

DEVELOPMENT OF A TARGET SCREENING METHOD  
OF MICRO-POLLUTANTS IN WATER SAMPLES USING  
SOLID-PHASE EXTRACTION AND TIME-OF-FLIGHT  
MASS SPECTROMETRY AND APPLICATION TO  
VIETNAMESE AQUATIC ENVIRONMENT

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by

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Chau Thi Cam Hong

March 2018

Kitakyushu, Japan



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## Abstract

This thesis can be divided into two major parts: 1) Development of a comprehensive screening method for more than three hundred organic chemicals in water samples using a combination of solid-phase extraction (SPE) and liquid chromatography time-of-flight mass spectrometry (LC/TOF-MS), 2) Application the new method to monitor organic micro-pollutants in the aquatic environment in Vietnam.

In this study, a comprehensive screening method for 311 LC-MS-amenable organic chemicals (LOCs) with a wide range of physicochemical properties ( $\log P_{ow}$ :  $-2.2 - 8.53$ ) in water samples was developed by combining SPE with LC/TOF-MS. First, method optimization using 128 pesticides revealed that tandem extraction with styrene-divinylbenzene polymer and activated carbon solid-phase extraction cartridges and setting sample water pH 7.0 provided the highest recovery. The following spike recovery test of 190 model compounds showed average recovery of 80.8 % and average relative standard deviations (RSD) of 13.5 % from spiked reagent water at  $0.20 \mu\text{g L}^{-1}$ , and 87.1 % recovery and 10.8 % RSD at  $0.05 \mu\text{g L}^{-1}$  and proved the accuracy. Spike-recovery testing ( $0.20 \mu\text{g L}^{-1}$ ) using sewage treatment plant effluents resulted in an average recovery and the average RSD of 190 model compounds of 77.4 % and 13.1 %, respectively and proved this method could be applied to wastewater as well. The method was applied to the influent and effluent of five sewage treatment plants in Kitakyushu, Japan, and 29 chemicals were detected out of 311 analytes at least once. As the results of those experiments, it was confirmed the well effectiveness of the combination of the tandem SPE and LC/TOF-MS-TIM method for screening LOCs in environmental samples. The developed target screening method reduces analytical time and cost, the consumption of solvent and the emission of toxic wastes compared to the conventional methods because it is possible to determine a huge number of pollutants in one analysis. Therefore this proposed method is expected to be very efficient for primary screening surveys of previously uninvestigated waters. This method can grasp a more complete pollution picture compared to the usual selective chemical analysis because wide range of chemicals are analyzed at once and it is applicable for emergency surveys after natural disasters such as earthquakes as well as the accidental release of pollutants. In addition,

data obtained by this LC/TOF-MS-TIM method can be used for non-target analysis and retrospective analysis because of the accurate mass spectra.

Because of the effectiveness of this developed screening method, we applied the method to determination of 311 LOCs in rivers of the major Vietnamese cities. In Vietnam, it is known that rivers and lakes are polluted with untreated household wastewater and industrial water, but the monitoring of chemical substances is limited to a small number of known-pollutants. Therefore, there is an urgent need to examine a large number of chemicals to prevent impacts from expanding environmental pollution. In the present study, we determined 1153 substances to grasp a pollution picture of micro-contaminants in Vietnam to evaluate the environmental risk of the detected chemicals. To achieve this objective, we have used two comprehensive analytical methods: 1) the analytical method developed in this study, and 2) SPE and GC-MS analysis. We collected water samples from 5 areas from north to south (the Red River, Hanoi, Hue, Danang, and Ho Chi Minh City (HCMC)) in February 2013 (dry season). One hundred and sixty five compounds were detected at least once. The compounds detected highly frequently (>40% samples) were sterols (cholesterol, beta-sitosterol, stigmasterol, and coprostanol), phthalates (bis (2-ethylhexyl) phthalate and di-n-butyl phthalate), and pharmaceuticals and personal care products (PPCPs, caffeine and metformin). These contaminants were detected with a high frequency in other countries. The results revealed that surface waters in Vietnam, particularly in the center of large cities, are polluted by a large number of organic micropollutants from households and business activities as the major sources.

In further survey to obtain the pollution status of LOCs in rivers in the large cities, we also collected samples in Hanoi and HCMC in September 2013 (rainy season). Eighteen groundwater samples were also collected in Hanoi. The results of the comparison between dry and rainy seasons showed that 22 compounds were found with total concentrations of 3.2 – 13  $\mu\text{g L}^{-1}$  in the dry season, and 24 compounds with total concentrations of 0.16 – 11  $\mu\text{g L}^{-1}$  in the rainy season in Hanoi. In HCMC samples, 22 compounds were detected with total concentrations of 0.86 – 12  $\mu\text{g L}^{-1}$  in the dry season,

and 30 compounds with total concentrations of  $0.59 - 15 \mu\text{g L}^{-1}$  in the rainy season. This study confirms that rivers in Hanoi and HCMC were heavily polluted with a large number of LOCs; particularly, concentrations of PPCPs (cotinine, lincomycin, sulfamethoxazole and acetaminophen) were higher than those of known international studies. It might be caused by the lack of sufficient wastewater treatment in Vietnam. Pesticides were detected more in suburban areas than city areas. Both the number and total concentrations of pesticides increased in the rainy season. Especially, the number of pesticides found in suburban areas of HCMC increased 6 times (30 compounds) in the rainy season from 5 compounds in the dry season and the total concentrations of these increased 6 times to  $1.2 \mu\text{g L}^{-1}$  because of agricultural activities.

As the result of evaluation of the environmental risk, the risk quotients (MEC/PNEC values) for sulfamethoxazole, ampicillin, acetaminophen, erythromycin and clarithromycin were higher than one, suggesting these chemicals may be causing ecological harm. Further detailed field study is required to confirm this hypothesis.

Results for the LOCs measured in the 18 groundwater samples showed that 36 compounds (one industrial chemical, four PPCPs and 31 pesticides) were detected with total concentrations of  $\text{ND} \sim 1270 \text{ ng L}^{-1}$ . The most frequently detected compounds in groundwater were lidocaine (89%) and dicyclohexylamine (67%) with the maximum concentrations of 81 and 39  $\text{ng L}^{-1}$ , respectively. The sources of contaminants are largely unknown.

In summary, the developed method was very effective for environmental survey of 311 kinds of LOCs in aquatic environment, and it can be used not only for target screening but also for non-target analysis. Many pharmaceuticals and agricultural chemicals were detected at high concentrations in the Vietnamese rivers and it became obvious that some detected chemicals could effect on aquatic ecosystems.

## Table of Contents

Acknowledgements	
Abstract .....	I
Table of Contents .....	IV
List of Tables .....	VII
List of Figures .....	VIII
Abbreviations .....	IX
Chapter 1 GENERAL INTROCDUCTION .....	1
1.1 Organic micro pollutants .....	1
1.1.1 Pharmaceuticals and personal care products .....	1
1.1.2 Pesticides .....	3
1.2 Monitoring of micro-organic pollutants in aquatic environment .....	4
1.3 Water pollution in Vietnam.....	5
1.4 Objectives of this study .....	6
Chapter 2 DEVELOPMENT OF A TARGET SCREENING METHOD OF MICRO-POLLUTANTS IN WATER SAMPLES USING SOLID-PHASE EXTRACTION AND TIME-OF-FLIGHT MASS SPECTROMETRY .....	7
2.1 Introduction .....	7
2.2 Materials .....	8
2.2.1 Reagents and equipment.....	8
2.1.1 Solid-phase extraction materials .....	9
2.1 Experimental .....	10
2.1.1 Model compounds .....	10
2.1.2 Solid-phase extraction .....	25
2.1.3 LC-TOF/MS analysis .....	25
2.2 Results and discussion.....	26
2.2.1 Selection of solid-phase materials .....	26
2.2.2 Selection of extraction apparatus and syringe filter .....	27



2.2.3	Recovery tests.....	28
2.2.3.1	Recovery tests using reagent water.....	28
2.2.3.2	Recovery tests using effluents of sewage treatment plants.....	30
2.2.4	Reliable identification based on in-source fragment ions .....	30
2.2.5	Surrogate compounds and matrix effects .....	32
2.2.6	Application to influents and effluents of sewage treatment plants.....	33
2.3	Conclusions .....	35
Chapter 3 APPLICATION OF THE DEVELOPED SCREENING METHOD TO VIETNAMESE AQUATIC ENVIRONMENT.....		36
3.1	Introduction .....	36
3.2	Study areas .....	37
3.2.1	Red River Delta .....	37
3.2.2	Hanoi city .....	38
3.2.3	Thua Thien Hue.....	39
3.2.4	Danang city.....	39
3.2.5	Saigon River .....	40
3.2.6	Dongnai River .....	41
3.2.7	Ho Chi Minh city.....	42
3.3	Sampling.....	43
3.3.1	Sampling sites.....	43
3.3.2	Sampling method.....	47
3.4	Experimental .....	48
3.4.1	Materials .....	48
3.4.2	Extraction methods.....	48
3.4.3	Analysis methods .....	49
3.4.4	Analytical quality control.....	51

3.5	Results and discussion.....	51
3.5.1	Detection of micro-pollutants in surface water samples .....	51
3.5.2	Distribution of micro-pollutants in surface waters .....	58
3.5.3	Correlations between organic compounds detected in surface waters .....	59
3.5.4	Most frequently detected compounds in surface waters .....	60
3.5.5	Environmental risk assessment of micro-organic compounds .....	63
3.5.6	Polar organic pollutants in surface water and groundwater .....	64
3.5.6.1	Detection of polar organic pollutants in surface water .....	64
3.5.6.1.1	Red River .....	65
3.5.6.1.2	Hue city.....	66
3.5.6.1.3	Danang city .....	66
3.5.6.1.4	Hanoi city.....	67
3.5.6.1.5	Saigon River and Dongnai River .....	68
3.5.6.1.6	Ho Chi Minh city .....	70
3.5.6.1.7	Description of the most frequently detected contaminants in big cities	71
3.5.6.2	Detection of polar organic pollutants in groundwater .....	73
3.6	Conclusions .....	77
Chapter 4 GENERAL CONCLUSIONS .....		78
REFERENCES .....		80
RESEARCH PUBLICATIONS .....		90
CONFERENCE PARTICIPATION .....		91
APPENDICES .....		92

## List of Tables

### Chapter 1

Table 1.1 Toxicity of seven major groups of human drugs to the aquatic environment (Jones 2002).....	3
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### Chapter 2

Table 2-1 Solid-phase extraction materials studied .....	10
Table 2-2 Model compounds including surrogate compounds and their recoveries ..	12
Table 2-3 LC-TOF/MS conditions .....	26
Table 2-4 Summary of results in test of selection of solid-phase materials using 128 pesticides.....	27
Table 2-5 Summary of results in recovery tests using reagent water and effluent .....	29

### Chapter 3

Table 3-1 Sampling record of samples.....	46
Table 3-2 GC-MS conditions for comprehensive analysis.....	50
Table 3-3 GC-MS-MS conditions for comprehensive analysis .....	50
Table 3-4 Concentrations (mg/L) of the chemicals found and the numbers of chemicals found (in parentheses).....	54
Table 3-5 List of most frequently detected compounds in 42 samples .....	62
Table 3-6 The MEC/PNEC ratios of detected compounds.....	64
Table 3-7 Summary of the number and total concentrations of compounds detected in study areas.....	65
Table 3-8 Frequency of compounds detected in Hanoi and HCMC samples (both the dry and rainy seasons, n=22) .....	72
Table 3-9 Analytical results for water-soluble chemicals in Hanoi groundwater.....	76

## List of Figures

### Chapter 1

Fig.1-1 Possible sources and entry pathways of human and veterinary pharmaceuticals into environment (John-Joseph 2007)..... 2

### Chapter 2

Fig. 2-1 Confirmation of identification of metformin using in-source fragment ions ..... 31

Fig. 2-2 Confirmation of false identification of siduron using in-source fragment ions ..... 32

Fig. 2-3 Substances detected in influent and effluent of a sewage treatment plant in Kitakyushu..... 34

### Chapter 3

Fig. 3-1 Location of 42 sampling sites ..... 45

Fig.3-2 Concentrations and number of compounds detected at each sampling site ... ..... 52

Fig. 3-3 Percentages of concentrations of compounds detected at each location .. 58

Fig.3-4 Correlation between groups of detected organic compounds ..... 60

Fig.3-5: Total concentrations of PPCPs and pesticides found in Hue, Danang and Red river..... 66

Fig.3-6: Total concentrations of PPCPs and pesticides found in Hanoi samples... 67

Fig.3-7: Total concentrations of PPCPs and pesticides found in Dongnai River samples and Saigon River samples of HCMC ..... 69

Fig.3-8: Total concentrations of PPCPs and pesticides found in HCMC samples . 71

Fig.3-9: Total concentrations of PPCPs and pesticides found in Hanoi groundwater ..... 74

## Abbreviations

AIQS	Automated Identification and Quantification System
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DBP	Di-n-butyl phthalate
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DEHA	Di(2-ethylhexyl)adipate
DEHP	Bis(2-ethylhexyl)phthalate
DEP	Diethyl phthalate
DO	Dissolved Oxygen
EPA	United States Environmental Protection Agency
FWHM	Full peak width at one-half maximum
GC-MS	Gas chromatography–mass spectrometry
HCH	Hexachlorocyclohexanes
HCMC	Ho Chi Minh City
HPLC	High performance liquid chromatography
IS	Internal standards
LC-MS	Liquid chromatography–mass spectrometry
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
LC-QTOF/MS	Liquid chromatography-quadrupole-time-of-flight mass spectrometry
LC-TOF/MS	Liquid chromatography time-of-flight mass spectrometry
LLE	Liquid - liquid extraction
LOCs	LC-MS-amenable organic chemicals

LOD	Limit of detection
log Pow	logarithm of the octanol–water partition coefficient
MCs	Model compounds
MDL	Method detection limits
MEC	Measured environmental concentration
OCPs	Organochlorine pesticides
OMPs	Organic micro pollutants
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
Pest	Pesticides
PNEC	Predicted no effect concentration
POCs	Polar organic compounds
PPCPs	Pharmaceuticals and personal care products
RSD	Relative standard deviations
RT	Retention time
SDR	Saigon-Dongnai River
SIM	Selected ion monitoring
SPE	Solid-phase extraction
SRM	Selected reaction monitoring
SS	Suspended solids
STP	Sewage treatment plants
SVOCs	Semi-volatile organic compounds
TOF	The time of flight mass spectrometer
TPP	Triphenylphosphate
TSS	Total suspended solids

## Chapter 1 GENERAL INTROCDUCTION

### 1.1 Organic micro pollutants

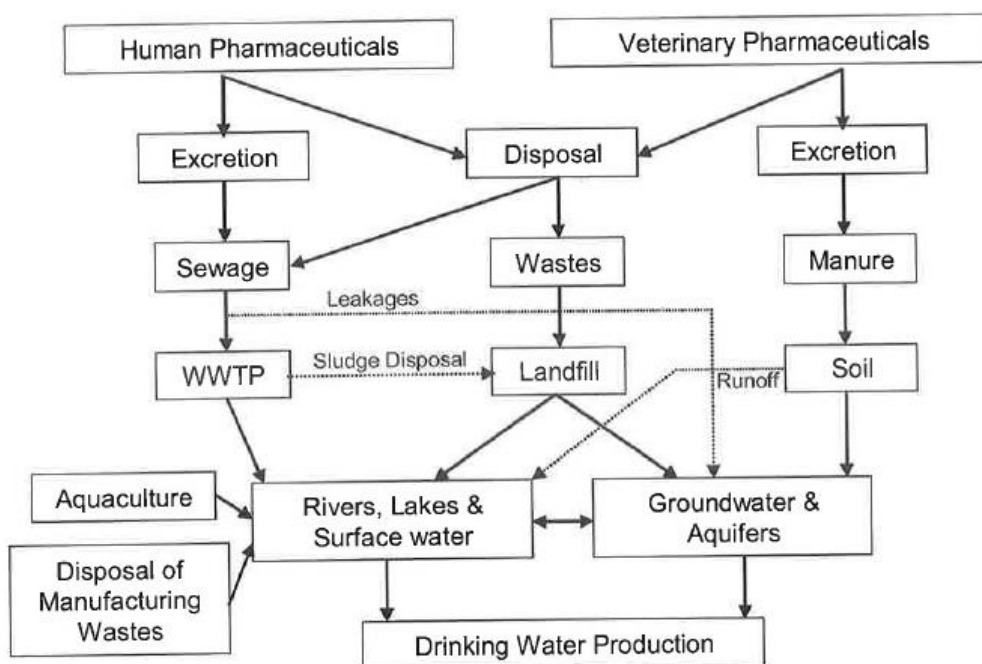
During the last decades, a large number of organic micro pollutants (OMPs) have been released into the environment as a result of anthropogenic activities. Environmental contaminants of recent concern are pharmaceuticals, pesticides (especially their transformation products), estrogens and other endocrine disrupting chemicals, such as degradation products of surfactants, algal and cyanobacterial toxins, disinfection by - products, and metalloids (Zwiener and Frimmel 2004).

