Precursor and product ions of SRM (continued)

No	Compound	IS[a]	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
			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	IS-5	289.92	219.94	20	22.4	23.4
			291.92	219.94	20	22.4	23.4
15	PCB #28	IS-5	255.96	185.97	20	22.83	23.83
			257.96	185.97	20	22.83	23.83
16	PCB #33	IS-5	255.96	185.97	20	23.03	24.03
			257.96	185.97	20	23.03	24.03
17	Heptachlor	IS-5	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	IS-5	255.96	185.97	20	23.23	24.23
			257.96	185.97	20	23.23	24.23
19	PCB #52	IS-6	289.92	219.94	20	23.69	24.69
			291.92	219.94	20	23.69	24.69
20	PCB #49	IS-6	289.92	219.94	20	23.78	24.78
			291.92	219.94	20	23.78	24.78
21	PCB #104	IS-6	323.88	253.91	20	24.02	25.02
			325.88	255.91	20	24.02	25.02
22	Aldrin	IS-6	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	IS-6	289.92	219.94	20	24.15	25.15
			291.92	219.94	20	24.15	25.15
24	PCB #37	IS-6	255.96	185.97	20	24.31	25.31
			257.96	185.97	20	24.31	25.31
25	Heptachlor epoxide (B)	IS-6	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	IS-6	386.79	322.83	15	25.03	26.03
27	PCB #74	IS-6	289.92	219.94	20	25.05	26.05
			291.92	219.94	20	25.05	26.05

Table S2.3 Precursor and product ions of SRM (continued)

No	Compound	IS^a	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
28	PCB #70	IS-6	289.92	219.94	20	25.16	26.16
			291.92	219.94	20	25.16	26.16
29	PCB #95	IS-6	323.88	253.91	20	25.2	26.2
			325.88	255.91	20	25.2	26.2
30	PCB #155	IS-6	357.84	287.88	25	25.51	26.51
			359.84	289.87	25	25.51	26.51
31	trans-Chlordane	IS-6	372.81	265.87	13	25.6	26.6
32	o,p'-DDE	IS-6	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	IS-6	323.88	253.91	20	25.78	26.78
			325.88	255.91	20	25.78	26.78
34	PCB #99	IS-6	323.88	253.91	20	25.88	26.88
			325.88	255.91	20	25.88	26.88
35	cis-Chlordane	IS-6	372.81	265.87	13	25.91	26.91
			409.8	374.81	5	25.91	26.91
36	trans-Nonachlor	IS-6	406.78	299.94	20	25.99	26.99
			408.78	301.83	20	25.99	26.99
37	PCB #119	IS-6	323.88	253.91	20	26.01	27.01
			325.88	255.91	20	26.01	27.01
38	PCB #87	IS-6	323.88	253.91	20	26.39	27.39
			325.88	255.91	20	26.39	27.39
39	PCB #81	IS-6	289.92	219.94	20	26.43	27.43
			291.92	219.94	20	26.43	27.43
40	p,p'-DDE	IS-6	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	IS-6	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	IS-6	323.88	253.91	20	26.6	27.6
			325.88	255.91	20	26.6	27.6
43	o,p'-DDD	IS-6	234.97	164.98	17	26.61	27.61
			236.97	164.98	20	26.61	27.61
44	PCB #77	IS-6	289.92	219.94	20	26.67	27.67
			291.92	219.94	20	26.67	27.67
45	PCB #151	IS-6	357.84	287.88	25	26.86	27.86
			359.84	289.87	25	26.86	27.86

Table S2.3 Precursor and product ions of SRM (continued)

No	Compound	IS[a]	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
46	Endrin	IS-6	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	IS-6	357.84	287.88	25	27.15	28.15
			359.84	289.87	25	27.15	28.15
48	PCB #123	IS-6	323.88	253.91	20	27.16	28.16
			325.88	255.91	20	27.16	28.16
49	PCB #118	IS-6	323.88	253.91	20	27.25	28.25
			325.88	255.91	20	27.25	28.25
50	cis-Nonachlor	IS-7	406.78	299.84	20	27.44	28.44
			408.78	301.83	20	27.44	28.44
51	p,p'-DDD	IS-7	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	IS-7	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	IS-7	323.88	253.91	20	27.48	28.48
			325.88	255.91	20	27.48	28.48
54	PCB #188	IS-7	391.81	321.84	25	27.52	28.52
			393.8	323.84	25	27.52	28.52
55	PCB #153&168	IS-7	357.84	287.88	25	27.74	28.74
			359.84	289.87	25	27.74	28.74
56	PCB #105	IS-7	323.88	253.91	20	27.83	28.83
			325.88	255.91	20	27.83	28.83
57	p,p'-DDT	IS-7	234.94	164.96	16	28.34	29.34
			234.94	198.95	15	28.34	29.34
58	PCB #138&158	IS-7	357.84	287.88	25	28.38	29.38
			359.84	289.87	25	28.38	29.38
59	PCB #178	IS-7	391.81	321.84	25	28.49	29.49
			393.8	323.84	25	28.49	29.49
60	PCB #126	IS-7	323.88	253.91	25	28.6	29.6
			325.88	255.91	25	28.6	29.6
61	PCB #187	IS-7	391.81	321.84	25	28.69	29.69
			393.8	323.84	25	28.69	29.69
62	PCB #183	IS-7	391.81	321.84	25	28.82	29.82
			393.8	323.84	25	28.82	29.82
63	PCB #128	IS-7	357.84	287.88	25	28.95	29.95
			359.84	289.87	25	28.95	29.95
64	PCB #167	IS-7	357.84	287.88	25	29.02	30.02
			359.84	289.87	25	29.02	30.02

Table S2.3 Precursor and product ions of SRM (continued)

No	Compound	IS[a]	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
65	PCB #177	IS-7	391.81	321.84	25	29.33	30.33
			393.8	323.84	25	29.33	30.33
66	PCB #202	IS-7	427.77	357.8	25	29.39	30.39
			429.76	357.8	25	29.39	30.39
67	PCB #171	IS-7	391.81	321.84	25	29.45	30.45
			393.8	323.84	25	29.45	30.45
68	PCB #156	IS-7	357.84	287.88	25	29.52	30.52
			359.84	289.87	25	29.52	30.52
69	PCB #201	IS-7	427.77	357.8	25	29.57	30.57
			429.76	357.8	25	29.57	30.57
70	PCB #157	IS-7	357.84	287.88	25	29.62	30.62
			359.84	289.87	25	29.62	30.62
71	PCB #180	IS-7	391.81	321.84	25	29.87	30.87
			393.8	323.84	25	29.87	30.87
72	PCB #191	IS-7	391.81	321.84	25	29.98	30.98
			393.8	323.84	25	29.98	30.98
73	PCB #169	IS-7	357.84	287.88	25	30.37	31.37
			359.84	289.87	25	30.37	31.37
74	PCB #170	IS-7	391.81	321.84	25	30.5	31.5
			393.8	323.84	25	30.5	31.5
75	PCB #199	IS-7	427.77	357.8	25	30.65	31.65
			429.76	357.8	25	30.65	31.65
76	PCB #189	IS-7	391.81	321.84	25	31.16	32.16
			393.8	323.84	25	31.16	32.16
77	PCB #208	IS-7	461.73	391.77	25	31.39	32.39
			463.73	393.77	25	31.39	32.39
78	PCB #194	IS-8	427.77	357.8	25	31.89	32.89
			429.76	357.8	25	31.89	32.89
79	PCB #205	IS-8	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	IS-8	495.69	425.73	25	33.28	34.28
			497.69	427.73	25	33.28	34.28