#### 1.1.1 Pharmaceuticals and personal care products

Pharmaceuticals and personal care products (PPCPs) are a large and growing class of bioactive chemicals including veterinary and human antibiotics, analgesics, anti-inflammatory drugs, lipid regulators, psychiatric drugs, hormones, etc. There are about 6 million PPCPs commercially available worldwide and the use of PPCPs is continuously creasing 3-4% by weight per year (Daughton 2004). Antibiotics are an important group of pharmaceuticals in today's medicine. They are used extensively in human and veterinary medicine for the purpose of preventing or treating microbial infections. Several hundred different antibiotics are used in human and veterinary medicine. Antibiotics have also used to control certain bacterial disease of high-value fruit, vegetable, and ornamental plants. Specific production rates of antibiotics, besides other drugs, are not reported in the literature. However, it is estimated that Germany used over 600 tons per year of antibiotics with some 300 tons per year used in France, Italy and Spain (Ellis 2006); and about 210 000 tons in 2005 in China (Bing Shao 2009). Over 3000 active substances are licensed for use within the UK with acetaminophen (2000 tons per year), acetylsalicylic acid (770 tons per year) and metformin ( 106 tons per year) being the highest usage drugs (Ellis 2006).

PPCPs are relatively water-soluble and nonvolatile. Most of PPCPs have shorter environmental half-lives than conventional pollutants, low natural background levels. Sources of PPCPs in environment are mainly due to hospitals, household,

pharmaceutical industries, disposal of expired or unused medicine, aquaculture and animal feeding. PPCPs and their metabolites predominantly end up in rivers, streams and fjords via the sewage network that focuses the excreted compounds through sewage treatment plants. They have been found in a wide range of environmental samples including surface water, groundwater and drinking water. (Fig. 1-1).



**Fig.1-1** Possible sources and entry pathways of human and veterinary pharmaceuticals into environment (John-Joseph 2007)

PPCPs often occur in low concentrations, but effects from biologically active compounds after exposure to environmental contaminants in the low ng/l range cannot be excluded a priori. This has become obvious from the past experiences with other biologically active compounds such as pesticides, antifouling agents and endocrine disrupters. And antibiotics are seen to be the most toxic group of PPCPs in aquatic environment (Table1.1).



**Table 1.1** Toxicity of seven major groups of human drugs to the aquatic environment (Jones 2002)

Substances	Extremely toxic EC <sub>50</sub> <0.1 mgL <sup>-1</sup>	Very toxic EC <sub>50</sub> <0.1-1 mgL <sup>-1</sup>	Toxic EC <sub>50</sub> <1-10 mgL <sup>-1</sup>	Harmful EC <sub>50</sub> <10-100 mgL <sup>-1</sup>	Non toxic EC <sub>50</sub> >100 mgL <sup>-1</sup>
Analgesics			D	D, E	
Antibiotics	A	B			
Antidepressants		D			
Anti-epileptics			C		D, E
Cardiovascular drugs		D			
Cytostatics		A		D, E	
X-ray contrast media					A, B, D, E

Most sensitive taxonomic groups: A-Microorganisms; B- Algae; C- Cnidaria; D- Crustacea; E- Fish

### 1.1.2 Pesticides

Pesticides became an important component of worldwide agriculture systems during the last century, allowing for a noticeable increase in crop yields and food production (Alexandratos and Bruinsma 2012). Worldwide pesticide production increased at a rate of about 11% per year, from 0.2 million tons in 1950s to more than 5 million tons by 2000 (FAO 2017). Pesticides include several groups of compounds, namely organochlorine, organophosphate, carbamate, pyrethroids, growth regulators, neonicotinoids, and now biopesticides, which have been developed one after the other. Pesticide sales have increased for all types of pesticides, but herbicides were the group that expanded the most followed by insecticides and fungicides (Roser and Ortiz-Ospina 2017).

Pesticides are widespread contaminants in agricultural crops as well as surface and waste waters. The released pesticides into the environment and their impacts on many species have been known for a long time. Persistent and bio-accumulative chemical compounds, such as DDT, HCH, toxaphene, aldrin, and dieldrin that affected birds and other wild species, were banned from agricultural use, and have been replaced by environmentally friendly and less bio-accumulative chemicals. This has been the trend over the last decades, and it was driven by the toxicity of chemical residues present in food to humans as well as to chemicals' persistence in the environment and

toxicity to nonhuman biota. However, the intensive use of pesticide leads to an increased risk of contamination of the environment and harmful effects on biodiversity, food security, and water resources (Malaj et al. 2014, Queyrel et al. 2016).

## **1.2 Monitoring of micro-organic pollutants in aquatic environment**

Due to the huge number of potential organic pollutants that could be present in the environment, development of new and more sensitive analytical methods for the detection of chemicals is necessary. Screening methods should be able to detect the presence of as many contaminants as possible in a sample, preferably with little sample manipulation.

Non-polar hazardous compounds were the focus of interest and awareness as priority pollutants, thus the analysis of environmental samples was traditionally dominated by the use of gas chromatography–mass spectrometry (GC-MS). For example, Kadokami et al. (2005) has developed a new, fully automated identification and quantification database system to permit quantification of nearly 1000 chemical substances using GC-MS.

Because most of organic contaminants, and even more their metabolites and transformation products, are highly polar and water-soluble, liquid chromatography–mass spectrometry (LC-MS) has become the method of choice for their determination. With recent advances in mass spectrometry, the time of flight mass spectrometer (TOF) has become available. The benefits of using TOF analyzer relies on its measuring principle, that allows to perform full scan acquisitions with superior sensitivity and high mass accuracy (2–5 ppm). These characteristics together with its higher mass resolving power (>10,000 FWHM (full peak width at one-half maximum)) are very attractive when developing analytical methodology for screening, confirmation, and elucidation of organic pollutants at relevant environmental levels.

Liquid - liquid extraction (LLE) or solid - phase extraction (SPE) have been the

most widely used methods in sample pre-concentration for different compound classes, like pesticides, pharmaceuticals, or estrogens. However, nowadays, for aqueous samples, LLE has been almost completely replaced by SPE. Using SPE, smaller sample volumes are needed and a large number of polar compounds can be efficiently extracted with little solvent consumption.

### **1.3 Water pollution in Vietnam**

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.

Water pollution is worsened by leachate from open dumps and medical waste. Most of the 1000 hospitals all over the country fail to have wastewater treatment facilities (Fredskilde 2006). Each hospital discharges hundreds of cubic meter of untreated wastewater into the environment a day. The medical wastewater carries a lot of germs and bacteria which are the main threat to public health. Untreated medical wastewater, industrial wastewater and municipal wastewater are combined in municipal sewage system and then discharged to channels and rivers. On average, there are 3.1 million m<sup>3</sup> of municipal, industrial and medical wastewater discharged into the environment per day. Water pollution is also found in rural areas as well. The main reason for water pollution in rural areas is pesticide and fertilizer residuals. Due to poor cropping practices, pesticides and fertilizers are often over used. Pesticide consumption increased from 14 000 tons under 837 trade names in 1990 to 50 000 tons under more than 3000 trade names in 2008. Consequently, run-off through crop fields forms considerable non-point source pollution.

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; Schechter et al., 1989, 2001; Kishida et al., 2001; Nhan et al., 2001; Hung & Thiemann, 2002; Toan et al., 2007; To et al., 2007).

#### **1.4 Objectives of this study**

As it has commented before, the more number of OMPs present in the environment, the more necessary screening methods develop for detection of a large number of OMPs. The aim of this study is to develop a comprehensive screening method for more than three hundred organic chemicals including PPCPs and pesticides in water samples using a combination of solid-phase extraction (SPE) and liquid chromatography time-of-flight mass spectrometry (LC-TOF/MS). This developed method allows detecting a huge number of potential contaminants in a sample without re – analysis. It provides full scan spectra with high sensitivity and mass accuracy, thus it can be applied for target and non - target screening.

Monitoring data for PPCPs and pesticides are generally poor in Vietnam, because it is difficult to carry out organic chemical analysis due to problems of inadequate facilities, impure reagents, and financial constraints. Therefore we applied the developed methods to monitor hundreds of micro-organic pollutants in surface water and groundwater from Vietnam. The results of this study are expected to be helpful in clarifying the water pollution by micro-organic pollutants, especially by polar organic pollutants in Vietnam; assessing and minimizing the environmental impact of these contaminants.

## Chapter 2

**DEVELOPMENT OF A TARGET SCREENING METHOD OF MICRO-POLLUTANTS IN WATER SAMPLES USING SOLID-PHASE EXTRACTION AND TIME-OF-FLIGHT MASS SPECTROMETRY****2.1 Introduction**

Although the number of all chemicals used in commerce is estimated to be 70 000-100 000 (UNEP 2006), the number of chemicals that are routinely examined in environmental samples is very limited. For example, in Japan, only 53 substances (Ministry of the Environment, Japan (MOE)), are monitored regularly in the aquatic environment, which is not enough to adequately evaluate the safety of the environment and to protect aquatic life and human health. In that context, it is particularly important to be able to quickly assess pollution caused by accidents and natural disasters, such as earthquakes (Tanabe et al. 2011). Historically, when assessing large numbers of organic substances, many analytical methods have had to be employed, which is time consuming, costly, resource intensive and may also result in large amounts of wastes. Preliminary screening of samples using rapid assessment tools is thus an increasingly attractive prospect for water environment managers. In that context, we have developed an Automated Identification and Quantification System with a GC-MS Database (AIQS) (Kadokami et al. 2004; 2005) that can determine the concentrations of nearly 1000 semi-volatile organic compounds (SVOCs). In turn, comprehensive screening methods for these SVOCs in water, soil and sediment samples have been developed (Jinya et al. 2011, Jinya et al. 2013; Kadokami et al. 2012) and applied to actual environmental samples (Duong et al. 2014; Pan et al. 2014; Kong et al. 2015).

The recent rapid progress of liquid chromatography-mass spectrometry (LC-MS) has allowed environment researchers and managers to understand pollution by emerging chemicals including polar pharmaceuticals and personal care products (PPCPs) (Bester 2007; Brack et al. 2015) and other emerging chemicals in environmental waters (Kümmerer 2009; Luo et al. 2014; Kolpin et al. 2002; Nakada et al. 2007). Most analytical methods using LC-MS/MS for environmental surveys utilize selected reaction monitoring (SRM), which limits the number of chemical

targets to less than one hundred (Okuda et al. 2009; Petrovic et al. 2010; United States Environmental Protection Agency (EPA) 2007; Rodil et al. 2009; Shao 2009; Gracia-Lor et al. 2011). To overcome this restriction on the number of target chemicals, LC-time-of-flight/MS (LC-TOF/MS) and LC-quadrupole-TOF/MS (LC-QTOF/MS) are used for determination of large numbers of compounds (Gómez et al. 2010; Ferrer and Thurman 2012; Martínez Bueno et al. 2012; Hernández et al. 2012; Masiá et al. 2013, Robles-Molina et al. 2014). However, although LC-QTOF/MS has great quantification and identification capabilities because of the ability to obtain accurate mass measurements of the molecular ions in TOF mode and of the product ions obtained in SRM mode, the high cost of these instruments reduces its availability in environmental laboratories.

Solid-phase extraction (SPE) has become a popular way to remove sample matrix materials before chemical analysis because using SPE, small sample volumes are needed and a large number of polar compounds can be efficiently extracted with little solvent consumption, and simultaneous extraction by the SPE technique has been reported for numerous analytes measurable by LC-MS (Okuda et al. 2009; EPA 2007; Rodil et al. 2009; Shao 2009; Gracia-Lor et al. 2011; Gómez et al. 2010; Ferrer and Thurman 2012; Masiá et al. 2013). This study was undertaken in order to develop a low-environmental-load simultaneous analytical method for LC-MS-amenable organic chemicals (LOCs) in water samples. For this purpose, SPE conditions suitable for the simultaneous extraction of LOCs from water samples were investigated, and the effectiveness of the SPE method used together with LC-TOF/MS measurement was confirmed.

## **2.2 Materials**

### **2.2.1 Reagents and equipment**

Chemical standards were purchased from Kanto Chemical (Tokyo, Japan) and Hayashi Pure Chemical (Osaka, Japan). Analytical-grade pharmaceuticals were obtained from Kanto Chemical, Funakoshi (Tokyo, Japan), Tokyo Chemical Industry (Tokyo, Japan), Wako Pure Chemical Industries (Osaka, Japan), Dr. Ehrenstorfer GmbH (Augsburg, Germany), LKT laboratories (St Paul, MN, USA), Sigma-Aldrich

Japan (Tokyo, Japan) and Santa Cruz Biotechnology (Dallas, TX, USA). LC/MS-grade methanol and acetonitrile and pesticide-grade dichloromethane were purchased from Kanto Chemical (Tokyo, Japan). Stock solutions ( $1000 \mu\text{g L}^{-1}$ ) of each substance were prepared with methanol or acetonitrile and kept at  $-20 \text{ }^\circ\text{C}$  in a freezer. Working mixed standard solutions were made by diluting the stock solutions with methanol. The deuterium labeled standards that were used as internal standards (IS), surrogates and for evaluating matrix effects were purchased from Kanto Chemical, Wellington Laboratories Japan (Tokyo, Japan), Hayashi Pure Chemical, Cambridge Isotope Laboratories (Andover, MA, USA), and Sigma-Aldrich Japan. The HPLC-grade ammonium acetate ( $1 \text{ mol L}^{-1}$ ) used for HPLC mobile phase was obtained from Wako Pure Chemical Industries (Osaka, Japan). Special-grade disodium hydrogenphosphate ( $\text{Na}_2\text{HPO}_4$ ) and anhydrous sodium dihydrogenphosphate ( $\text{NaH}_2\text{PO}_4$ ) were purchased from Kanto Chemical (Tokyo, Japan) and used to prepare the  $1 \text{ mol L}^{-1}$   $\text{NaH}_2\text{PO}_4$ –  $\text{Na}_2\text{HPO}_4$  (pH 7.0) buffer solution that was used for adjusting the pH of samples. The SPE cartridges used were Waters Sep-Pak PS2 and Waters Sep-Pak AC2 (Nihon Waters, Tokyo, Japan). Whatman GMF-150 glass fiber filters (47 mm diameter) were purchased from GE Healthcare Japan (Tokyo, Japan). A GL-SPE vacuum manifold system was purchased from GL Sciences (Tokyo, Japan). An Agilent 1200 HPLC with a 6220 MSD (Agilent, Santa Clara, CA, USA) was used for chemical separation and determination. All glassware and plastic ware were cleaned with detergent and water, washed in an ultrasonic cleaner, dried and rinsed with methanol before use.

### 2.1.1 Solid-phase extraction materials

In this study, five commercial SPE cartridges (Table 2-1) that contain different absorbent were examined to find absorbents that can simultaneously extract the large number of LOCs being examined. These SPE cartridges were conditioned by passing 10 mL of dichloromethane, 10 mL of methanol and 10 mL of purified water through them before use. In order to select SPE cartridges suitable for simultaneous extraction of target compounds, 200 mL of purified water was spiked with 128 pesticides at  $0.5 \mu\text{g L}^{-1}$  and extracted using the five different SPE cartridges.

**Table 2-1** Solid-phase extraction materials studied

Code	Commercial name	Sorbent type	Sorbent weight, mg	Manufacture
C18	Sep-Pak C18 Plus	Octadecyl silica (ODS)	360	Nihon Waters
PS2	Sep-Pak PS2Plus	Styrenedivinylbenzene (SDB)	300	Nihon Waters
HLB	Oasis HLB Plus	Styrenedivinylbenzene (SDB) + N-vinylpyrrolidone	225	Nihon Waters
AC2	Sep-Pak AC2Plus	Activated carbon	400	Nihon Waters
PLS-3	InertSep PLS-3	Styrenedivinylbenzene (SDB) + N-methacrylate	200	GL Science

The recovery rates were calculated using the following equation:

$$\text{Recovery, \%} = 100 \times (A - B) / C \quad (1)$$

where A = detected concentration,  $\mu\text{g L}^{-1}$ ; B = blank concentration,  $\mu\text{g L}^{-1}$ ; and C = spiked concentration,  $\mu\text{g L}^{-1}$ .

In order to evaluate applicability of the developed method to real samples, we also carried out recovery tests using effluents collected from sewage treatment plants (STP); such samples are considered difficult to analyze due to large amounts of matrix they contain. Effluents of five STPs sampled from Kitakyushu City were spiked with 190 MCs at  $0.20 \mu\text{g L}^{-1}$  and extracted by the final developed SPE method and analyzed. Unspiked samples were also analyzed. The recoveries were calculated using equation (1).

## 2.1 Experimental

### 2.1.1 Model compounds

All of the target compounds examined in this study are listed in Table S2-1. It is, however, impractical to examine all of those standards during method development. Therefore, 190 substances were selected as model compounds (MCs) (Table 2-2). These MCs have a wide range of log Pow (logarithm of the octanol–water partition



coefficient; from  $-2.20$  to  $8.53$ ) covering the range of targets examined using this method. In experiments conducted for selection of SPE materials and recovery tests using reagent water and wastewater in sewage treatment plants, 128 pesticides (log Pow:  $-2.20 - 5.03$ , Table S2-2,) and 190 MCs (log Pow:  $-2.20 - 8.53$ , Table 2-2) were used, respectively.

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
1	PPCP	Sulfadiazine	20	8.05	-0.09	79.6	11.6	81.7	10.4	98.1	11.9	99.9	7.3	24.8	20.8
2	PPCP	Acetaminophen <sup>a</sup>	20	8.31	0.46	77.9	8.9	45.7	10.9	93.2	4.4	47.3	12.4	48.2	19.9
3	PPCP	Terbutaline	8	8.97	0.90	87.6	5.7	81.5	10.2	94.0	4.3	101.7	4.9	52.3	18.0
4	PPCP	Sulfamethizole	8	9.03	0.54	84.5	9.7	85.3	9.2	89.0	15.4	90.8	6.3	28.1	6.0
5	PPCP	Sotalol	8	9.08	0.24	91.6	6.1	82.3	10.1	116.7	4.1	94.4	25.9	118.2	11.3
6	PPCP	Salbutamol	80	9.30	0.01	90.0	6.0	85.3	11.6	ND	ND	ND	ND	71.2	18.4
7	PPCP	Atenolol <sup>a</sup>	8	9.80	0.16	90.2	5.9	89.1	8.2	110.2	3.4	104.5	5.0	86.4	0.6
8	PPCP	Sulfamethoxazole <sup>a</sup>	20	10.40	0.89	87.9	7.3	82.9	11.0	100.3	9.1	101.8	7.2	82.8	18.2
9	PPCP	Sulfathiazole	20	10.62	0.05	80.5	12.9	86.1	17.8	87.6	15.4	100.1	7.6	45.2	11.0
10	Pest	Nitenpyram	8	10.89	-0.66	72.8	13.6	79.7	12.1	87.7	15.7	87.8	11.1	60.2	17.5
11	PPCP	Sulfapyridine <sup>a</sup>	8	11.41	0.35	88.0	8.7	84.8	11.1	100.7	13.3	99.0	6.7	89.1	18.2
12	PPCP	Sulfamerazine	8	11.55	0.14	90.1	8.6	84.9	11.6	101.5	11.5	99.2	6.6	53.5	20.6
13	Pest	Flumetsulam	8	11.64	-0.68	84.8	7.5	93.6	7.5	108.3	2.4	97.6	6.1	62.8	17.4
14	PPCP	Sulfamonomethoxine	8	11.78	-0.04	89.4	7.7	84.4	9.4	103.1	10.1	99.9	6.7	75.4	12.0
15	PPCP	Sulpiride <sup>a</sup>	20	12.21	0.57	92.9	5.3	93.3	4.7	112.6	3.5	105.4	4.8	353.8	31.8
16	PPCP	Cotinine <sup>a</sup>	8	12.21	-0.23	82.4	15.4	80.0	17.6	111.5	15.7	98.1	3.7	60.9	11.8
17	PPCP	Ranitidine	20	12.52	0.27	39.9	15.2	40.6	13.1	42.6	5.5	48.9	13.7	67.8	12.9

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
18	Pest	Pymetrozin	8	12.98	-0.18	78.3	7.7	84.5	9.4	92.9	20.4	88.4	8.4	55.5	21.6
19	PPCP	Cimetidine	8	13.34	0.40	57.3	18.3	12.9	18.6	25.9	8.8	16.7	15.9	76.0	21.9
20	Pest	Thifensulfuron-methyl	80	13.88	0.02	83.7	4.8	95.0	8.8	ND	ND	ND	ND	69.0	13.6
21	Pest	Metsulfuron-methyl	80	13.89	0.02	82.5	6.1	92.1	8.3	ND	ND	ND	ND	74.4	9.4
22	Pest	Imazaquin	8	14.65	0.34	81.4	7.2	68.5	14.7	106.9	4.6	83.9	9.4	44.6	24.3
23	Pest	Florasulam	80	14.70	-1.22	89.7	5.9	92.5	6.7	ND	ND	ND	ND	69.2	11.9
24	Pest	Azimsulfuron	80	14.72	0.04	82.9	5.1	83.2	10.0	ND	ND	ND	ND	49.6	18.3
25	PPCP	Carbadox	80	15.04	-1.37	66.9	12.0	91.8	8.6	ND	ND	ND	ND	63.1	15.7
26	Pest	Chlorsulfuron	80	15.09	-0.99	81.3	5.9	88.6	9.3	ND	ND	ND	ND	64.5	19.0
27	Pest	Imidacloprid	40	15.21	0.57	82.9	6.7	85.2	7.9	110.9	5.6	93.4	7.4	81.7	8.8
28	PPCP	Antipyrine	8	15.41	0.38	83.9	11.0	78.3	19.2	110.5	13.4	97.6	3.4	71.5	16.4
29	Pest	Clofencet	80	15.43	-2.20	75.6	9.4	75.1	21.5	ND	ND	ND	ND	34.0	20.7
30	PPCP	Sulfadimethoxine	8	15.47	1.63	88.4	7.8	87.0	7.5	103.5	10.6	100.1	4.5	51.8	17.9
31	Pest	Cinosulfuron	80	15.53	2.04	86.2	5.4	93.2	9.1	ND	ND	ND	ND	78.2	9.0
32	PPCP	Pirenzepine	8	15.75	0.60	90.1	6.5	88.8	7.4	109.0	3.2	97.4	5.0	106.5	7.5
33	Pest	Foramsulfuron	80	15.89	0.17	85.4	5.7	106.2	11.3	ND	ND	ND	ND	70.3	14.0

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
34	Pest	Thiabendazole metabolite	8	16.06	1.73	82.0	5.4	94.6	9.3	90.8	5.5	87.2	7.7	51.9	12.5
35	Pest	Flazasulfuron	80	16.11	-0.06	82.3	3.6	83.9	11.5	ND	ND	ND	ND	72.5	7.7
36	Pest	Sulfosulfuron	80	16.29	1.00	91.8	5.6	96.8	7.7	ND	ND	ND	ND	85.0	7.9
37	Pest	Acetamiprid	8	16.35	0.80	93.5	4.7	93.5	12.0	113.0	10.7	96.0	7.8	71.3	14.1
38	PPCP	Scopolamine	8	16.43	0.98	93.4	5.9	95.9	8.6	103.2	3.5	99.3	3.5	72.4	12.2
39	Pest	Triasulfuron	80	16.59	1.10	88.9	4.8	101.3	8.7	ND	ND	ND	ND	85.4	9.2
40	PPCP	Trimethoprim <sup>a</sup>	8	16.66	0.91	94.7	5.3	97.0	7.3	103.4	4.3	102.5	6.5	90.9	9.3
41	Pest	Chloridazon	8	16.71	1.19	87.7	5.0	91.7	11.3	111.1	5.7	90.6	9.6	65.1	13.7
42	PPCP	Metoclopramide	8	16.85	2.62	91.3	6.3	92.1	11.4	99.0	4.7	94.7	12.9	89.3	9.5
43	Pest	Tribenuron methyl	40	16.89	0.78	60.6	10.0	22.8	12.9	87.2	16.2	54.1	16.6	90.9	13.6
44	Pest	Fenthion oxon sulfoxide	8	16.90	-0.11	91.6	8.4	99.3	15.8	114.7	1.0	105.0	8.0	78.2	15.7
45	PPCP	Candesartan <sup>a</sup>	8	16.92	5.01	91.0	7.9	91.1	9.4	99.1	9.4	101.6	5.7	84.7	20.8
46	Pest	Imazosulfuron	8	17.11	1.72	83.8	5.6	84.2	14.1	96.7	10.3	94.8	8.1	71.8	8.4
47	PPCP	Pentoxifylline	20	17.44	0.29	99.9	5.5	90.0	16.0	123.8	8.1	105.4	4.7	83.5	9.1
48	Pest	Mesosulfuron-methyl	80	17.45	1.17	87.6	5.8	111.3	11.3	ND	ND	ND	ND	78.5	8.8
49	PPCP	Ifosfamide	8	17.52	0.86	95.2	5.9	84.3	17.2	106.5	11.9	98.0	10.2	73.7	8.7
50	PPCP	Disopyramide <sup>a</sup>	8	17.55	2.58	94.5	5.2	98.7	6.0	110.5	3.4	104.5	6.8	111.2	12.1

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
51	PPCP	Ormetoprim	8	17.62	1.55	90.9	3.3	93.1	3.7	111.4	5.0	104.0	5.0	72.8	10.9
52	Pest	Carbendazim <sup>a</sup>	8	17.70	1.51	86.9	7.9	83.6	21.6	106.6	13.4	92.1	10.8	85.6	10.6
53	Pest	Ethametsulfuron-methyl	80	17.71	0.89	93.8	5.6	101.6	7.4	ND	ND	ND	ND	70.7	8.0
54	PPCP	Metoprolol	8	17.76	1.88	93.6	6.1	95.7	8.9	107.6	4.5	102.0	3.6	79.7	8.6
55	PPCP	Dicyclohexylamine <sup>a</sup>	8	18.03	3.69	86.2	12.4	87.8	13.2	109.4	8.1	99.9	3.0	63.7	59.9
56	Pest	Pyrazosulfuron-ethyl	80	18.24	3.16	87.4	4.8	88.8	12.2	ND	ND	ND	ND	64.3	17.7
57	Pest	Trifloxysulfuron-sodium	80	18.27	-0.43	91.3	4.4	103.0	8.3	ND	ND	ND	ND	61.8	10.3
58	PPCP	Cyclophosphamide	8	18.35	0.80	90.3	6.6	85.5	17.4	98.7	9.9	100.4	9.5	75.1	20.3
59	Pest	Thiacloprid	8	18.38	0.55	90.8	6.0	90.5	13.3	105.4	4.1	96.7	7.3	66.8	13.6
60	Pest	Iodosulfuron-methyl-sodium	80	18.45	-0.70	91.0	4.1	89.1	9.9	ND	ND	ND	ND	104.5	12.2
61	PPCP	Phenacetin	8	18.54	1.58	83.6	10.8	90.2	16.0	110.8	16.7	97.5	3.1	69.5	11.1
62	Pest	Halosulfuron-methyl	80	18.57	-0.02	85.8	6.6	85.3	11.7	ND	ND	ND	ND	65.7	7.1
63	Pest	Tricyclazole	8	18.91	1.42	82.1	8.3	81.5	21.8	113.3	16.4	91.7	8.1	66.6	12.8
64	PPCP	Warfarin	8	19.10	2.27	90.1	6.2	82.6	13.2	99.1	4.2	102.9	5.3	73.7	10.6
65	Pest	Metosulam	80	19.39	2.46	87.4	6.2	105.7	8.9	ND	ND	ND	ND	85.6	9.9
66	Pest	Penoxsulam	80	19.54	-0.35	88.6	5.5	101.8	7.0	ND	ND	ND	ND	87.1	9.2
67	Pest	Tepraloxydim	20	19.58	2.88	77.5	13.3	67.4	25.4	93.2	11.4	83.1	20.0	73.8	10.7