[a] Internal standard group

Table S2.3 Precursor and product ions of SRM (continued)

Internal standard

No	Compound	Precursor ion	Product ion	Collision energy, eV	Start time, min	Stop time, min
IS-4	Acenaphthene-d10	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
IS-5	Phenanthrene-d10	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
IS-6	Fluoranthene-d10	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
IS-7	Chrysene-d12	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
IS-8	Perylene-d12	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 S4.1 Concentrations (μg L^{-1}) of OMPs in groundwaters of Hanoi and Ho Chi Minh City (S1 and S2 represent sample taken in September, 2013 and August, 2014, respectively)

No	Name	LOD	HN1		HN2		HN3	HN3	HN3	HN4		HN5		HN6		HN7		HN8		HN9		HN10		HN11	
		(μg L^{-1})	S1	S2	S1	S2	S1	S2	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
1	2(3H)-Benzothiazolone	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	2-(Methylthio)-benzothiazol	0.01	0.01	nd	0.05	nd	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.04	nd	nd	nd	nd	nd	nd	nd
3	2-Ethyl-1-hexanol	0.01	0.16	nd	0.15	nd	0.15	nd	nd	0.10	nd	0.11	nd	0.14	nd	0.12	nd	0.12	nd	0.08	nd	0.15	nd	0.14	nd
4	3- & 4-tert-Butylphenol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
5	4-Chloro-2-nitroaniline	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	4-Cymene	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01	nd
7	4-tert-Octylphenol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
8	3,5-Dimethylphenol	0.01	nd	0.17	nd	0.04	nd	0.17	0.29	nd	0.10	nd	0.38	nd	0.08	nd	0.23	nd	0.23	nd	0.18	nd	0.09	nd	0.14
9	4-Chloro-3-methylphenol	0.01	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	Acetophenone	0.01	0.02	nd	0.02	nd	0.12	0.02	0.06	0.03	nd	0.02	0.07	0.02	nd	0.02	0.02	nd	0.02	nd	0.02	0.02	nd	0.03	nd
11	alpha-Terpineol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	Benzothiazole	0.01	nd	nd	0.01	nd	0.01	nd	0.02	nd	nd	nd	nd	0.01	nd	nd	nd	0.01	nd	nd	0.03	nd	nd	0.01	nd
13	Benzyl alcohol	0.01	0.12	0.30	nd	0.97	0.30	2.14	1.85	0.05	0.83	0.22	2.16	nd	1.60	0.10	0.50	0.09	0.26	0.05	1.21	0.12	0.90	3.59	0.66
14	Bis(2-ethylhexyl) sebacate	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13	nd	nd
15	Bis(2-ethylhexyl)phthalate	0.01	0.55	4.68	2.12	nd	0.79	nd	nd	1.51	nd	0.60	nd	1.37	nd	0.71	nd	1.34	nd	1.18	0.48	0.83	nd	1.12	nd
16	Bisphenol A	0.01	0.04	nd	0.02	nd	0.04	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	nd	nd	nd	nd	nd
17	Butyl benzyl phtalate	0.01	0.02	0.02	0.01	nd	0.01	0.04	nd	nd	nd	0.04	nd	nd	nd	nd	nd	0.07	0.03	0.04	nd	0.05	0.05	0.10	nd
18	Caffeine	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
19	Campesterol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.07	nd	nd	nd	nd	nd	0.16	nd	nd	nd	nd
20	Cholestanol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.35	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
21	Cholesterol	0.01	0.63	0.19	0.78	0.03	0.10	0.88	0.23	0.24	0.26	0.11	0.54	0.48	0.83	0.12	0.27	0.40	0.20	0.45	0.34	0.20	0.46	0.09	0.25
22	beta-Sitosterol	0.01	0.18	nd	0.41	nd	nd	0.13	nd	nd	nd	nd	nd	0.62	0.53	nd	nd	0.17	nd	0.59	nd	nd	nd	nd	nd
23	Ergosterol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.34	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
24	Stigmasterol	0.01	5.82	nd	0.86	nd	nd	nd	nd	nd	nd	nd	nd	0.78	nd	nd	nd	0.17	nd	0.02	nd	nd	nd	nd	nd
25	Di(2-ethylhexyl)adipate	0.01	0.04	0.06	0.05	nd	0.04	0.42	nd	0.06	0.39	0.05	0.08	0.03	0.31	0.06	0.01	0.05	0.04	0.04	0.09	0.04	0.18	0.03	nd
26	Diethyl phthalate	0.01	0.06	nd	0.06	nd	0.06	0.71	0.40	0.06	0.37	0.06	0.14	0.08	0.32	0.06	nd	0.07	nd	0.05	0.43	0.06	0.49	0.04	nd
27	Diethyltoluamide	0.01	nd	nd	nd	nd	nd	0.09	nd	nd	0.40	0.04	nd	nd	nd	nd	nd	nd	nd	0.03	nd	nd	0.07	nd	nd
28	Diisobutyl phthalate	0.01	0.05	nd	0.07	nd	0.80	nd	nd	0.12	nd	0.12	nd	0.07	nd	0.11	nd	0.15	nd	0.21	nd	0.08	nd	0.10	nd
29	Dimethyl phthalate	0.01	nd	nd	nd	nd	0.01	0.01	0.04	nd	nd	nd	nd	0.01	nd	nd	nd	0.01	nd	nd	0.02	nd	nd	nd	nd
30	Di-n-butyl phthalate	0.01	0.07	0.59	0.13	nd	0.12	0.83	0.36	0.21	3.97	0.14	0.47	0.11	10	0.15	0.53	0.25	nd	0.16	0.02	0.12	0.16	0.10	nd
31	Diphenylamine	0.01	nd	nd	nd	nd	nd	nd	0.07	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
32	e-Caprolactam	0.01	nd	0.07	nd	nd	nd	0.11	0.07	nd	0.08	nd	0.04	nd	nd	nd	0.04	nd	0.02	nd	0.10	nd	0.05	nd	0.09
33	Ethanol, 2-phenoxy-	0.01	0.07	nd	0.03	nd	0.02	0.04	0.02	0.02	0.01	0.03	nd	0.04	nd	0.03	nd	0.02	nd	0.03	nd	0.03	nd	0.21	nd

Table S4.1 Concentrations (μg L^{-1}) of OMPs in groundwaters of Hanoi and Ho Chi Minh City (S1 and S2 represent sample taken in September, 2013 and August, 2014, respectively) (continued)

No	Name	LOD (μg L^{-1})	HN1		HN2		HN3	HN3	HN3	HN4		HN5		HN6		HN7		HN8		HN9		HN10		HN11	
			S1	S2	S1	S2	S1	S2	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
34	Isophorone	0.01	nd	nd	nd	nd	nd	nd	0.05	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	nd	0.04	nd	nd	0.01	nd
35	L-Menthol	0.01	0.01	nd	0.01	nd	0.01	nd	0.02	nd	nd	0.02	nd	0.01	0.01	0.02	nd	0.02	nd	0.03	nd	0.02	nd	0.04	nd
36	Longifolene	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	nd	0.09	nd
37	Safrole	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
38	Squalane	0.01	0.01	nd	0.04	nd	nd	nd	nd	0.03	nd	0.01	nd	nd	nd	0.02	nd	0.02	nd	nd	nd	0.01	nd	nd	nd
39	Methyl palmitoleate	0.01	nd	nd	nd	0.13	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
40	Nitrobenzene	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.10	nd	nd	nd	nd	nd	nd	nd	nd
41	Phenylethyl alcohol	0.01	nd	nd	nd	nd	nd	nd	0.01	nd	nd	nd	0.02	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
42	trans-Decahydronaphthalene	0.01	0.15	nd	0.10	nd	0.07	nd	nd	0.07	nd	0.09	nd	0.15	nd	0.08	nd	0.08	nd	0.04	nd	0.14	nd	0.13	nd
43	Tributyl phosphate	0.01	nd	nd	nd	nd	nd	1.45	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	nd	0.02	nd	0.05	nd	0.06	nd
44	trans-Chlordane[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
45	cis-Chlordane[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
46	trans-Nonachlor[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
47	Endrin[a]	0.4	nd	nd	nd	nd	nd	0.50	nd	nd	0.65	nd	1.7	nd	nd	nd	nd	0.53	nd	nd	nd	1.1	nd	nd	nd
48	Dieldrin[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
49	Hexachlorobenzene[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
50	Heptachlor epoxide (B)[a]	0.4	nd	nd	nd	nd	nd	1.2	0.72	nd	5.9	nd	nd	nd	nd	nd	nd	nd	1.2	nd	nd	nd	1.3	nd	0.55
51	a-HCH[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
52	g-HCH[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
53	p,p'-DDT[a]	0.1	nd	nd	nd	nd	nd	12	nd	nd	7.5	nd	1.1	nd	0.66	1.8	nd	nd	0.57	nd	0.48	nd	1.1	nd	3.7
54	p,p'-DDE[a]	0.1	nd	nd	nd	nd	nd	0.33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
55	p,p'-DDD[a]	0.1	nd	nd	nd	nd	nd	0.55	nd	nd	0.18	nd	0.20	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.12
56	o,p'-DDT[a]	0.2	nd	nd	nd	nd	nd	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.38
57	o,p'-DDD[a]	0.1	0.31	nd	0.20	nd	0.14	0.32	2.4	nd	0.16	0.21	6.4	nd	0.14	nd	nd	0.16	nd	0.11	nd	0.11	nd	0.10	nd
58	PCB#8[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.10	nd
59	PCB#74[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
60	PCB#70[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
61	PCB#66[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
62	PCB#60[a]	0.1	nd	nd	nd	nd	0.32	nd	nd	nd	nd	nd	nd	nd	0.25	0.58	0.18	nd	0.33	0.30	nd	nd	0.11	nd	nd
63	PCB#52[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
64	PCB#44[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table S4.1 Concentrations (µg L^{-1}) of OMPs in groundwaters of Hanoi and Ho Chi Minh City (S1 and S2 represent sample taken in September, 2013 and August, 2014, respectively) (continued)

No	Name	LOD (µg L^{-1})	HN1		HN2		HN3	HN3	HN3	HN4		HN5		HN6		HN7		HN8		HN9		HN10		HN11	
			S1	S2	S1	S2	S1	S2	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
65	PCB#41[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
66	PCB#4&10[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
67	PCB#37[a]	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
68	PCB#33[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
69	PCB#28[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.46	nd
70	PCB#22[a]	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
71	PCB#19[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
72	PCB#18[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.16	nd
73	PCB#15[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
74	PCB#1[a]	0.1	0.11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a] Compounds presented concentrations in ng L^{-1}.

[b] Duplicate analyses.

Table S4.1 Concentrations (μg L^{-1}) of OMPs in groundwaters of Hanoi and Ho Chi Minh City (S1 and S2 represent sample taken in September, 2013 and August, 2014, respectively) (continued)

No	Name	LOD	HN12		HN13		HN14			HN14	HN14	HN15		HN16		HN17		HN18		HCM1	HCM2	HCM3	HCM4
		(μg L^{-1})	S1	S2	S1	S2	S1	S2-1^{b}	S2-2^{b}	S2	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S1	S1	S1
1	2(3H)-Benzothiazolone	0.01	nd	nd	nd	nd	nd	0.23	0.39	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	2-(Methylthio)-benzothiazol	0.01	nd	nd	nd	nd	0.11	0.08	0.09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	2-Ethyl-1-hexanol	0.01	0.12	nd	0.32	nd	0.18	nd	nd	nd	nd	0.11	nd	0.07	nd	nd	nd	0.11	nd	0.06	0.12	0.16	0.19
4	3- & 4-tert-Butylphenol	0.01	nd	nd	nd	nd	0.04	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
5	4-Chloro-2-nitroaniline	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	4-Cymene	0.01	nd	nd	0.03	nd	6.75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01	nd	0.02
7	4-tert-Octylphenol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	nd	nd	nd	nd	nd	nd	0.06	nd	nd
8	3,5-Dimethylphenol	0.01	nd	0.13	nd	0.13	nd	0.13	0.16	0.13	0.14	nd	0.11	nd	0.18	nd	0.12	nd	0.12	nd	nd	nd	nd
9	4-Chloro-3-methylphenol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	Acetophenone	0.01	nd	nd	0.05	nd	nd	nd	nd	nd	nd	0.03	nd	0.01	0.03	nd	nd	0.02	nd	0.01	0.03	0.04	0.03
11	alpha-Terpineol	0.01	nd	nd	nd	nd	0.65	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	Benzothiazole	0.01	0.01	nd	0.03	nd	0.02	0.14	0.13	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd	0.02	0.02	0.04	0.02
13	Benzyl alcohol	0.01	0.09	1.60	0.08	0.81	0.30	0.79	0.97	0.61	0.78	0.10	0.78	0.06	1.12	nd	0.47	0.04	1.02	nd	nd	nd	nd
14	Bis(2-ethylhexyl) sebacate	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	0.01	nd	nd
15	Bis(2-ethylhexyl)phthalate	0.01	0.70	nd	1.34	5.99	2.65	1.0	1.1	0.12	0.44	0.76	nd	1.67	6.16	1.05	5.93	0.92	nd	2.45	1.34	3.62	3.19
16	Bisphenol A	0.01	nd	nd	nd	nd	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17	Butyl benzyl phtalate	0.01	0.05	0.01	0.06	0.11	0.05	0.02	0.01	nd	nd	0.05	0.03	0.09	nd	0.04	0.02	nd	nd	0.07	0.09	0.09	0.09
18	Caffeine	0.01	nd	nd	nd	nd	2.71	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.17	nd
19	Campesterol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
20	Cholestanol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
21	Cholesterol	0.01	0.12	0.19	0.12	0.62	0.70	0.32	0.31	0.30	0.58	0.10	0.36	0.05	0.48	0.27	0.25	0.17	0.12	0.24	0.08	1.00	0.20
22	beta-Sitosterol	0.01	nd	nd	nd	nd	0.06	nd	nd	nd	nd	nd	nd	nd	nd	0.02	nd	nd	nd	nd	nd	nd	nd
23	Ergosterol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
24	Stigmasterol	0.01	nd	nd	nd	nd	0.03	nd	nd	nd	nd	nd	nd	nd	nd	0.05	nd	nd	nd	nd	nd	nd	nd
25	Di(2-ethylhexyl)adipate	0.01	0.05	0.34	0.05	0.95	0.07	0.05	0.25	0.06	0.02	0.03	0.10	0.05	0.76	0.04	0.89	0.04	nd	0.05	0.05	0.07	0.04
26	Diethyl phthalate	0.01	0.08	0.46	0.07	0.25	0.08	0.12	0.12	0.26	0.08	0.05	nd	0.07	0.34	0.05	0.41	0.05	0.27	0.07	0.08	0.09	0.06
27	Diethyltoluamide	0.01	nd	0.37	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	nd	nd
28	Diisobutyl phthalate	0.01	0.15	nd	0.16	nd	0.10	nd	nd	nd	nd	0.07	nd	0.13	nd	0.08	nd	0.06	nd	0.15	0.15	0.23	0.36
29	Dimethyl phthalate	0.01	nd	nd	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
30	Di-n-butyl phthalate	0.01	0.18	0.25	0.20	0.14	0.18	nd	nd	0.42	0.31	0.08	nd	0.18	0.50	0.12	0.05	0.08	0.13	0.25	0.18	0.28	0.39
31	Diphenylamine	0.01	nd	nd	nd	nd	nd	nd	nd	0.05	0.02	nd	nd	nd	nd	nd	nd	nd	0.04	nd	nd	nd	nd
32	e-Caprolactam	0.01	nd	0.09	nd	0.03	nd	0.05	0.06	0.03	0.02	nd	0.10	nd	0.08	nd	0.07	nd	0.09	nd	nd	nd	nd