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
68	PPCP	Tolbutamide	20	19.62	2.34	91.9	6.0	83.1	13.4	105.4	8.9	100.5	4.3	79.9	17.0
69	Pest	Chlorimuron-ethyl	80	19.86	0.11	85.3	6.4	97.2	16.3	ND	ND	ND	ND	84.0	9.3
70	PPCP	Carazolol	8	19.96	3.59	90.2	5.5	95.2	9.2	101.5	2.3	101.9	7.9	82.2	10.2
71	PPCP	Bisoprolol	8	19.97	2.14	93.7	6.3	95.3	7.9	105.4	3.7	109.3	8.9	96.4	11.1
72	PPCP	Epinastine	8	20.14	3.51	93.4	5.5	91.9	11.4	105.0	4.4	106.2	4.9	112.4	11.1
73	Pest	Diclosulam	40	20.33	0.85	90.8	6.3	88.2	5.7	99.9	6.2	93.1	10.2	78.3	14.1
74	Pest	Cyanazine	8	20.47	2.24	84.9	6.5	83.9	17.3	102.3	7.9	93.2	5.7	70.1	11.5
75	Pest	Metribuzin	8	20.58	1.60	72.4	16.1	84.4	14.7	96.6	12.8	83.9	12.0	60.9	10.9
76	PPCP	Flumequine	40	20.65	2.41	93.7	6.5	78.6	14.3	96.7	10.8	111.3	22.1	73.1	13.5
77	Pest	Bromacil	40	20.77	2.14	86.3	7.4	94.3	17.0	100.7	10.2	92.9	21.2	81.1	9.4
78	Pest	Sulfentrazone	80	20.79	1.48	88.7	4.4	93.3	11.4	ND	ND	ND	ND	77.5	10.3
79	PPCP	Ifenprodil	8	20.97	4.25	91.3	5.7	95.7	7.4	84.4	2.9	115.1	17.0	103.8	13.8
80	PPCP	Lincomycin	80	21.01	0.91	89.3	6.6	86.1	7.7	ND	ND	ND	ND	70.6	8.3
81	Pest	Thiabendazole <sup>a</sup>	8	21.02	2.39	82.1	5.9	91.1	12.7	96.5	8.7	88.7	7.8	72.0	7.1
82	PPCP	Mepirizole	8	21.30	1.01	80.8	13.4	76.1	14.3	97.6	15.2	82.2	9.1	74.6	16.0
83	Pest	Clodinafop	80	21.32	2.49	87.9	6.0	94.4	15.7	ND	ND	ND	ND	79.2	11.5
84	Pest	Carbofuran	8	21.42	1.52	82.6	15.7	96.8	15.7	112.0	18.5	101.8	8.6	74.9	10.7

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
85	Pest	Fluazifop	80	21.50	1.98	86.4	5.4	87.8	17.7	ND	ND	ND	ND	83.6	8.0
86	PPCP	Betaxolol	8	21.57	2.69	92.3	6.7	93.6	8.8	105.6	4.1	106.2	6.0	96.7	8.9
87	Pest	Isouron	20	21.60	1.98	78.1	13.5	87.1	21.0	107.5	19.5	88.0	11.1	83.3	12.9
88	Pest	Tebuthiuron	8	21.72	1.82	78.4	13.5	81.6	25.4	110.3	19.3	90.7	10.7	76.8	13.5
89	PPCP	Propranolol	8	21.76	3.48	91.1	6.7	91.9	10.1	112.0	7.7	101.7	6.5	91.2	7.8
90	PPCP	Carbamazepin <sup>a</sup>	8	21.90	1.51	91.8	5.4	82.0	16.3	104.2	7.8	101.9	4.2	94.8	8.7
91	Pest	Bensulfuron-methyl	80	22.13	0.79	87.1	4.9	94.2	9.9	ND	ND	ND	ND	87.3	7.1
92	PPCP	Prednisolone	8	22.16	1.62	93.7	5.9	97.0	9.1	108.0	7.7	102.9	3.6	80.6	11.2
93	Pest	Fenthion sulfoxide	8	22.21	1.81	98.4	6.1	96.5	18.6	121.9	5.5	108.1	9.6	96.9	13.0
94	PPCP	Propyphenazole	8	22.77	1.74	82.9	9.7	92.0	3.2	87.9	18.2	80.3	17.2	92.6	11.1
95	PPCP	Losartan <sup>a</sup>	8	23.13	6.10	82.4	8.7	87.3	7.6	94.4	13.7	97.0	4.9	59.0	17.4
96	PPCP	Diphenidol	8	23.25	4.30	90.7	7.0	94.4	6.9	105.2	4.7	100.1	3.9	97.2	10.3
97	PPCP	Tolperisone	8	23.38	3.81	85.6	10.1	84.3	13.2	99.9	7.5	93.4	7.0	66.8	20.3
98	Pest	Dimethirimol	8	23.39	2.79	75.5	13.8	86.7	17.7	93.9	13.9	87.6	12.0	90.0	13.7
99	Pest	Pirimicarb	8	23.40	1.70	77.6	12.2	85.4	14.8	91.6	19.2	89.0	13.4	83.8	11.5
100	Pest	Furametpyr	8	23.63	2.36	84.8	7.8	88.5	17.4	106.2	12.5	93.1	8.6	89.6	10.7
101	Pest	Cyclosulfamuron	80	23.64	1.41	84.9	4.1	91.5	9.6	ND	ND	ND	ND	95.5	5.8

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
102	PPCP	Dexamethasone	8	23.64	1.83	96.1	5.7	104.6	6.5	103.8	4.2	104.9	6.6	91.1	11.0
103	Pest	Methabenzthiazuron	8	23.82	2.64	71.9	15.2	85.3	12.8	107.6	29.5	84.1	13.1	85.6	15.6
104	Pest	Fomesafen	40	23.92	2.90	91.0	6.7	98.7	11.2	99.2	6.6	100.1	17.9	88.7	8.3
105	Pest	Mepanipyrim_metabolite	8	23.97		82.0	8.0	85.2	15.3	107.5	15.5	91.8	10.2	96.3	14.9
106	Pest	Forchlorfenuron	8	23.98	3.20	82.7	5.0	92.9	6.7	100.3	4.5	90.7	9.5	74.7	10.2
107	PPCP	Griseofulvin	8	24.11	2.18	89.4	5.1	85.2	10.0	103.2	4.0	100.3	4.4	85.1	8.7
108	PPCP	Etodolac <sup>a</sup>	8	24.20	2.50	76.2	10.3	65.4	19.6	88.7	6.3	85.6	12.4	68.0	12.5
109	PPCP	Dextromethorphan	20	24.22	3.60	90.4	7.7	85.6	10.6	102.8	4.8	100.4	2.3	105.1	11.6
110	Pest	Diuron <sup>a</sup>	8	24.23	2.85	86.0	6.6	85.9	21.6	104.0	14.5	91.6	9.6	97.6	12.2
111	PPCP	Lidocaine <sup>a</sup>	8	24.37	2.44	77.8	17.2	82.0	13.2	97.7	9.2	96.0	5.4	105.4	16.9
112	PPCP	Virginiamycin M1	20	24.40	-0.66	83.8	8.0	86.8	5.3	97.5	12.2	94.0	8.9	69.6	1.7
113	PPCP	Paroxetine	8	24.54	3.60	79.5	10.3	76.0	14.0	79.5	9.3	90.0	15.0	56.7	10.8
114	Pest	Metominostrobin (E)	8	24.58	2.32	82.5	8.2	81.6	15.6	109.9	15.2	91.4	11.7	82.2	15.2
115	PPCP	Haloperidol	8	25.08	4.30	86.9	6.2	89.8	6.6	97.6	3.2	95.7	3.5	74.4	18.5
116	PPCP	Fluvoxamine	8	25.18	3.20	53.2	17.5	51.2	19.3	62.9	9.2	69.8	16.0	40.6	21.6
117	Pest	Fenobucarb	8	25.23	2.79	72.4	13.8	77.9	16.8	87.9	8.2	89.5	15.3	71.5	11.2
118	Pest	Propanil	80	25.40	3.12	89.7	10.0	64.9	42.7	ND	ND	ND	ND	93.4	13.5



## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
119	PPCP	Erythromycin	8	25.50	3.06	90.4	5.4	91.4	7.6	90.7	6.3	95.6	6.7	132.2	12.0
120	Pest	Inabenfide	20	25.52	3.13	85.6	5.6	90.5	9.1	98.5	6.8	92.5	8.7	83.4	9.4
121	Pest	Siduron	8	25.58	3.80	90.5	5.3	90.6	17.9	107.8	7.1	107.3	12.2	93.8	9.6
122	Pest	Sethoxydim	8	25.61	4.51	43.3	16.1	32.6	19.2	64.5	12.1	47.5	17.1	68.3	11.5
123	PPCP	Fluoxetine	8	25.76	4.05	81.1	9.0	81.9	15.1	75.8	11.9	89.6	4.8	57.8	15.6
124	Pest	Ametryn	8	25.94	2.98	68.8	15.8	69.6	20.3	93.8	14.2	80.3	16.6	88.1	9.1
125	Pest	Fluridone	8	26.00	1.87	85.6	7.6	88.1	8.9	118.1	4.2	97.0	8.0	93.6	18.4
126	Pest	Linuron	40	26.00	3.00	78.0	19.9	77.0	17.3	94.8	17.9	83.2	14.3	93.1	16.1
127	PPCP	Diazepam	8	26.04	2.91	83.9	7.7	71.9	15.6	96.2	11.2	98.1	5.4	91.2	12.7
128	PPCP	Imipramine	8	26.04	4.80	84.4	8.3	81.1	8.3	90.6	7.7	91.9	3.2	79.9	9.5
129	Pest	Azoxystrobin	8	26.07	2.50	85.1	7.8	80.1	11.4	108.1	5.6	86.6	18.3	87.0	12.6
130	Pest	Dimethomorph(E)	8	26.17	2.63	82.0	7.0	76.4	13.0	89.4	14.8	87.1	10.5	83.6	10.4
131	Pest	Fenamidone	8	26.27	2.80	82.3	6.5	77.3	15.1	94.8	5.3	84.4	15.9	85.9	11.9
132	Pest	Boscalid	40	26.31	2.96	81.3	7.4	78.0	18.6	100.7	11.7	90.0	11.2	85.9	10.6
133	Pest	Pyriminobac-methyl (Z)	4	26.46	2.11	113.7	14.4	79.4	15.6	104.8	18.3	89.7	7.9	45.2	17.8
134	PPCP	Testosterone	40	26.62	3.32	85.5	8.2	80.0	22.6	103.1	21.7	104.8	7.1	86.0	11.9
135	Pest	Dimethomorph(Z)	8	26.67	2.73	94.9	3.8	89.6	14.1	109.2	6.5	96.3	6.2	90.2	9.5

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
136	Pest	Dymron	8	26.69	2.70	89.7	5.3	89.2	10.0	103.6	4.9	93.1	7.7	93.0	12.8
137	PPCP	Verapamil	8	26.71	3.79	87.5	6.1	82.2	5.6	98.7	5.9	92.0	6.4	85.4	7.5
138	Pest	Ferimzone(E) <sup>a</sup>	8	26.81	2.83	58.5	11.6	53.4	18.4	82.4	12.4	60.7	17.4	61.7	17.2
139	Pest	Fenhexamid	80	26.91	3.51	85.4	7.3	88.6	16.4	ND	ND	ND	ND	84.2	10.9
140	Pest	Cumyluron	8	26.95	2.61	85.5	5.1	84.2	13.8	97.3	8.4	91.4	8.1	78.2	14.4
141	Pest	Benzobicyclon	8	26.96	3.10	79.8	4.9	78.9	13.5	86.3	7.0	72.9	12.9	56.2	17.2
142	Pest	Chloroxuron	8	26.98	3.20	83.3	15.0	84.6	18.5	100.4	10.8	90.0	7.4	86.5	14.6
143	Pest	Ferimzone(Z) <sup>a</sup>	8	27.07	2.83	75.0	12.2	73.2	20.9	107.4	15.6	76.2	6.5	86.4	17.0
144	Pest	Triticonazole	8	27.16	3.29	83.2	5.4	85.7	18.3	93.9	8.9	92.0	10.2	87.4	13.6
145	Pest	Triflumizole metabolite	8	27.18		64.4	23.0	70.7	21.1	90.2	23.3	83.1	16.6	64.3	10.2
146	Pest	Tetraconazole	8	27.21	3.56	106.1	12.5	80.4	15.7	94.4	12.9	80.1	16.1	82.8	11.0
147	PPCP	Clarithromycin <sup>a</sup>	8	27.23	3.16	87.4	6.3	88.2	6.8	94.8	7.2	93.8	7.7	78.5	23.7
148	PPCP	Diltiazem <sup>a</sup>	8	27.35	2.80	88.0	6.1	84.2	5.9	101.9	4.1	96.0	7.5	100.7	22.2
149	Pest	Simeconazole	8	27.56	3.20	76.3	11.1	81.4	19.7	95.6	12.1	91.6	9.4	84.6	10.9
150	Pest	Prometryn	8	27.59	3.10	86.9	18.1	67.3	19.4	89.2	13.8	77.3	21.7	75.2	12.1
151	Pest	Thifluzamide	8	27.64	4.10	116.1	17.1	104.5	19.5	128.9	9.8	93.8	19.2	89.6	9.8
152	Pest	Flufenacet	8	27.67	3.20	73.4	11.2	84.6	18.2	89.1	12.6	83.9	14.8	73.8	15.3

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL						Effluent, 200mL					
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>			
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %		
153	Pest	Cyazofamid	8	27.69	3.20	67.1	8.8	65.2	13.8	89.4	9.9	69.7	10.4	34.3	15.1		
154	Pest	Butafenacil	8	27.70	3.20	83.9	4.6	82.2	13.2	103.4	7.1	90.5	4.8	83.9	10.5		
155	Pest	Fipronil	40	27.91	4.00	87.6	6.2	83.2	26.1	97.4	7.1	96.0	8.5	84.5	11.4		
156	Pest	Chromafenozide	8	27.92	2.70	88.6	4.9	88.6	10.3	104.5	4.7	96.1	7.0	93.5	4.6		
157	Pest	Epoxiconazole	8	27.94	3.44	75.2	5.4	79.4	15.4	92.5	12.9	89.0	11.4	90.4	7.1		
158	PPCP	Amitriptyline	8	28.07	4.92	82.1	9.5	80.0	12.4	90.4	9.9	92.1	6.2	73.8	12.7		
159	Pest	Mepanipyrim	8	28.12	3.28	65.9	11.2	62.5	14.5	76.1	12.9	79.5	15.8	67.2	13.7		
160	PPCP	Roxithromycin <sup>a</sup>	8	28.18	1.70	85.5	6.8	83.0	7.5	92.7	5.3	90.1	8.1	81.6	9.2		
161	Pest	Bensulide	8	28.29	4.20	84.2	3.3	80.1	12.6	97.4	7.1	89.7	8.8	84.6	10.4		
162	Pest	Diflubenzuron	8	28.31	3.89	78.1	7.8	77.3	17.7	92.2	14.1	83.9	13.1	75.9	12.4		
163	Pest	Tebuconazole	8	28.31	3.70	99.8	13.0	78.5	19.0	92.8	10.5	89.8	12.2	91.4	8.5		
164	PPCP	Dipyridamole	8	28.42	1.50	41.0	14.4	31.4	14.6	44.3	17.6	35.2	14.3	78.6	11.0		
165	Pest	Fenoxycarb	8	28.81	4.07	72.6	8.4	76.4	11.1	76.3	14.5	77.1	11.9	71.9	16.9		
166	Pest	Naproanilide	20	28.81	4.31	71.0	10.0	70.0	19.6	73.9	11.7	71.3	2.7	72.4	12.7		
167	Pest	Etobenzanid	8	29.03	3.68	76.5	16.3	56.5	15.1	57.0	15.6	57.8	8.0	69.5	24.4		
168	Pest	Anilofos	40	29.16	3.81	77.1	8.8	73.0	8.9	95.9	15.5	81.8	18.5	82.3	15.5		