Table S4.1 Concentrations (μg L^{-1}) of OMPs in groundwaters of Hanoi and Ho Chi Minh City (S1 and S2 represent sample taken in September, 2013 and August, 2014, respectively) (continued)

No	Name	LOD (μg L^{-1})	HN12		HN13		HN14			HN14	HN14	HN15		HN16		HN17		HN18		HCM1	HCM2	HCM3	HCM4
			S1	S2	S1	S2	S1	S2-1[b]	S2-2[b]	S2	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S1	S1	S1
33	Ethanol, 2-phenoxy-	0.01	0.06	0.01	0.07	nd	0.05	nd	nd	nd	nd	0.03	nd	0.07	0.01	0.02	nd	0.05	nd	0.12	0.14	0.07	0.30
34	Isophorone	0.01	nd	nd	0.01	nd	0.02	0.06	0.07	0.08	0.20	nd	nd	nd	nd	nd	0.02	0.01	0.15	nd	nd	0.01	nd
35	L-Menthol	0.01	0.06	0.02	0.04	nd	nd	nd	nd	nd	nd	0.02	nd	nd	nd	nd	0.01	0.03	nd	0.01	0.05	0.02	0.02
36	Longifolene	0.01	nd	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
37	Safrole	0.01	nd	nd	nd	nd	0.69	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
38	Squalane	0.01	0.02	nd	0.02	nd	0.12	nd	nd	nd	nd	0.01	nd	nd	nd	0.01	nd	nd	nd	0.05	nd	0.14	nd
39	Methyl palmitoleate	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
40	Nitrobenzene	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
41	Phenylethyl alcohol	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
42	trans-Decahydronaphthalene	0.01	0.14	nd	0.17	nd	0.15	nd	nd	nd	nd	0.09	nd	0.03	nd	nd	nd	0.13	nd	0.02	0.15	0.21	0.34
43	Tributyl phosphate	0.01	nd	nd	0.50	nd	nd	nd	nd	nd	nd	0.03	nd	0.02	nd	nd	nd	0.04	nd	nd	0.13	0.19	0.43
44	trans-Chlordane[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.0	nd	nd
45	cis-Chlordane[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.7	nd	nd
46	trans-Nonachlor[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.72	nd	nd
47	Endrin[a]	0.4	nd	nd	1.2	0.81	nd	0.42	0.44	nd	nd	1.3	nd	nd	0.57	nd	nd	nd	0.78	nd	nd	nd	nd
48	Dieldrin[a]	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.53	nd	nd	2.8	nd	nd
49	Hexachlorobenzene[a]	0.1	nd	nd	0.35	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.15	nd	nd
50	Heptachlor epoxide (B)[a]	0.4	nd	nd	nd	0.79	nd	nd	nd	nd	nd	nd	nd	nd	0.45	nd	nd	nd	nd	nd	nd	nd	nd
51	a-HCH[a]	0.4	nd	nd	1.9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
52	g-HCH[a]	0.4	nd	nd	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
53	p,p'-DDT[a]	0.1	nd	nd	1.3	1.5	2.4	nd	nd	nd	0.77	nd	nd	nd	nd	nd	nd	nd	nd	1.2	3.6	2.0	nd
54	p,p'-DDE[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.11	nd	nd
55	p,p'-DDD[a]	0.1	nd	nd	nd	nd	0.11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.46	nd	nd
56	o,p'-DDT[a]	0.2	nd	nd	0.38	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.22	nd	nd
57	o,p'-DDD[a]	0.1	nd	nd	nd	0.12	2.7	nd	nd	nd	nd	0.17	nd	nd	0.31	0.11	nd	0.13	0.16	0.13	0.64	0.52	0.15
58	PCB#8[a]	0.1	nd	nd	0.35	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.35	nd	nd
59	PCB#74[a]	0.1	nd	nd	0.10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13	nd	nd
60	PCB#70[a]	0.1	nd	nd	0.11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.11	nd	nd
61	PCB#66[a]	0.1	nd	nd	0.11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.12	nd	nd
62	PCB#60[a]	0.1	nd	nd	nd	0.18	nd	nd	nd	nd	nd	nd	nd	nd	0.15	nd	0.11	nd	nd	nd	1.1	0.16	nd

Table S4.1 Concentrations (μg L^{-1}) of OMPs in groundwaters of Hanoi and Ho Chi Minh City (S1 and S2 represent sample taken in September, 2013 and August, 2014, respectively) (continued)

No	Name	LOD (μg L^{-1})	HN12		HN13		HN14			HN14	HN14	HN15		HN16		HN17		HN18		HCM1	HCM2	HCM3	HCM4
			S1	S2	S1	S2	S1	S2-1[b]	S2-2[b]	S2	S2	S1	S2	S1	S2	S1	S2	S1	S2	S1	S1	S1	S1
63	PCB#52[a]	0.1	nd	nd	0.33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.46	nd	nd
64	PCB#44[a]	0.1	nd	nd	0.22	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.25	nd	nd
65	PCB#41[a]	0.1	nd	nd	0.29	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.34	nd	nd
66	PCB#4&10[a]	0.1	nd	nd	0.10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.29	nd	nd
67	PCB#37[a]	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.20	nd	nd
68	PCB#33[a]	0.1	nd	nd	0.37	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.40	nd	0.13
69	PCB#28[a]	0.1	nd	nd	1.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.8	nd	0.58
70	PCB#22[a]	0.2	nd	nd	0.29	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.30	nd	nd
71	PCB#19[a]	0.1	nd	nd	0.15	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
72	PCB#18[a]	0.1	nd	nd	0.78	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.64	nd	0.27
73	PCB#15[a]	0.1	nd	nd	0.17	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.19	nd	nd
74	PCB#1[a]	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a] Compounds presented concentrations in ng L^{-1}.

[b] Duplicate analyses.

Table S5.1 Concentrations (ngg^{-1} dry–wt) of the detected chemicals and volatile organic contents (%) at each site

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
1	n-C9H20	N.D.	27	37	49	36	N.D.	N.D.	N.D.	24	8	21	31	22	5	N.D.	N.D.	11	29
2	n-C10H22	10	N.D.	11	100	432	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	25	42	49	N.D.	N.D.
3	n-C11H24	367	297	438	418	971	N.D.	N.D.	214	110	120	107	385	320	185	434	444	351	331
4	n-C12H26	62	N.D.	75	193	460	N.D.	22	N.D.	N.D.	N.D.	N.D.	11	N.D.	182	481	395	N.D.	760
5	n-C13H28	214	47	215	261	969	27	78	34	N.D.	N.D.	28	N.D.	N.D.	525	1051	911	N.D.	912
6	n-C14H30	78	N.D.	115	419	1030	N.D.	84	N.D.	N.D.	N.D.	34	85	N.D.	623	516	547	2	679
7	n-C15H32	N.D.	N.D.	N.D.	N.D.	1842	N.D.	203	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	821	642	572	N.D.	826
8	n-C16H34	93	32	485	186	1985	14	208	65	N.D.	14	87	254	32	795	297	316	44	1139
9	n-C17H36	394	155	659	1712	3724	100	728	431	26	26	N.D.	391	137	2138	2091	1846	80	4624
10	n-C18H38	46	N.D.	89	349	2257	5	25	N.D.	N.D.	N.D.	N.D.	13	N.D.	914	203	198	N.D.	N.D.
11	n-C19H40	51	1	61	363	2391	27	91	39	14	N.D.	12	61	11	586	247	260	8	178
12	n-C20H42	101	42	121	211	2245	N.D.	118	39	13	3	N.D.	163	111	627	403	390	5	303
13	n-C21H44	72	7	86	682	2707	56	124	56	30	2	19	111	29	1200	619	660	19	615
14	n-C22H46	245	236	292	342	2428	160	322	247	141	122	122	354	226	1054	785	797	159	1011
15	n-C23H48	172	125	206	880	2615	309	407	264	29	N.D.	27	563	65	1199	905	933	25	990
16	n-C24H50	330	328	394	1530	3276	428	550	321	148	112	137	624	211	1725	1050	1282	324	1167
17	n-C25H52	317	341	378	N.D.	3458	620	705	563	63	30	96	1159	126	1611	2050	2001	47	1561
18	n-C26H54	325	365	533	435	2387	302	456	331	N.D.	N.D.	116	831	221	1378	1820	1606	N.D.	1882
19	n-C27H56	662	878	1118	2220	3458	914	1326	862	176	167	257	2403	295	1516	2053	1965	53	2500
20	n-C28H58	326	405	1365	887	2770	428	733	452	N.D.	N.D.	N.D.	982	N.D.	1066	1228	1168	N.D.	1211
21	n-C29H60	200	137	2003	2959	4707	1579	2262	242	N.D.	67	42	3473	773	1842	2082	1791	67	3458
22	n-C30H62	450	476	537	1878	2932	507	760	589	83	138	128	1669	323	1539	1447	1291	N.D.	1994
23	n-C31H64	1740	1468	2078	1489	5106	1867	2715	2027	108	45	475	3962	1181	2266	2582	2531	163	3221
24	n-C32H66	604	597	721	4454	3386	781	1191	877	169	202	197	1699	502	1930	2356	2841	644	2550
25	n-C33H68	N.D.	N.D.	N.D.	2792	4265	1440	2237	1652	6	N.D.	349	3096	820	1574	2228	2015	N.D.	2855
26	4-Cymene	30	N.D.	30	123	351	18	169	4	N.D.	N.D.	N.D.	5	N.D.	106	34	29	N.D.	8
27	Pentamethylbenzene	1.4	N.D.	1.7	77	53	N.D.	1.7	N.D.	0.40	N.D.	N.D.	N.D.	N.D.	115	84	79	0.67	50
28	Pentachlorobenzene	N.D.	N.D.	N.D.	0.63	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.55	0.48	N.D.	0.46
29	1,4-Dichlorobenzene	3.5	2.2	3.7	5.4	7.7	0.37	N.D.	0.77	1.2	N.D.	0.58	0.86	0.50	0.83	4.4	4.9	0.84	0.64
30	1,2,4-Trichlorobenzene	N.D.	N.D.	N.D.	N.D.	3.1	N.D.	N.D.	1.1	N.D.	N.D.	N.D.	1.0	1.9	N.D.	11	12	N.D.	N.D.
31	1,3-Dimethylnaphthalene	10	3.2	6.9	250	340	3.4	11	5.0	2.1	0.96	3.0	21	2.4	378	205	198	4.9	162
32	1,4-&2,3-Dimethylnaphthalene	6.1	1.9	25	35	172	1.8	5.2	2.7	0.98	0.70	1.3	20	0.92	176	100	105	2.6	55

Table S5.1 Concentrations (ngg^{-1} dry–wt) of the detected chemicals and volatile organic contents (%) at each site (continued)