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
169	PPCP	Chlorpromazine	8	29.80	5.41	45.8	16.5	39.5	13.6	54.9	13.6	51.8	19.0	30.5	17.3
170	Pest	Difenoconazole	20	29.81	4.40	91.8	14.0	71.9	19.3	84.3	12.6	79.6	22.7	81.6	10.4
171	Pest	Pencycuron	40	29.82	4.68	72.7	8.1	76.8	18.7	82.6	11.8	78.2	24.3	78.0	18.7
172	Pest	Cyprodinil	40	29.84	4.00	56.8	16.7	59.9	14.3	62.1	7.4	58.6	12.0	50.4	17.5
173	Pest	Pyraclostrobin	40	30.00	3.99	71.7	9.4	70.0	7.2	79.6	14.6	78.1	15.8	75.4	14.9
174	Pest	Cyflufenamid	40	30.06	4.70	67.8	7.3	69.8	11.4	79.3	6.0	83.1	15.5	73.7	10.2
175	PPCP	Norgestimate	8	30.32	5.00	60.7	6.3	61.4	20.3	53.5	13.9	74.0	10.6	73.3	5.8
176	Pest	Indoxacarb	80	30.57	4.65	64.3	5.0	69.9	15.0	ND	ND	ND	ND	72.6	10.7
177	Pest	Fenoxaprop-ethyl	40	30.90	4.58	57.7	11.8	55.1	16.6	49.9	19.3	53.7	11.0	52.4	18.1
178	Pest	Oxaziclomefone	40	30.99	4.01	65.5	12.9	59.9	18.7	84.7	6.7	74.8	21.5	71.3	10.6
179	Pest	Benfuracarb	40	31.05	4.22	51.8	13.3	54.8	11.1	57.3	16.6	45.0	13.5	62.3	12.9
180	Pest	Imibenconazole	40	31.30	4.94	61.3	6.8	70.5	11.0	64.0	17.6	66.4	28.0	73.4	15.4
181	Pest	Quizalofop-ethyl	40	31.32	4.28	59.0	14.4	54.3	12.2	53.6	18.0	56.0	0.6	59.6	16.2
182	Pest	Benzofenap	40	31.32	4.69	68.0	8.1	73.6	22.7	72.0	16.7	70.3	31.7	73.6	16.4
183	PPCP	Fenofibrate <sup>a</sup>	8	31.45	5.30	51.8	11.1	49.8	13.5	37.0	19.8	45.5	19.4	44.2	17.2
184	Pest	Furathiocarb	40	31.54	4.60	59.7	13.6	61.3	14.5	60.1	18.3	69.3	11.2	61.2	15.3
185	Pest	Clomeprop	40	31.61	4.80	52.2	13.1	63.0	42.3	56.3	34.9	53.9	52.2	53.4	12.6

## Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>Pow</i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
186	Pest	Chlorfluazuron	40	32.97	5.80	35.5	10.2	37.6	15.6	41.3	11.0	48.8	38.5	47.1	12.9
187	Pest	Fenpyroximate	80	33.52	5.01	33.7	10.6	32.7	17.8	ND	ND	ND	ND	52.2	6.0
188	Pest	Spinosyn A	4	34.52	4.50	36.8	11.1	44.5	17.3	59.2	13.1	40.3	16.6	53.7	13.9
189	Pest	Spinosyn D	8	34.92	4.50	40.7	14.8	26.8	20.9	56.2	15.2	31.4	22.6	46.6	18.6
190	PPCP	Salinomycin	8	35.51	8.53	73.9	6.8	69.0	8.9	89.1	9.0	76.6	6.2	82.6	14.6
1	Surrogate	Methamidophos-d6		4.22	-0.78	71.8	20.7	77.8	16.2	NT		NT		75.8	12.9
2	Surrogate	Sulfamethoxazole-d4		9.83	0.66	81.1	9.9	85.4	9.7	NT		NT		48.5	18.3
3	Surrogate	Sulfadimethoxine-d6		15.14	1.60	85.3	8.0	86.1	5.9	NT		NT		51.8	18.2
4	Surrogate	Simazine-d10		20.64	2.30	77.7	16.7	79.0	27.5	NT		NT		76.8	12.3
5	Surrogate	Diflubenzuron-d4		27.44	3.70	69.4	8.9	69.3	27.2	NT		NT		83.0	12.3
6	Surrogate	Ethofenprox-d5		34.32	7.30	24.2	23.1	37.5	40.0	NT		NT		29.7	22.9
1	Matrix	Cimetidine-d3		13.27	0.26	NT		99.1	3.8	NT		NT		64.1	10.2
2	Matrix	Clothianidin-d3		14.42	-0.15	NT		99.7	2.1	NT		NT		49.4	22.6
3	Matrix	Imidacloprid-d4		14.57	0.33	NT		102.6	2.9	NT		NT		77.8	10.6
4	Matrix	Carbendazim-d4		17.13	1.51	NT		100.7	2.2	NT		NT		77.6	6.8
5	Matrix	Carbofuran-d3		20.46	1.70	NT		99.4	2.7	NT		NT		86.5	4.5
6	Matrix	Diuron-d6		23.32	2.70	NT		98.7	3.1	NT		NT		101.1	3.4

Chapter 2

**Table 2-2** Model compounds including surrogate compounds and their recoveries (continued)

No.	Class	Compound	LOD, ng L <sup>-1</sup>	RT, min	log <i>P<sub>ow</sub></i>	Reagent water, 200 mL								Effluent, 200mL	
						200 ng L <sup>-1</sup>				50 ng L <sup>-1</sup>				200 ng L <sup>-1</sup>	
						HLB+AC2		PS2+AC2		HLB+AC2		PS2+AC2		PS2+AC2	
						Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=7)	RSD, %	Avg, % (n=5 <sup>b</sup> )	RSD, %
1	Internal standard	Methomyl-d3		11.91											
2	Internal standard	Pirimicarb-d6		22.75											
3	Internal standard	Imazalil-d5		28.40											

LOD: limit of detection; RT: retention time; log *P<sub>ow</sub>*: octanol-water partition coefficient; NT: not tested; ND: not detected

<sup>a</sup>: Detected in effluents used for recovery test

<sup>b</sup>: Recovery test was done using 5 effluents collected from 5 sewage treatment plants.

### 2.1.2 Solid-phase extraction

Phosphate buffer (0.4 mL; 1 mol L<sup>-1</sup>; pH 7.0) and surrogate standards (5 µg mL<sup>-1</sup>, 40 µL, Table 2-2) were added to water sample (200 mL), and the mixture then filtered with a 47 mm glass microfiber filter (Whatman, GF/C). The pH of samples was adjusted to 7.0 because Jinya et al. (2011), Rodil et al. (2009) and Gómez et al. (2010) have shown that pH 7.0 is the optimal pH for extraction of organic compounds with a wide range of physicochemical properties. The aqueous filtrate was then passed sequentially through a Sep-Pak PS2 cartridge and a Sep-Pak AC2 cartridge at a flow rate of 10 mL min<sup>-1</sup>. The AC2 cartridges were then dried by passing nitrogen through the cartridges for 40 min, and then the LOCs were eluted from the AC2 side with 5 mL of methanol and 3 mL of dichloromethane. The suspended solids (SS) remaining on the filter paper were subjected to sonication extraction (Ultrasonic cleaner USK-3R, AS ONE, Osaka, Japan) with 3 mL of methanol twice. After combining the eluates and the extract from SS extraction, the mixture was concentrated to 200 µL under a gentle stream of nitrogen. Mixed internal standards (5 µg mL<sup>-1</sup>, 40 µL, Table 2-2) were added and the mixture reconstituted to 400 µL with methanol. The sample extract was filtered with a syringe filter (Milliex LG, Merck Millipore, Darmstadt, Germany) prior to LC-TOF/MS analysis.

### 2.1.3 LC-TOF/MS analysis

LC-TOF/MS measurement conditions are showed in Table 2-3. Samples were measured twice using different fragmentor voltages: 100 V and 100, 150, 200 and 250 V. The 100 fragmentor voltage was used for quantification and the remaining 4 voltages used for identification of in-source generated fragment ions.

MCs and surrogate compounds were determined by the internal standard (IS) method using calibration curves. The calibration curves were prepared by measuring 2 µL of calibration standards (methanol solutions) containing 0, 0.004, 0.010, 0.020, 0.040, 0.10, 0.20, 0.40 or 1.0 µg mL<sup>-1</sup> of the MCs and surrogate compounds, and 0.20 µg mL<sup>-1</sup> of IS (methomyl-d3, pirimicarb-d6 and imazalil-d5).

Since the method developed in the present study aimed to comprehensively

analyze a large number of LOCs with a wide range of physicochemical properties, acceptable target analyte recovery was set at more 50%. Target method detection limit was set  $0.01 \mu\text{g L}^{-1}$  by the consideration of instrumental detection limit of the LC-TOF/MS used in the study and a criterion concentration that meets the European Medicines Agency requirement for the environmental risk assessment for pharmaceuticals ((EMA 2006).

**Table 2-3** LC-TOF/MS conditions

LC : Agilent 1200	
Column	GL Sciences Inertsil ODS-4 (2.1×150mm, 3 $\mu$ m)
Mobile phase	A: 5 mmol CH <sub>3</sub> COONH <sub>4</sub> in H <sub>2</sub> O B: 5 mmol CH <sub>3</sub> COONH <sub>4</sub> in CH <sub>3</sub> OH
Gradient profile	A95:B5 (0 min) - A5:B95 (30 min-50 min)
Column temp	40 °C
Flow rate	0.3 mL min <sup>-1</sup>
Injection volume	2 $\mu$ L
MS : Agilent 6220 MSD	
Ionization	ESI-Positive
Measurement mode	Scan
Fragmentor Voltage	100 V for quantification 100, 150, 200 and 250 V for identification
VCap voltage	3500 V
Drying gas	10 L min <sup>-1</sup> at 325 °C
Nebulizer gas pressure	50 psi
Reference ion (m/z)	121.050873, 922.009798
Scan range (m/z)	50-1000
Mass tolerance	5 ppm

## 2.2 Results and discussion

### 2.2.1 Selection of solid-phase materials

There were clear differences in the recovery of the LOCs extracted by each of the 5 cartridge types evaluated (Table 2-4 and Table S2-2). Recoveries of the pesticides with log Pow < 2 were low when using C18, whereas PS2, HLB and PLS-3 were able to extract pesticides with log Pow below 0 to over 4. Also, the AC2 cartridge had



high recoveries of 20 pesticides that were not extracted with high recoveries by other four cartridges. From these results, it was inferred that tandem extraction using a combination of either PS2, HLB or PLS-3 and AC2 was most suitable for the simultaneous extraction of the widest range of LOCs.

**Table 2-4** Summary of results in test of selection of solid-phase materials using 128 pesticides

Average recovery, %	AC-2	C18	PS-2	HLB	PLS-3
All substances	35	52	60	60	61
log Pow <0	26	31	64	68	63
0 < log Pow <1	28	47	70	76	73
1 < log Pow <2	32	50	57	58	58
2 < log Pow <3	39	58	62	63	62
3 < log Pow <4	41	60	62	61	63
log Pow >4	37	37	47	38	45
Unknown log Pow	32	62	64	66	68

### 2.2.2 Selection of extraction apparatus and syringe filter

Although little attention is usually paid to the extraction apparatus and syringe filters in SPE method development, selection of such equipment is important for obtaining high recovery rates of target LOCs. There are two types of apparatuses for passing water samples through cartridges: pressure and suction types. Some substances can adsorb onto the surface of the fluorocarbon polymer tubes used in pressurized SPE apparatuses. Similarly some syringe filters can adsorb some substances during the filtering of a sample. Consequently we examined adsorption of substances in two types of SPE apparatuses (Aqua loader twin, SPL 698T (GL Sciences) and GL-SPE manifold system) by carrying out recovery tests on deionized water spiked with 128 pesticides using the SPE-based sample preparation method, albeit without filtration using the syringe filter. It was observed that the recoveries of pesticides with log Pow > 4 were lower than those of hydrophilic substances, indicating that hydrophobic substances were being adsorbed in the flow path of the pressure type SPE apparatus.

The adsorption of LOCs onto syringe filters was examined using the 128 pesticide mixture and three syringe filters (Millex LG (hydrophilic PTFE membrane, 0.20  $\mu\text{m}$  pore size), Millex GS (mixed cellulose esters membrane, 0.22  $\mu\text{m}$  pore size, Merck Millipore, Darmstadt, Germany) and 13CP020AS (cellulose acetate membrane, 0.20  $\mu\text{m}$  pore size, Advantec, Tokyo, Japan)). A comparison before and after filtration suggests that pesticides with  $\log P_{ow} > 4$  were being adsorbed by the syringe filters, particularly the Millex GS and 13CP020AS filters. Although the amount of adsorption decreased with increasing ratio of methanol in mobile phase, some of the pesticides with  $\log P_{ow} > 4$  were still being adsorbed at 50% methanol in the mobile phase.

### **2.2.3 Recovery tests**

#### **2.2.3.1 Recovery tests using reagent water**

The extraction performance of two tandem SPE systems (HLB + AC2 and PS2 + AC2) was examined by recovery testing using reagent water spiked with 190 MCs at two concentrations (0.05 and 0.2  $\mu\text{g L}^{-1}$ ). At the higher spiked concentration, both the HLB + AC2 and PS2 + AC2 combinations produced recoveries of over 50% for 182 and 178 out of the 190 MCs, respectively, with average recoveries (average relative standard deviation, RSD, %) of 81.1 % (8.7 %) and 80.8 % (13.5 %), respectively (Tables 2-2 and 2-5). Recoveries and precisions in the recovery test at 0.05  $\mu\text{g L}^{-1}$  were similar to those of the 0.20  $\mu\text{g L}^{-1}$  test. These results indicated that the extraction ability of the developed SPE method is more than adequate for screening a large number of substances with a broad range of physicochemical properties.

The limit of detection (LOD) of the developed method was estimated from the lowest concentration in the calibration curves, and ranged from 0.004 to 0.40 (average, 0.039)  $\mu\text{g L}^{-1}$  for the 311 LOCs (Table S2-1). The LODs of 174 of these LOCs were acceptable ( $<0.01 \mu\text{g L}^{-1}$ ). The low ( $<50\%$ ) recoveries of some MCs might be attributable to their high water solubility (low extraction efficiency) or high hydrophobicity (adsorption on vessels). These compounds should be analyzed individually by another method.

**Table 2-5** Summary of results in recovery tests using reagent water and effluent

Compound class	Reagent water, 200 mL				Effluent, 200mL
	200 ng L <sup>-1</sup>		50 ng L <sup>-1</sup>		200 ng L <sup>-1</sup>
	HLB+AC2, n=7	PS2+AC2, n=7	HLB+AC2, n=7	PS2+AC2, n=7	PS2+AC2, n=5 <sup>c</sup>
	Average recovery, % (Average RSD, %)	Average recovery, % (Average RSD, %)	Average recovery, % (Average RSD, %)	Average recovery, % (Average RSD, %)	Average recovery, % (Average RSD, %)
Model compound	81.1 -8.7	80.8 -13.5	93.6 -10.5	87.1 -10.8	77.4 -13.1
Surrogate	68.3 -14.6	72.5 -21.1	- -	- -	60.9 -16.2
Matrix <sup>a</sup>	- -	100 -2.8	- -	- -	76.1 -9.7
Model compound	Number of compound	Number of compound	Number of compound	Number of compound	Number of compound
< or = 50 % of recovery	8	12	6	10	14
(> or = 20 % of RSD <sup>b</sup> )	-1	-17	-5	-13	-15
> 50 % of recovery	182	178	152	148	176
(< 20 % of RSD)	-189	-173	-153	-145	-175
> 70 % of recovery	160	154	139	136	134
(< 10 % of RSD)	-133	-58	-80	-88	-46

<sup>a</sup>: Matrix are substances that were spiked to a final concentrate for evaluating the matrix effects.