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
33	1-Methylphenanthrene	N.D.	N.D.	N.D.	35	125	N.D.	4.2	1.7	0.39	N.D.	N.D.	N.D.	0.85	48	27	27	N.D.	11
34	2,3-Benzofluorene	7.2	4.2	8.6	129	227	20	8.6	5.0	N.D.	N.D.	N.D.	9.3	N.D.	93	146	157	N.D.	84
35	2,6-Diisopropylnaphthalene	10	6.3	N.D.	35	26	3.2	3.4	6.8	2.5	3.9	3.1	94	N.D.	N.D.	N.D.	N.D.	6.2	111
36	2,6-Dimethylnaphthalene	20	5.0	24	499	305	19	30	9.3	2.6	N.D.	2.9	45	N.D.	290	245	235	4.6	243
37	2-Methylnaphthalene	4.0	N.D.	29	65	63	N.D.	3.5	1.5	N.D.	N.D.	N.D.	3.4	N.D.	44	47	45	0.60	30
38	2-Methylphenanthrene	5.5	0.62	39	75	160	3.9	5.2	2.1	0.19	N.D.	0.34	N.D.	0.91	56	57	56	N.D.	41
39	2-Phenylnaphthalene	6.0	1.1	7.2	72	135	9.0	7.4	3.7	N.D.	N.D.	0.70	5.3	1.1	565	61	59	N.D.	40
40	Acenaphthene	1.2	N.D.	7.3	12	16	3.4	1.5	N.D.	N.D.	0.06	0.42	3.3	N.D.	13	13	11	N.D.	7.3
41	Anthracene	1.7	0.23	6.8	17	35	3.5	2.6	0.87	0.10	0.10	0.20	2.4	0.29	15	17	15	0.14	11
42	Benzo(a)anthracene	4.1	1.5	43	57	223	23	13	1.4	0.31	0.32	0.54	5.5	0.86	36	103	96	0.72	56
43	Benzo(a)pyrene	4.6	1.0	42	86	275	25	12	1.6	0.13	0.15	0.47	6.2	0.39	38	148	154	N.D.	53
44	Benzo(e)pylene	21	7.2	279	324	669	61	41	7.9	1.2	1.0	1.5	24	3.4	169	374	304	N.D.	173
45	Benzo(ghi)perylene	4.6	0.87	60	N.D.	115	10	6.3	1.6	0.16	0.13	0.40	5.5	0.91	43	108	96	N.D.	N.D.
46	Benzo(j&b)fluoranthene	10	5.7	105	146	310	30	24	4.3	0.44	0.41	0.90	11	2.1	78	187	180	0.86	89
47	Chrysene & Triphenylene	7.5	2.7	87	125	258	21	16	2.4	0.27	0.10	0.62	10	1.4	67	132	153	0.76	80
48	Fluoranthene	12	2.0	89	237	447	44	31	6.7	0.46	0.19	2.5	20	2.8	161	200	168	2.1	142
49	Fluorene	3.4	0.78	8.2	26	31	3.7	4.4	2.2	0.22	N.D.	0.86	5.2	0.60	24	22	26	0.21	15
50	Indeno(1,2,3-cd)pyrene	4.4	1.5	45	N.D.	127	13	10	2.0	0.19	N.D.	0.58	6.8	0.99	30	92	87	N.D.	N.D.
51	Naphthalene	6.5	0.10	56	73	125	0.26	5.0	0.91	N.D.	N.D.	N.D.	6.8	0.34	166	66	70	0.24	17
52	Perylene	293	2896	188	90	521	301	337	562	22	0.98	155	670	339	86	454	420	N.D.	484
53	Phenanthrene	13	1.5	53	136	272	16	16	5.7	0.40	N.D.	2.1	14	2.2	128	115	130	1.7	73
54	Pyrene	9.3	5.4	114	267	459	34	24	4.3	0.49	0.27	1.6	30	2.3	183	209	184	2.1	139
55	1-Methylnaphthalene	1.7	0.19	10	31	36	0.25	1.7	0.60	0.08	0.10	0.07	1.5	0.10	28	25	23	0.40	14
56	3-Methylphenanthrene	4.4	0.38	36	84	139	2.6	3.8	0.85	N.D.	0.36	0.14	N.D.	0.27	50	57	50	N.D.	34
57	9-Methylphenanthrene	2.7	1.3	26	122	127	N.D.	2.3	0.64	0.15	N.D.	0.22	N.D.	0.37	48	43	36	N.D.	28
58	Benzo(k)fluoranthene	1.9	0.35	21	33	74	10	7.5	0.51	0.07	0.12	0.21	1.4	0.28	11	52	57	0.23	26
59	PCB#1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.70	0.83	N.Q.	N.D.
60	PCB#3	N.D.	N.D.	0.04	N.D.	0.04	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	N.D.	0.17	0.18	0.23	N.Q.	0.06
61	PCB#4&10	N.D.	N.D.	0.05	0.13	0.05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.04	N.D.	N.D.	1.0	1.3	N.Q.	0.33
62	PCB#8	N.D.	N.D.	0.43	1.8	0.41	N.D.	N.D.	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	0.09	2.8	2.3	N.Q.	1.1
63	PCB#15	N.D.	N.D.	0.35	0.98	0.33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	0.28	1.5	1.8	N.Q.	0.62
64	PCB#18	N.D.	N.D.	1.5	4.2	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.13	0.06	0.38	6.1	6.5	N.Q.	3.2
65	PCB#19	N.D.	N.D.	0.17	0.32	0.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	0.07	1.8	1.9	N.Q.	0.42

Table S5.1 Concentrations (ngg^{-1} dry–wt) of the detected chemicals and volatile organic contents (%) at each site (continued)

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
66	PCB#22	N.D.	N.D.	0.47	1.2	0.33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.06	0.03	0.15	1.3	1.3	N.Q.	0.76
67	PCB#28	0.08	0.03	2.9	6.3	1.9	0.06	0.03	0.09	0.03	N.D.	N.D.	0.32	0.26	1.1	10	17	N.Q.	4.6
68	PCB#33	0.03	N.D.	0.96	2.3	0.56	0.03	0.02	0.03	N.D.	N.D.	N.D.	0.06	0.06	0.28	2.3	2.7	N.Q.	1.3
69	PCB#37	0.03	N.D.	0.78	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	0.09	0.03	N.D.	1.5	1.5	N.Q.	1.3
70	PCB#44	0.02	N.D.	1.6	2.0	1.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.18	0.02	N.D.	3.0	2.1	N.Q.	2.8
71	PCB#49	0.03	N.D.	1.6	1.9	1.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.36	0.03	0.90	7.8	8.3	N.Q.	3.5
72	PCB#52	0.11	N.D.	1.5	2.8	3.3	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	0.30	0.03	N.D.	4.6	3.7	N.Q.	3.1
73	PCB#54	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.41	0.67	N.Q.	0.08
74	PCB#70	0.06	N.D.	1.5	1.6	2.3	0.02	N.D.	0.02	N.D.	N.D.	N.D.	0.14	0.04	1.1	N.D.	N.D.	N.Q.	2.0
75	PCB#74	0.03	N.D.	1.1	1.2	1.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.08	0.04	N.D.	0.03	0.02	N.Q.	1.0
76	PCB#77	N.D.	N.D.	0.22	0.17	0.26	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.04	N.D.	0.22	0.18	0.43	N.Q.	0.21
77	PCB#87	0.04	N.D.	1.3	N.D.	2.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.07	N.D.	N.D.	1.4	1.4	N.Q.	1.1
78	PCB#95	0.07	N.D.	1.5	0.99	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.19	N.D.	N.D.	1.0	N.D.	N.Q.	0.69
79	PCB#99	0.07	N.D.	N.D.	N.D.	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	0.16	N.D.	N.D.	0.09	0.11	N.Q.	N.D.
80	PCB#101	0.05	N.D.	1.4	1.1	2.1	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	0.17	N.D.	0.66	2.9	4.1	N.Q.	1.7
81	PCB#105	0.05	N.D.	1.3	1.3	2.2	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	0.74	1.2	2.0	N.Q.	0.91
82	PCB#110	0.09	0.02	2.7	1.9	3.5	0.05	0.02	N.D.	0.02	N.D.	N.D.	0.27	0.03	1.6	3.7	5.2	N.Q.	2.4
83	PCB#114	N.D.	N.D.	0.05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	0.03	0.08	N.Q.	0.07
84	PCB#118	0.11	N.D.	3.1	2.6	4.5	0.05	0.03	0.02	N.D.	N.D.	N.D.	0.17	N.D.	1.2	2.9	3.2	N.Q.	2.3
85	PCB#128	0.03	N.D.	0.69	0.74	0.89	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.06	N.D.	0.29	1.1	1.3	N.Q.	0.85
86	PCB#138&158	0.09	0.02	1.6	1.4	1.9	0.02	0.02	N.D.	N.D.	N.D.	N.D.	0.20	N.D.	0.74	4.9	4.4	N.Q.	2.9
87	PCB#149	0.08	N.D.	1.4	0.98	2.0	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	0.30	N.D.	N.D.	7.7	8.4	N.Q.	3.5
88	PCB#151	N.D.	N.D.	0.42	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.17	3.0	3.8	N.Q.	1.2
89	PCB#155	N.D.	N.D.	0.02	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	N.D.	N.D.	N.D.	0.03	N.Q.	0.06
90	PCB#153&168	0.07	N.D.	1.4	1.2	1.7	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	0.25	N.D.	0.57	6.0	7.5	N.Q.	3.2
91	PCB#156	N.D.	N.D.	0.28	0.28	0.39	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.09	0.63	0.83	N.Q.	0.41
92	PCB#157	N.D.	N.D.	0.08	0.04	0.06	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	0.07	0.08	N.Q.	0.03
93	PCB#167	N.D.	N.D.	0.07	0.10	0.16	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	0.25	0.30	N.Q.	0.15
94	PCB#169	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.Q.	N.D.
95	PCB#170	0.04	N.D.	0.54	N.D.	0.46	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.17	N.D.	N.D.	4.6	3.9	N.Q.	N.D.
96	PCB#171	N.D.	N.D.	0.10	0.05	0.06	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	N.D.	0.03	0.83	1.1	N.Q.	0.42