<sup>b</sup>: Relative standard deviation

<sup>c</sup>: Recovery test was done using 5 effluents collected from 5 sewage treatment plant

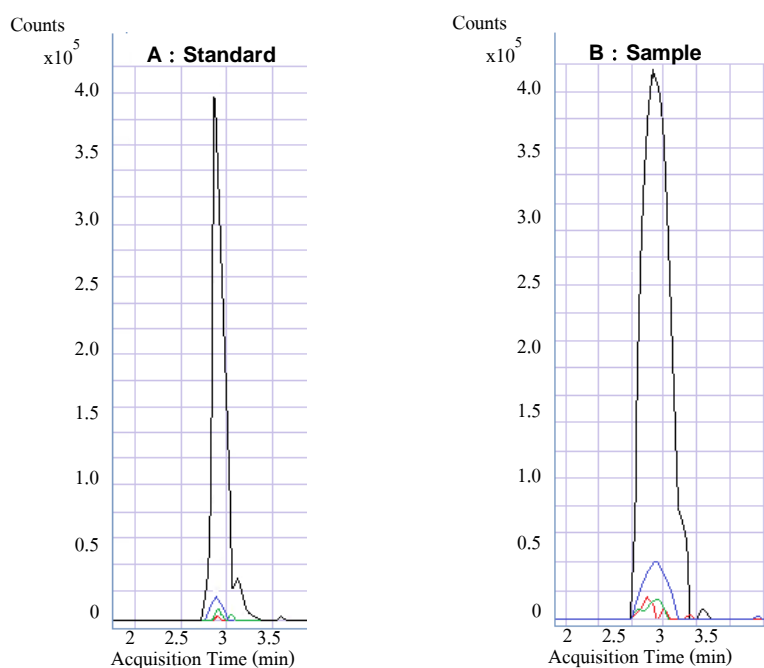
### 2.2.3.2 Recovery tests using effluents of sewage treatment plants

The recoveries of 176 out of 190 MCs were over 50 % with an average recovery and an average RSD of 77.4 % and 13.1 %, respectively (Tables 2-2 and 2-5). Twenty-five out of 190 MCs used in this testing were detected in at least one unspiked effluent. Notably, the concentrations of sulphiride were 5 times as high as the spiked concentration ( $0.20 \mu\text{g L}^{-1}$ ) ranging 0.79 to  $1.24 \mu\text{g L}^{-1}$ ; the high concentrations may be the cause of its high recovery rate. Although recoveries of some compounds were low, the results of the real sample recovery test confirmed that the developed SPE method can quantitatively extract a wide range of target LOCs in samples containing a large amount of matrix.

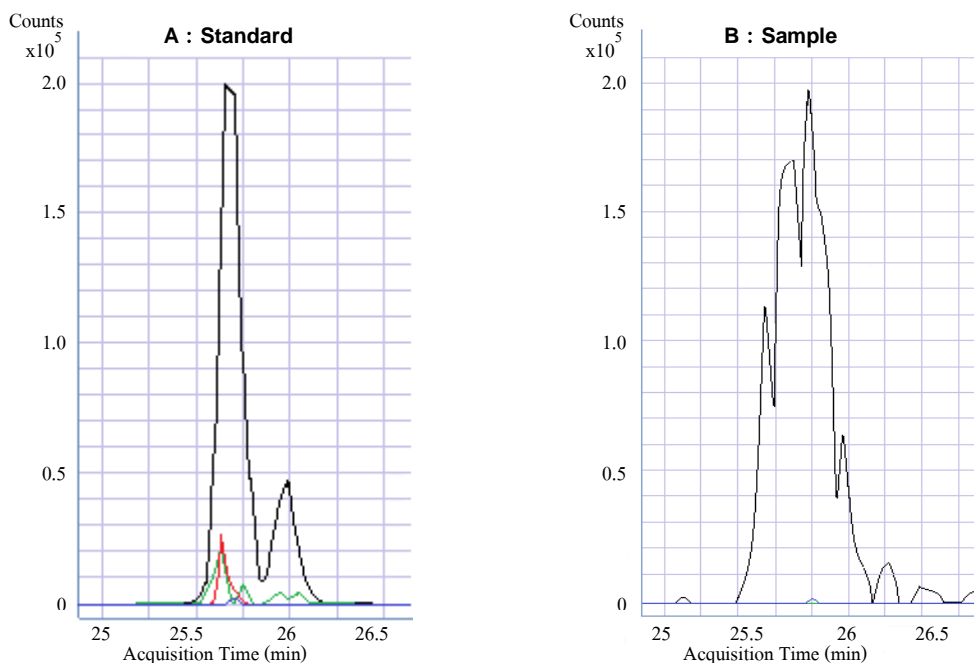
### 2.2.4 Reliable identification based on in-source fragment ions

LC-TOF/MS provides high-resolution mass spectra, which are useful for accurate identification of target substances coupled with retention times. However the possibility of mis-identification is relatively high compared to that of capillary GC-MS because of low reproducibility of retention times in LC analysis and there being only one characteristic ion. For example, siduron (a herbicide) was mis-identified in a STP influent even using high-resolution MS (see below), which indicates the need for additional information for reliable identification. In the present study, we used in-source fragment ions (Gómez et al. 2010; Saito et al. 2012; Ferrer and Thurman 2007), which were obtained at fragmentor voltages 150, 200 and 250 V, to achieve reliable identification. For instance, since peaks of the fragment ions of metformin (an antidiabetic) were found in the chromatograms of both standard (Fig. 2-1A) and sample (Fig. 2-1B), metformin was correctly identified. However, when peaks of fragment ions that were found in a chromatogram of a standard (e.g. siduron; Fig. 2-2A) were not found in a chromatogram of the sample (Fig. 2-2B), this indicated that the peak in the sample chromatogram was not derived from siduron. We measured all the target substances at four fragmentor voltages (100, 150, 200 and 250 V) and obtained one or more than one fragment ions from 284 out of 311 target substances (89%, Table S2-1, Supporting Information). In order to confirm

universality of the in-source fragment ions, we compared them to the product ions obtained by LC-MS/MS-SRM that are listed in the official method for pesticides residues in agricultural products (Pharmaceutical and Food Safety Bureau, Japan (PFSB) 2005). The product ions of 135 pesticides listed in the official method were the same as the fragment ions obtained in this study, a general conclusion consistent with reports by Weinmann et al. (2000) using SRM, although the intensity of fragment ions was not as high as that obtained by SRM.



**Fig. 2-1** Confirmation of identification of metformin using in-source fragment ions  
(A) Extracted ion chromatogram of standard ( $m/z=130.1087$  (black),  $113.0822$  (red),  $88.0869$  (green),  $71.0604$  (blue))  
(B) Extracted ion chromatogram of sample



**Fig. 2-2** Confirmation of false identification of siduron using in-source fragment ions  
 (A) Extracted ion chromatogram of standard (m/z= 233.1648 (black), 94.0657 (red), 137.0715 (green), 120.0449 (blue))  
 (B) Extracted ion chromatogram of sample

### 2.2.5 Surrogate compounds and matrix effects

Surrogate compounds are a very useful way to validate sample analysis through all procedures. Therefore, a set of deuterium-labeled surrogate compounds (Table 2-2) was spiked into all samples before extraction. Although the surrogate compounds did not cover the entirety of the physicochemical range of the targets, confirmation of their recoveries allowed the performance of the simultaneous extraction and the degree of matrix effects for each sample to be checked. Their average recovery and average RSD of the recovery tests with the PS2 + AC2 SPE system using reagent water and effluents of STPs were 72.5 and 60.9 % and 21.1 and 16.2 %, respectively (Table 2-2 and Table 2-5), which seems to be acceptable for a screening analysis without extensive clean-up of samples.

The lower recoveries of the LOCs from STP effluents are probably due to matrix effects. Ion suppression by matrix effects is a major problem in quantitative analysis of dirty samples by LC/MS measurement (Stahnke et al. 2009). Therefore, clean-up procedures are usually performed to remove matrix from samples in conventional

target analysis. But in screening analysis for a large number of compounds with a broad range of physicochemical properties, clean-up of samples is not adopted because there is a risk of removal of some target chemicals. Isotope dilution using chemicals labeled with  $^{13}\text{C}$  or deuterium, or determination by standard addition and matrix-matched standards are ways to compensate for matrix effects. However, the isotope dilution method is very costly and can be applied to only a limited number of chemicals. Determination by standard addition or matrix matched standards is time consuming and target substances free samples are needed, which is difficult for environmental samples.

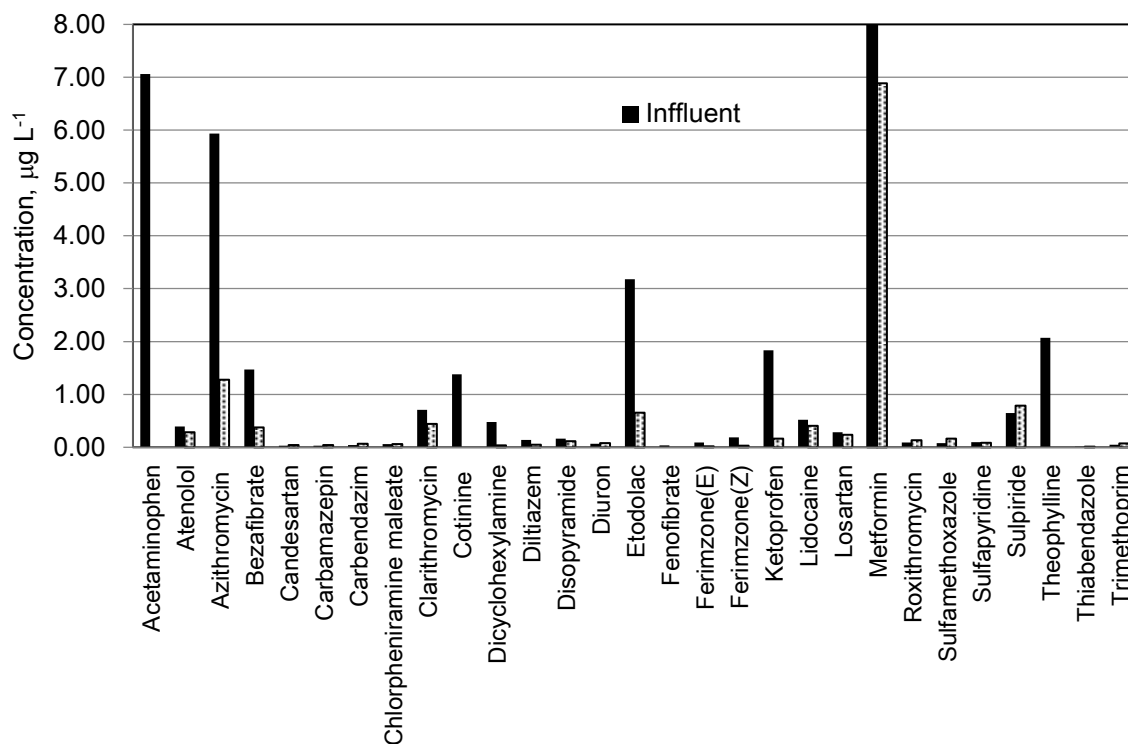
In order to examine the degree of the matrix effects, we spiked 6 deuterium-labeled compounds (Matrix in Table 2-2) into the final concentrates obtained in the recovery tests. No matrix effects were observed in reagent water samples whereas matrix effects were found for LOCs whose retention times are less than 20 min in effluent samples (Table 2-2). However, since the decrease in detected concentrations due to the matrix effects in dirty samples is below 30 % compared to concentrations observed in reagent water due to the compensatory effect of using the internal standards, this is an acceptable level in screening analysis.

### **2.2.6 Application to influents and effluents of sewage treatment plants**

In order to confirm the usefulness of the developed screening method, we analyzed influents and effluents of five sewage treatment plants in Kitakyushu. The number of compounds detected at least once was 29 (Fig. 2-3), and all of them were identified by using fragment ions and retention times. About half of the detected substances have also been detected in other areas in Japan (Okuda et al. 2009; Narimiya et al. 2009). There is, however, no report of detection of metformin in Japan, although it is an antidiabetic drug with one of the highest consumption rates of all pharmaceuticals worldwide (Scheurer et al. 2012). The reason for the lack of previous reports in Japan may be the analytical challenges of determining this chemical by conventional methods, e.g. using SPE with a conventional SPE cartridge and measurement by HPLC with an ODS column. Since metformin is highly hydrophilic ( $\log P_{ow} -0.5$ ), the combination of direct injection (Trautwein et al.

2012) or SPE using a cation-exchange resin (Scheurer et al. 2012) and HPLC analysis using a HILIC column is used for its analysis (EPA 2007; Scheurer et al. 2012). Therefore its true concentrations in the present study may be higher than the detected concentration because of low recovery by the developed screening method.

Recoveries of the surrogates ranged from 46 to 106 % (average recovery 67 %), which is lower than those of reagent water because of probable matrix effects. The observed differences between sample duplicates for the 26 detected substances ranged from 0 to 62.6 % (averages of both results), although for 23 of those substances the difference between the two results was below 30 %. Consequently, it was confirmed that the accuracy and reproducibility of the developed method is enough for screening pollution of wastewater and environmental waters. In addition, the method provides for a more complete picture of pollution as well as for non-target detection of pollutants.



**Fig. 2-3** Substances detected in influent and effluent of a sewage treatment plant in Kitakyushu



### 2.3 Conclusions

The experimental results clearly showed the effectiveness of the combination of the tandem SPE and LC-TOF/MS-TIM methods for the screening analysis of LOCs in real environmental samples. The developed screening analytical method saves on the cost of labor required to run multiple tests, and decreases both the consumption of solvent and the emission of toxic wastes (green analysis), while making it possible to quickly determine a huge number of pollutants in one analysis.

This proposed method is expected to be very efficient for primary screening surveys of previously uninvestigated waters, for a more complete grasp of a pollution picture, particularly by the combination with the comprehensive methods using AIQS (Jinya et al. 2011; 2013), and for emergency surveys after natural disasters such as earthquakes as well as the accidental release of pollutants. In addition, data obtained by this method can be used for non-target analysis and retrospective analysis.

## Chapter 3

**APPLICATION OF THE DEVELOPED SCREENING METHOD  
TO VIETNAMESE AQUATIC ENVIRONMENT****3.1 Introduction**

Urbanization, industrialization, and intensive farming are having a negative impact on Vietnam's environment. As a result, surface water of rivers running through residential and industrial areas has been increasingly polluted by organic contaminants (Ministry of Natural Resources and Environment (MONRE) 2010). Untreated medical, industrial and municipal wastewater are combined in municipal sewage systems and then discharged to canals and rivers (Pham et al. 2002). In particular, water pollution problems originating in domestic wastewater were clearly evidenced in large cities (MONRE 2010). For example, Ho Chi Minh City [HCMC, the most densely populated city in Vietnam (GSO 2013)], discharges 413 000 m<sup>3</sup> of wastewater per day, Hanoi discharges 155 000 m<sup>3</sup>/day, and Hue –Danang discharge 58 800 m<sup>3</sup>/day.

Water pollution was also found in rural or suburban areas of these cities. The main cause of water pollution in rural areas is pesticide and fertilizer residuals (Dang et al. 2002; Anyusheva et al. 2012). Statistical data show that pesticide consumption rapidly increased from 66 000 tons in 2005 to 124 000 tons in 2012 (GSO 2013). Because of poor cropping practices, pesticides and fertilizers are often overused and enter waterways. High-density industrial development and agricultural activities in certain major river basins may also pollute rivers. For example, surface water of the Red River and Saigon-Dongnai River (SDR) is extensively used for irrigation, drinking and cooking. Therefore water pollution may affect large numbers of the population. The Red River is one of the main sources of water in northern Vietnam and has the second largest basin, covering 26% of the area of Vietnam (MONRE 2006). Another important basin is that of the SDR; this basin encompasses the southeast principal economic zone including HCMC, Binhduong, Dongnai and Baria-Vungtau provinces. These provinces comprise the most important industrial

area in the country, with a high rate of economic growth.

In Vietnam, there have been few studies focusing on a small number of organochlorine pesticides, PCBs, PAHs, and others in surface or in sediments (e.g., Nhan et al. 2001; Dang et al. 2002; Nguyen et al. 2007; Duong et al. 2008; Pham et al. 2010; Lamers et al. 2011). Owing to rapid economic growth and urbanization, monitoring of a large number of chemicals is needed to prevent expansion of environmental pollution. However, it is difficult to analyze such large numbers using existing methods because of the substantial time and expense involved with operating multiple definitive tests. We have developed novel screening methods that can measure hundreds of chemicals simultaneously (Jinya et al. 2013). In the present study, we applied the methods to river water in Vietnam and analyzed 1153 substances composed of 843 semi-volatile organic compounds (SVOCs) and 310 polar organic compounds (POCs), to elucidate the pollution status of the aquatic environment in Vietnam. From the results, a complete pollution picture of the aquatic environment in the country is portrayed.

## **3.2 Study areas**

### **3.2.1 Red River Delta**

Red River is the second largest river in Vietnam after Mekong River (south of Vietnam). It begins in China's Yunnan province and flows through northern Vietnam to the Gulf of Tonkin with 1149 km long. This river has the largest river basin of Vietnam, covering 26% of the territory (Aquastat, water report 37-2012), and is one of the main sources of water supply for agricultural activities in northern Vietnam, which has an important role in the agricultural production of the country as well as the Mekong Delta in the southern part. 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 26 provinces with a population of 21 million people (GSO 2016). Surface water in 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.

### 3.2.2 Hanoi city

Hanoi is the capital of Vietnam and the country's second largest city with population is 7.3 million and covers a total area of 3324 km<sup>2</sup> (GSO 2016). It comprised 10 districts, one town and 18 suburban districts. Hanoi stood the second nationwide in population number and ranks the first in Vietnam in terms of area. It is the most important political center, 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, the biggest city in Vietnam.

Hanoi has a tropical monsoon climate with two main seasons, the dry season and wet season. The dry season, which lasts from October to April, is cool with little rainfall. The wet season, which lasts from May to September is hot with heavy rains. The annual mean temperature was 26.5 °C, and the annual rainfall was 1243 mm (Bjuhr, 2007). Hanoi has a density river network with over 10 rivers which are running throughout the city. Among them, Red River is the biggest river in the North of Vietnam and is the second largest river in Vietnam. It plays an important role in agriculture development activity in the Northern part of Vietnam.

Tolich, Kim Nguu, Lu, Set and apart of the Nhue river are seemed to be wastewater channels of city. Untreated wastewater discharged from both domestic and industrial sources are the main causes of water pollution in these rivers. It was reported that 95% of capital's wastewater effluents are discharged without treatment and an estimated 450 000 m<sup>3</sup>/day are discharged untreated into the rivers Lu, Set, Tolich and Kim Nguu in Hanoi city (Hoai et al. 2010). 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. However there has been no comprehensive study on wide range of organic micro-pollutants carried out until now. In this study, three representative rivers in Hanoi were chosen for monitoring organic-micro pollutants: Red, Nhue and Tolich River. These rivers are the main rivers in Hanoi city and play an important role in providing irrigation water for suburban agricultural land as well as fish farm.

### 3.2.3 Thua Thien Hue

Thua Thien Hue is bounded by Quang Tri province to the North, by Da Nang to the South, by Laos to the West and by the sea to the East with the area of 5033.2 km<sup>2</sup> and the population of 1.1 million (GSO 2016). The province is divided into Hue city and 8 districts: Quang Dien, Phu Vang, Phu Loc, Phong Dien, Nam Dong, Huong Tra, Huong Thuy and A Luoi. Thua Thien – Hue has a best quality and purest surface water resources compared to other provinces. It also has 10 water factories with the total capacity of 99 200 m<sup>3</sup> per day. In 2010, the capacity was improved to 206 500 m<sup>3</sup> per day.

Thua Thien Hue has one economic zone which is Chan May-Lang Co (21,108 ha) and 6 Industrial zones which are Phong Dien IZ (400 ha), Phu Bai IZ (800 ha), Tu Ha IZ (250 ha), Phu Da IZ, La Son IZ and Quang Vinh IZ. Hue city, an ancient capital, preserves many cultural heritages in their original design (mausoleums of Nguyen dynasty's Kings, Huong River, Ngu mountain peak, Vong Canh hill...). In economic development plan of Thua Thien Hue province, Hue City will be a nuclear center generating urban services required for industrial development and services development of the province, Central Vietnam and Central Highlands. Beside urbanization and economic development, it is necessary to survey on aquatic environment to prevent pollution in future.

### 3.2.4 Danang city

Danang City is located in the middle of Central Vietnam, 759 km from Hanoi and 960 km from Ho Chi Minh City. The total area of the city is 1256 km<sup>2</sup>, including 5 urban districts (Hai Chau, Thanh Khe, Son Tra, Ngu Hanh Son, Lien Chieu) and two suburban ones (Hoa Vang, Hoang Sa). This region has a common border with Thua Thien Hue Province in the north and Quang Nam Province in the south. Danang is a major port city in the South Central Coast of Vietnam; it 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, and Laos, Cambodia, Thailand, Myanmar and Northeast Asian nations. Danang is in a typical tropical monsoon zone with high temperature and equable climate. The city's weather is a combination of climatic features of northern

and southern Vietnam, with the northern having the more distinct influence. There are two seasons, the rainy season lasts from August to December and the dry season from January to July. The population of Danang city is 1.0 million (GSO 2016).

There are two largest river basin systems in Danang City, Cude and Tuy Loan river basin. Cu De river basin is located in the northern part of Danang city. It originates in Truong Son Mountain and flows through Hoa Vang district to Lien Chieu district and finally runs into East Sea at Nam O mouth. The Cu De river basin with 38 km length supplies irrigation water for agricultural land. Tuy loan river basin is also important river of the city. It 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 11 river basin systems are very important, they are mainly water supply sources and for agriculture activities and aqua farming in Danang city. Danang city is the fourth biggest city in Vietnam, and also it is moving forward to urbanization and industrial expansion. It means that environmental pollution by toxic chemicals will become worse year by year. Hence, the pollution sources may affect water quality of the rivers in Danang city. 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.

### **3.2.5 Saigon River**

The Saigon River 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 HCMC 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 HCMC 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 HCMC, most of them don't have 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 also is polluted by industrial and agricultural waste water from small-sized enterprises operating along the river. In addition, every day the river receives over 748 000 cubic meters of waste water, discharged from residential areas in localities, with more than 90 % of the waste water coming from HCMC. Saigon and Dongnai river basin has an important role in social and economic development in Vietnam since these basins encompasses the southern principal economic zone including HCMC, 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.

### **3.2.6 Dongnai River**

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 HCMC), with the total area of about 48 000 km<sup>2</sup>, in which 47 683 km<sup>2</sup> are in the country's territory (99 %). Only a small part (the riverhead of Be River, Saigon River and Vam Co River) lies in Cambodia. This river basin ranks the third largest basin after Mekong River and Red River in Vietnam (Dao Xuan Hoc). 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. The basin has several dams and lakes such as Tri An hydropower plant, Dau Tieng reservoir and other hydropower plants including Don Duong, Dai Ninh in Dongnai River; Thac Mo, Srok Fuming, Can Don in Be River; Ham Thuan, Da Mi in La Nga River. After

construction of Tri An hydropower plant and Dau Tieng reservoir, the water flow increased by 4 – 5 times in the dry season (Feb., Mar. Apr.) and decreased by 50 % in the flood season.

Dongnai 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 Huy. 2004). Within Dongnai river basin, the current water supply capacity reaches 2350 m<sup>3</sup> per person per year and may decrease 1600 m<sup>3</sup> per person per year by 2025 if population continuous to grow as at present (MONRE 2006). The delta of Dongnai River system is known as a breeding area of aquatic species. Aquatic products contribute significantly to the local economy.

### **3.2.7 Ho Chi Minh city**

Ho Chi Minh City (HCMC) is the largest city in Vietnam with an area of approximately 2094 km<sup>2</sup> and population is 8.3 million (GSO 2016). It is located in the south of Vietnam, and borders Binh Duong Province in the north, Tay Ninh Province in the northwest, Dong Nai Province in the east and northeast, Ba Ria-Vung Tau Province in the southeast, and Long An and Tien Giang provinces in the west and southwest. HCMC is 1730 km away from Hanoi city by land and is at the crossroads of international maritime routes. It is the economic center of Vietnam and accounts for a large proportion of the economy of Vietnam.

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 1,800 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. The highest temperature sometimes reaches 39 °C around noon in late April, while the lowest may fall below 16 °C in the early mornings of late December. HCMC has a dense network of rivers and canals, hundreds of rivers and canals which flow through the city. Sai Gon and Dong Nai are two big river basins running throughout the city.

HCMC is facing serious water resources degradation problems in terms of quantity and quality. Rivers and canals passing HCMC receive all kinds of



wastewater (mostly untreated) from agricultural, domestic, and industrial activities. In addition, all kinds of wastes from floating markets, floating houses, and houses along the banks of canals and rivers also find their way to the water system. The daily volumes of domestic and industrial wastewater discharged to the canals in HCMC were 710 000 m<sup>3</sup> and 35 000 m<sup>3</sup>, respectively in 2000. The daily projected volume of domestic wastewater will be 2 100 000 m<sup>3</sup> in 2020. However, currently, only a small amount of municipal wastewater is conventionally treated at Binh Hung Hoa central wastewater treatment plant with a capacity of 30 000 m<sup>3</sup>/day. In addition, only 40%, approximately 15 000 m<sup>3</sup>/day, of industrial wastewater has been treated efficiently by the centralized wastewater treatment plants located inside the five industrial parks (including Tan Thuan, Linh Trung 1, Linh Trung 2, Tan Binh, Le Minh Xuan, and Tan Tao industrial parks). The other 10 industrial parks in the city are still in the progress of setting up the wastewater treatment plant.

### **3.3 Sampling**

#### **3.3.1 Sampling sites**

All 42 samples were collected in March 2013. Fourteen samples were collected from the Red River (Figure 3-1A, upstream to downstream). In Hanoi, three samples were taken in urban zones including the Kimnguu River (HN1), Lu River (HN2), and Tolich River (HN3). Another two samples (HN4, HN5) were collected from the Nhue River in a suburban zone of Hanoi (Fig. 3-1B). Figure 3-1C is for Hue (five samples, in an urban area HU4, and in a rural area HU1, HU2, HU3, HU5). Figure 3-1D is for Danang (seven samples, in an urban area DN3, DN7, and in a suburban area DN1, DN2, DN4, DN5, DN6). Four out of six HCMC samples were taken in the Thamluong (HCM7), Nhieuoc-Thinghe (HCM8), Logom (HCM9) and Tauhu (HCM10) canals (Fig. 3-1E), which appeared to be wastewater canals within urban areas. Since water from these canals has been collected and treated at wastewater treatment plants, water quality has improved (HCMC PC 2014). However, their surface water quality still does not meet national standards. Another two samples were taken from Anha (HCM6) and Kenhdoi (HCM11) canals in a suburban zone. For the SDR, three of five samples were collected from the Saigon River (HCM2,

HCM3, HCM4) and one from the Dongnai River (HCM1); there was one other sample from the downstream of these two rivers (HCM5) (Fig. 3-1E). Detailed information and figures of sampling sites are given in Duong et al. (2015).

Samples of Hanoi and HCMC, Saigon – Dongnai River were also collected Sep (rainy season) 2013 at the same sampling sites. And 18 samples of groundwater were taken from urban and suburban zones of Hanoi city. Well depths were generally shallow with such depths ranging from 16 to 100 m with a median depth of 20 m.

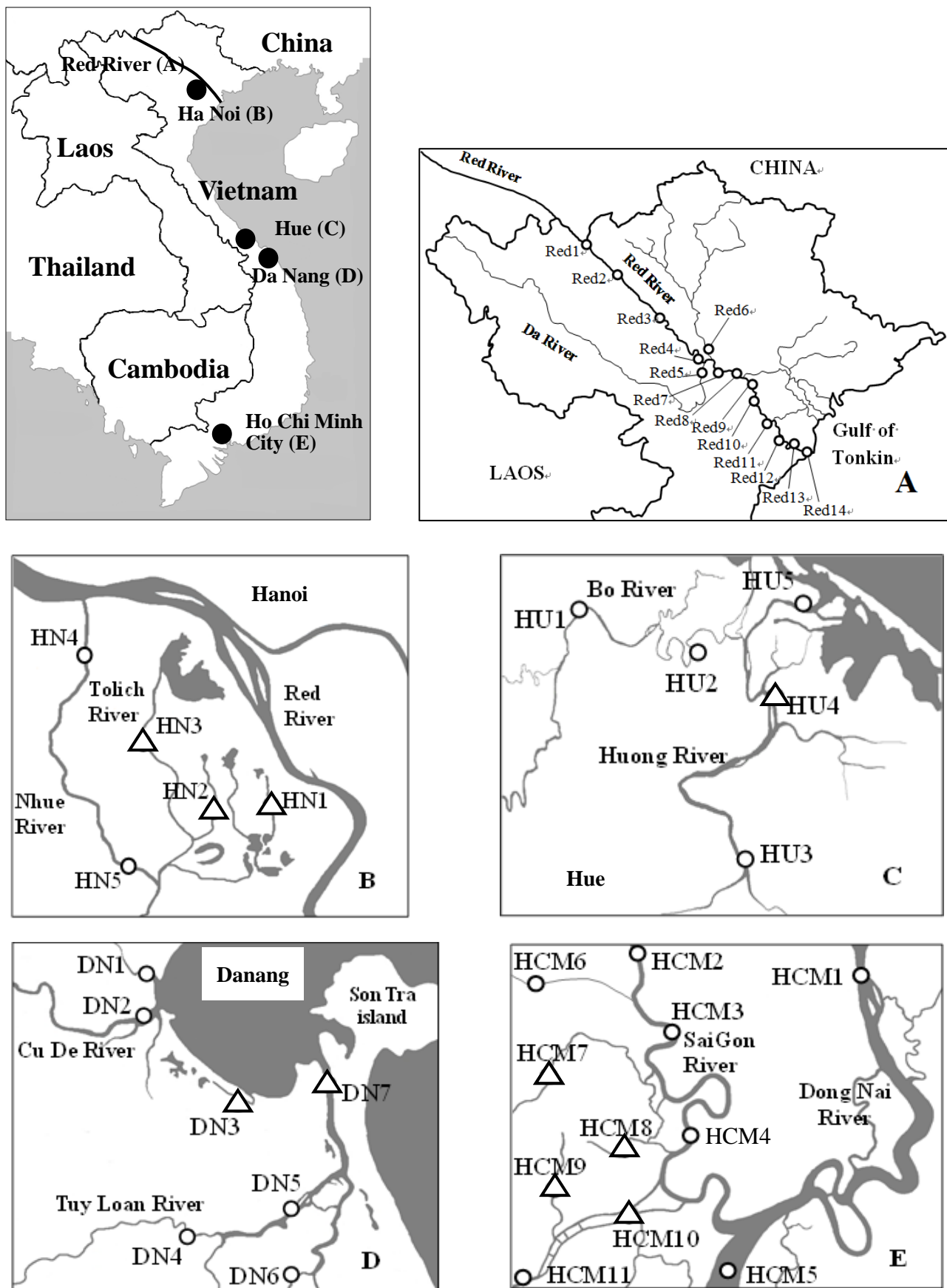


Fig. 3-1 Location of 42 sampling sites ( $\Delta$ : Urban area,  $\circ$ : Suburban area)