Table S5.1 Concentrations (ng g^{-1} dry–wt) of the detected chemicals and volatile organic contents (%) at each site (continued)

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
97	PCB#177	N.D.	N.D.	0.15	0.13	0.06	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	0.11	1.6	1.5	N.Q.	0.83
98	PCB#178	N.D.	N.D.	0.05	0.03	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	0.62	0.46	N.Q.	0.30
99	PCB#180	0.04	N.D.	0.38	0.36	0.24	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.14	N.D.	0.20	3.3	3.2	N.Q.	1.8
100	PCB#183	N.D.	N.D.	0.25	0.15	0.12	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.07	N.D.	0.09	1.6	2.1	N.Q.	0.89
101	PCB#187	0.02	N.D.	0.38	0.32	0.22	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.17	N.D.	0.21	3.5	3.8	N.Q.	1.7
102	PCB#189	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.13	0.14	N.Q.	0.06
103	PCB#191	N.D.	N.D.	N.D.	0.64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.10	0.31	N.Q.	0.04
104	PCB#194	N.D.	N.D.	N.D.	0.16	0.08	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.08	N.D.	0.08	1.9	2.1	N.Q.	0.85
105	PCB#199	N.D.	N.D.	0.1	0.12	0.05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.08	N.D.	0.07	1.6	1.2	N.Q.	0.86
106	PCB#201	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.16	0.16	N.Q.	0.06
107	PCB#202	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	0.16	0.24	N.Q.	0.07
108	PCB#205	N.D.	N.D.	0.1	0.13	0.07	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.Q.	0.09
109	PCB#206	N.D.	N.D.	0.02	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	N.D.	0.49	0.46	N.Q.	0.20
110	PCB#208	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.10	0.22	N.Q.	0.03
111	PCB#209	N.D.	N.D.	0.3	N.D.	0.09	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.04	N.D.	N.D.	0.98	1.2	N.Q.	0.78
112	Chlorpyrifos	N.D.	N.D.	N.D.	N.D.	N.D.	9.4	25	3.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
113	Deltamethrin	N.D.	N.D.	N.D.	N.D.	59714	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
114	Permethrin 1	N.D.	N.D.	6410	6346	4433	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	435	3990	3702	N.D.	2308
115	Permethrin 2	N.D.	N.D.	1444	1296	1874	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	162	1404	1320	N.D.	473
116	Piperonyl butoxide	N.D.	N.D.	12	33	64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.3	27	29	N.D.	9.2
117	Hexachlorobenzene	0.05	N.D.	3	3.8	0.79	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.19	1.6	1.4	N.Q.	1.4
118	a-HCH	0.1	N.D.	1	0.66	0.89	0.03	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.85	0.88	N.Q.	0.39
119	b-HCH	N.D.	N.D.	N.D.	0.04	0.28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.04	0.04	N.Q.	N.D.
120	g-HCH	N.D.	N.D.	2	0.70	N.D.	0.44	0.16	0.29	N.D.	N.D.	N.D.	N.D.	0.18	1.2	1.6	1.3	N.Q.	2.8
121	Aldrin	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	0.13	0.18	N.Q.	N.D.
122	Endrin	0.5	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	0.35	0.19	N.D.	0.23	0.10	N.D.	N.D.	N.D.	N.D.	N.Q.	0.43
123	Dieldrin	N.D.	0.05	3	N.D.	N.D.	0.15	0.27	0.26	0.14	N.D.	0.11	N.D.	0.22	N.D.	4.7	4.0	N.Q.	N.D.
124	oxy-Chlordane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.Q.	0.28
125	trans-Chlordane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.24	0.25	N.Q.	0.31
126	cis-Chlordane	N.D.	N.D.	0.1	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.90	0.82	N.Q.	0.50
127	trans-Nonachlor	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.47	0.33	N.Q.	0.21

Table S5.1 Concentrations (ng g^{-1} dry–wt) of the detected chemicals and volatile organic contents (%) at each site (continued)

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
128	cis-Nonachlor	N.D.	N.D.	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	0.38	0.41	N.Q.	0.07
129	Heptachlor	N.D.	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	0.02	N.Q.	N.D.
130	Heptachlorepoxide(B)	N.D.	N.D.	0.4	0.10	N.D.	0.07	N.D.	N.D.	0.05	N.D.	0.09	N.D.	0.10	N.D.	0.08	0.08	N.Q.	1.4
131	o,p'-DDE	0.1	N.D.	0.5	0.73	0.88	0.04	0.04	N.D.	N.D.	N.D.	N.D.	0.11	N.D.	0.03	3.3	3.0	N.Q.	0.24
132	p,p'-DDE	4	0.3	17	27	26	0.66	0.93	0.40	0.03	N.D.	0.29	2.1	0.20	1.3	62	54	N.Q.	6.7
133	o,p'-DDD	0.3	N.D.	6	4.9	2.3	0.15	0.36	0.07	0.02	N.D.	0.03	0.39	0.02	N.D.	8.0	6.5	N.Q.	1.2
134	p,p'-DDD	1	0.1	13	12	15	0.63	2.4	0.40	0.06	N.D.	0.09	1.2	0.11	N.D.	52	49	N.Q.	5.1
135	o,p'-DDT	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.Q.	N.D.
136	p,p'-DDT	0.1	N.D.	N.D.	N.D.	N.D.	0.06	0.11	0.13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.6	2.4	N.Q.	N.D.
137	Cholestane	10	N.D.	118	165	171	1	1	2	N.D.	6	N.D.	27	1	184	233	256	3	65
138	beta-Sitosterol	2810	184	5377	7820	11698	934	2181	538	115	48	274	1378	373	4173	7930	7803	153	4300
139	Stigmasterol	1521	265	4532	8636	5938	992	1758	726	97	20	272	1958	377	4340	6500	6225	275	6587
140	Cholesterol	2481	487	7836	9217	11477	1387	3160	1125	273	79	372	1787	534	5237	16522	18157	497	11186
141	Cholestanol	2662	754	7498	14462	11713	1253	2652	1085	220	78	288	2617	423	6493	10594	14176	551	16506
142	Coprostanol	5747	1347	14566	23398	21397	1011	2490	508	266	64	189	1975	246	8391	19063	16403	804	19143
143	Epicoprostanol	3514	591	7594	7300	10840	627	1531	331	124	21	113	952	113	6016	10148	10789	417	10845
144	Coprostanone	3452	700	7734	9048	10412	317	1055	238	59	3	84	675	104	8952	1973	1823	244	11092
145	Campesterol	1156	82	4508	5381	8797	1053	2168	560	55	16	149	1004	232	2709	6140	6606	198	3583
146	Di(2-ethylhexyl)phthalate	3539	697	8028	5426	7891	940	1553	362	400	87	523	3382	546	7060	7016	7966	906	5036
147	Butyl benzyl phtalate	N.D.	9	242	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3	N.D.	9	75	N.D.	N.D.	1	139
148	Diethyl phthalate	15	5	79	3	220	23	N.D.	57	57	N.D.	N.D.	5	N.D.	58	79	84	54	2
149	Diisobutyl phthalate	109	33	609	440	N.D.	34	34	35	3	20	26	33	N.D.	135	169	160	15	103
150	Dimethyl phthalate	3	N.D.	N.D.	19	25	2	N.D.	5	N.D.	N.D.	N.D.	4	N.D.	28	21	26	1	491
151	Di-n-butyl phthalate	62	3	877	365	641	54	70	69	N.D.	4	26	56	12	24	260	298	32	432
152	Di-n-octyl phthalate	N.D.	17	899	581	N.D.	N.D.	78	N.D.	3	66	140	163	9	322	N.D.	N.D.	9	191
153	Methyl dodecanoate	N.D.	2	N.D.	N.D.	N.D.	N.D.	6	N.D.	1	1	1	1	1	N.D.	N.D.	N.D.	1	N.D.
154	Methyl pentadecanoate	63	2	6	210	N.D.	110	290	72	20	N.D.	5	109	N.D.	N.D.	208	249	N.D.	290
155	Stearic acid methyl ester	3	4	4	N.D.	N.D.	14	N.D.	6	3	2	2	3	N.D.	N.D.	N.D.	N.D.	18	N.D.
156	3,5-di-tert-Butyl-4-hydroxybenzal	23	34	53	33	31	8	35	32	17	17	24	34	24	28	37	33	21	107
157	trans-Decahydronaphthalene	13	N.D.	15	187	191	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	10	N.D.	56	243	251	N.D.	66
158	Longifolene	9	N.D.	11	625	97	N.D.	N.D.	2	2	N.D.	1	16	N.D.	15	122	143	2	119

Table S5.1 Concentrations (ng g^{-1} dry–wt) of the detected chemicals and volatile organic contents (%) at each site (continued)

No	Name	HN 1	HN 2	HN 3	HN 4	HN 5	HP 1	HP 2	HP 3	HP 4	DN 1	DN 2	HCM 1	HCM 2	HCM 3	HCM 4–1	HCM 4–2	HCM 5	HCM 6
159	Diphenyl ether	1	1	21	71	43	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1	1	31	44	50	1	23
160	2,6-Di-tert-butyl-4-benzoquinone	149	N.D.	47	N.D.	N.D.	224	N.D.	N.D.	N.D.	6	N.D.	N.D.	N.D.	N.D.	348	372	52	N.D.
161	Benzanthrone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	12	N.D.	N.D.	N.D.	N.D.	18	3	N.D.	N.D.	N.D.	N.D.	N.D.
162	Isophorone	9	1	124	5	N.D.	7	N.D.	1	N.D.	N.D.	3	3	N.D.	N.D.	N.D.	N.D.	8	19
163	Acetophenone	8	N.D.	47	27	41	4	1	N.D.	N.D.	N.D.	N.D.	5	N.D.	51	21	28	N.D.	N.D.
164	2,6-Di-t-butyl-4-ethylphenol	228	346	332	242	388	19	134	N.D.	152	N.D.	71	239	161	50	98	110	N.D.	984
165	4-Methyl-2,6-di-t-butylphenol	5	12	16	215	285	3	4	N.D.	8	N.D.	N.D.	10	6	75	146	151	1	91
166	Phenol	N.D.	N.D.	34	1	27	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	13	N.D.	N.D.	N.D.	N.D.
167	3- & 4-tert-Butylphenol	1	1	N.D.	2	N.D.	N.D.	1	1	N.D.	N.D.	N.D.	2	N.D.	4	N.D.	N.D.	N.D.	5
168	Bisphenol A	N.D.	7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	714	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
169	4-tert-Octylphenol	N.D.	N.D.	N.D.	77	59	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	51	145	171	N.D.	N.D.
170	Nonylphenol	N.D.	N.D.	N.D.	4453	7769	N.D.	9	N.D.	7	N.D.	7	496	N.D.	5161	3946	3566	45	4246
171	Octanol	N.D.	6	N.D.	15	N.D.	N.D.	N.D.	12	N.D.	N.D.	N.D.	10	N.D.	N.D.	N.D.	N.D.	N.D.	21
172	alpha-Terpineol	7	4	28	35	N.D.	N.D.	13	4	N.D.	N.D.	4	11	1	27	25	28	N.D.	15
173	2-Butoxyethanol	N.D.	29	N.D.	40	N.D.	N.D.	24	N.D.	51	N.D.	55	42	46	N.D.	N.D.	N.D.	N.D.	31
174	2-Ethyl-1-hexanol	9	20	71	49	90	9	10	25	N.D.	N.D.	4	33	3	67	33	36	6	2
175	Benzyl alcohol	N.D.	N.D.	52	24	28	N.D.	22	N.D.	N.D.	N.D.	8	32	N.D.	10	N.D.	N.D.	N.D.	N.D.
176	L-Menthol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3	N.D.
177	Triclosan	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	211	240	N.D.	N.D.
178	Squalane	176	93	210	1361	1094	N.D.	N.D.	N.D.	67	N.D.	70	310	N.D.	N.D.	N.D.	N.D.	N.D.	889
179	Carbazole	6	N.D.	N.D.	22	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
180	2-(Methylthio)-benzothiazol	4	N.D.	86	N.D.	99	N.D.	9	N.D.	N.D.	N.D.	N.D.	N.D.	2	16	21	17	N.D.	N.D.
181	Benzothiazole	6	N.D.	59	N.D.	75	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	9	N.D.	23	22	25	N.D.	N.D.
182	Tris(2-ethylhexyl) phosphate	4	N.D.	N.D.	115	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	41	N.D.	N.D.	N.D.	N.D.	N.D.	119
183	Di(2-ethylhexyl)adipate	380	N.D.	1152	46	1205	605	204	3	12	N.D.	152	344	47	773	1016	1227	38	N.D.
184	Quinoline, 2,7-dimethyl-	N.D.	1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	14	N.D.	N.D.	37	43	N.D.	17
185	Biphenyl	13	2	17	61	63	4	10	7	ND	ND	1	9	1	50	38	38	2	29
	Total concentration, ng/g dry-wt	1007	523	2293	6862	11267	876	453	53	297	6	376	2343	271	6402	6151	6102	157	6490
	Volatile organic, %	6.6	7.3	12	10	17	5.9	7.7	7.1	1.4	1.0	1.6	11	11	7.3	10	10	3.4	13

N.Q.: not quantified.
N.D.: not detected.