**Table 3-1** Sampling record of samples

Site	No.	Sample	Latitude	Longitude	Feb, 2013	Sep, 2013
Hue	Hue_1	An Lo River	16°32'39.42"N	107°27'19.69"E	○	×
	Hue_2	Huong Can River	16°31'2.93"N	107°32'6.48"E	○	×
	Hue_3	Tuan River	16°23'41.04"N	107°34'34.32"E	○	×
	Hue_4	Cho Dinh River	16°29'34.93"N	107°35'33.67"E	○	×
	Hue_5	Dam Thao Long	16°32'49.99"N	107°37'1.40"E	○	×
Da Nang	DAN_1	Lien Chieu River	16° 8'36.99"N	108° 7'18.43"E	○	×
	DAN_2	Cu De River	16° 6'53.33"N	108° 6'16.53"E	○	×
	DAN_3	Phu Loc canal	16° 4'8.48"N	108°10'52.61"E	○	×
	DAN_4	Tuy Loan River	15°59'35.70"N	108° 8'37.90"E	○	×
	DAN_5	Cam Le River	16° 0'30.72"N	108°12'25.51"E	○	×
	DAN_6	Qua Giang River	15°58'20.54"N	108°12'31.99"E	○	×
	DAN_7	Song Han River	16° 4'19.93"N	108°13'36.44"E	○	×
Red River	Red_1	Coc Leu Bridge	22°30'11.61"N	103°58'6.90"E	○	×
	Red_2	Bao Ha Bridge	22°10'14.21"N	104°21'17.41"E	○	×
	Red_3	Yen Bai Bridge	21°41'41.45"N	104°52'13.90"E	○	×
	Red_4	Phong Chau Bridge	21°17'8.35"N	105°15'35.98"E	○	×
	Red_5	Trung Ha Bridge	21°14'4.15"N	105°21'4.61"E	○	×
	Red_6	Viet Tri Bridge	21°18'1.53"N	105°26'36.52"E	○	×
	Red_7	Vinh Thinh Ferry	21°10'0.39"N	105°29'7.40"E	○	×
	Red_8	Thang Long Bridge	21° 5'57.33"N	105°47'11.22"E	○	×
	Red_9	Thanh Tri Bridge	20°59'37.09"N	105°54'5.66"E	○	×
	Red_10	Chuong Duong Ferry	20°50'39.80"N	105°55'9.67"E	○	×
	Red_11	Yen Lenh Bridge	20°39'29.22"N	106° 2'5.38"E	○	×
	Red_12	Tan De Bridge	20°26'37.82"N	106°13'6.76"E	○	×
	Red_13	Sa Cao Ferry	20°22'12.39"N	106°20'38.83"E	○	×
	Red_14	Ba Lat estuary	20°17'29.68"N	106°32'57.05"E	○	×

○: collected    ×: uncollected

**Table 3-1** Sampling record of samples (continued)

Site	No.	Sample	Latitude	Longitude	Feb, 2013	Sep, 2013
Ho Chi Minh City	HCM_1	Dong Nai River (Dong Nai Bridge)	10°54'5.71"N	106°50'20.80"E	○	○
	HCM_2	Sai gon River - Ben Suc Bridge	11° 9'22.15"N	106°27'5.52"E		
	HCM_3	Sai gon River - Phu Long Bridge	10°53'25.06"N	106°41'31.30"E	○	○
	HCM_4	Sai gon River - Sai Gon Bridge	10°47'56.04"N	106°43'37.94"E	○	○
	HCM_5	Sai gon-Dong nai River - Binh Khanh Ferry	10°40'1.60"N	106°46'27.41"E	○	○
	HCM_6	An Ha canal: An ha Bridge	10°55'5.56"N	106°33'46.86"E	○	○
	HCM_7	Tham Luong-Vam Thuat canal: Tham Luong Bridge	10°49'29.06"N	106°37'40.64"E	○	○
	HCM_8	Nhieu Loc-Thi Nghe canal: Le Van Sy Bridge	10°47'9.22"N	106°40'52.70"E	○	○
	HCM_9	Tan Hoa canal -Lo Gom: Ong Buong Bridge	10°45'16.18"N	106°38'12.34"E	○	○
	HCM_10	Chu Y Bridge	10°45'2.44"N	106°41'2.10"E	○	○
	HCM_11	Binh Dien Bridge	10°42'5.92"N	106°35'50.31"E	○	○
Hanoi	HN_1	Kim Nguu river (Ku I or Voi bridge)	20°59'27.88"N	105°51'46.61"E	○	○
	HN_2	Lu river (Dinh Cong bridge)	20°58'58.77"N	105°50'5.18"E	○	○
	HN_3	To Lich river (Moc brige)	21° 0'31.89"N	105°48'48.58"E	○	○
	HN_4	Nhue river (Noi bridge)	21° 3'41.69"N	105°46'20.50"E	○	○
	HN_5	Nhue river (Mau Luong bridge)	20°57'39.81"N	105°47'46.65"E	○	○

○: collected    ×: uncollected

### 3.3.2 Sampling method

Surface water at the center of a stream was sampled from a bridge with a stainless steel bucket, which was pre-cleaned with solvents, purified water and sample water. Each water sample was stored in a 1 L glass bottle previously washed with solvents and purified water. Bottles containing water samples were kept in an icebox and transported to our laboratory.

## 3.4 Experimental

### 3.4.1 Materials

All solvents, n-hexane, acetone and dichloromethane (DCM) for pesticide residue analysis, methanol of LC-MS grade, Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> were supplied by the Kanto Chemical Company (Tokyo, Japan). Reagents of target compounds and internal standards were purchased from Wako Pure Chemical Industries (Osaka, Japan), Kanto Chemical Company and Sigma-Aldrich (Tokyo, Japan). Purified water was obtained using a Millipore Milli-Q Advantage system (Nihon Millipore K.K., Tokyo, Japan).

### 3.4.2 Extraction methods

The GC-MS and GC-MS-MS analytical method for 950 SVOCs was undertaken according to the method of Jinya et al. (2013). A water sample (1L), spiked with 1 mL of phosphate buffer (1M, pH7.0) to adjust the pH of each sample to 7, was fitted inside a vacuum manifold (3M Company, St. Paul, MN, USA) with flow rate less than 100mL/min in a sequence with a glass microfiber disk (GMF 150, 47 mm, Whatman, Maidstone, UK), a styrene-divinylbenzene disk (Empore™ SDB-XD, 47 mm, 3M Co.), and an active carbon disk (Empore™ AC, 47 mm, 3M Co.). These disks were pre-conditioned by passing 10 mL of DCM, 10 mL of acetone, 10 mL of methanol, and 20 mL of purified water through them before use. After passing water sample through the disks, water remaining in the disks was completely removed using a vacuum for 30 min. The GMF and XD disks were eluted together with 5 mL of acetone (twice), followed by 5 mL of DCM. The AC disk was eluted with 5 mL of acetone (twice). The eluates were combined and concentrated into 1 mL with a nitrogen stream. The concentrate was diluted with 10 mL of hexane and dehydrated by adding Na<sub>2</sub>SO<sub>4</sub> (preheated at 700 °C for 6 h). The dehydrated solution was concentrated to 1 mL, and then mixed internal standards (IS; 4-chlorotoluene-d<sub>4</sub>, 1,4-dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, fluoranthene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub>) were added prior to instrumental analysis [GC-MS-SIM/Scan (QP-2010 Plus, Shimadzu, Tokyo, Japan) and GC-MS-MS-SRM (TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama,

Japan)].

For the analysis of 310 POCs, 1 mL of phosphate buffer (1 M, pH 7.0) was added to a water sample (500 mL) and filtered with a 1.2- $\mu\text{m}$  glass fiber filter (Whatman, GF/C). Suspended solids (SS) were subjected to ultrasonic extraction with methanol twice. The filtrate was passed through a PS-2 Sep-Pak short cartridge (Waters Corporation) and an AC2 Sep-Pak (Waters) using a Chratec Sep-Pak Concentrator (SPC 10-C; Chratec, Kyoto, Japan) with a flow rate of 10 mL/min, and then rinsed with 10 mL of purified water. The cartridges were then dried with nitrogen to remove water for 40 min. The cartridges were eluted with methanol (5 mL) and DCM (3 mL). After combining the eluates and the extract from SS, the mixture was concentrated to 50  $\mu\text{L}$  and then spiked with 40  $\mu\text{L}$  of three IS (5  $\mu\text{g}\text{L}^{-1}$ , mixture of methomyl-d3, pirimicarb-d6, imazalil-d5). The concentrate was diluted to 1 mL with purified water, filtered through a 0.2- $\mu\text{m}$  syringe filter (Millex-LG) into an analysis vial and subsequently measured by LC-TOF/MS.

### 3.4.3 Analysis methods

A Shimadzu QP-2010 GC-MS were used for the analysis. 1  $\mu\text{L}$  of sample was injected (splitless for 1 min) with the help of auto sampler AOC-20s and auto injector AOC-20i (Shimadzu). The analytes were separated on J&W DB-5 ms capillary column (30m x 0.25mm i.d; Agilent Technologies, San Jose, CA, USA), coated with Phenyl Arylene polymer virtually equivalent to a (5%-Phenyl)-methylpolysiloxane at 0.25  $\mu\text{m}$  film thickness, which was used for construction of the database and for sample analysis. Helium gas was used as carrier gas at a flow rate of 1.56 ml/min with liner velocity flow control mode. The determination was carried out at injector, ion source and interface temperatures of 250, 200 and 300°C, respectively. The GC temperature program was set to 40°C (maintained for 2 minutes) before increasing to 310°C at the rate of 8°C/min and held at the final temperature for 4 minutes. Automated identification and quantification of contaminants were carried out by using gas chromatography-mass spectrometry database (AIQS-DB) (Table 3-2).

**Table 3-2** 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

Precise analysis of PCBs and OCPs was carried out on GC–MS–MS–SRM (Table S3-1) 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 3.3). The MDL of OCPs and PCBs measured by SRM for water samples ranged from 0.1–0.4 ng L<sup>-1</sup>, while for sediment the MDL of the targets was ≤ 0.02 ng g<sup>-1</sup> dry-wt.

**Table 3-3** GC–MS-MS conditions for comprehensive 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 <sup>-1</sup> , constant flow mode
Ionization method	EI
Emission current	50µA
Measurement method	1



The SVOCs (Table S3-1) were measured with a LC-TOF/MS (Agilent 1200 HPLC Systems equipped with an Agilent 6220 TOF mass spectrometer, Tokyo, Japan). The LC-TOF/MS conditions were shown in Table 2-3.

#### 3.4.4 Analytical quality control

Method accuracy and precision were studied by recovery studies using surface water and effluent of sewage treatment plants spiked at different concentrations. The procedure blanks were analyzed every 6 samples to check for cross-contamination and interference.

For SVOC analysis, quality control measures were as described by Jinya et al. (2011, 2013). Two hundred two SVOCs were selected as model compounds (MCs) having a wide range of physicochemical properties (structure, functional group, boiling points (145-536°C)). The MCs included polycyclic aromatic hydrocarbons (PAHs), amines, alkyl phenols, halogenated phenols, phthalates, benzenes, alcohols, and some classes of pesticides. Recoveries were determined by analyzing purified and environmental sample spiked standards at two concentrations (0.1 and 0.5  $\mu\text{gL}^{-1}$ ). Most of the model compounds, which are representative of the target SVOCs, had recoveries of over 50% (Jinya et al. 2013). Method detection limits (MDL) of chemicals measured by SIM and/or SRM were 0.0004–0.3  $\mu\text{gL}^{-1}$ . The MDL of compounds measured by TIM were 0.005 to 0.5  $\mu\text{gL}^{-1}$ .

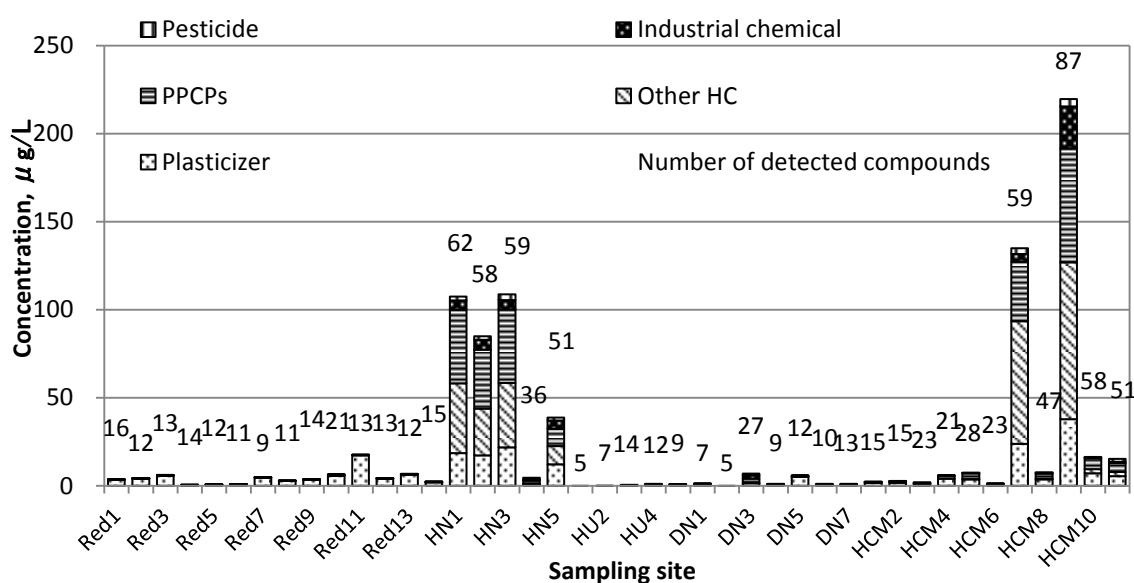
For the polar substance analysis, the recoveries of 264 MCs from spike experiments at 0.05 and 0.2  $\mu\text{gL}^{-1}$  were determined using purified water (replication  $n=7$  for each level of concentration) and effluent wastewater ( $n=5$ ) to be in the range 50–120%. The relative standard deviation (RSD) values for recovery tests using purified water were in the range 3-25% and the RSD of effluent samples between 5 - 30%. Quantitation was performed by IS method using a peak area obtained at 100V of fragmentor voltage. MDLs of POCs ranged from 0.008 to 0.4  $\mu\text{gL}^{-1}$ . The correlation coefficients of calibration curves are higher than 0.99 for all the compounds analyzed.

### 3.5 Results and discussion

#### 3.5.1 Detection of micro-pollutants in surface water samples

One hundred and sixty five out of 1153 target compounds were detected at least once in surface water samples (Table S3-1). The total number of compounds found in Hanoi and HCMC samples were similar (113 and 129 compounds, respectively; Table 3-4), and two to three times higher than at other sampling sites (Red River 58, Hue 46, Danang 56, SDR 61). Overall, the concentrations of substances detected in

Hanoi and HCMC were much higher than in Hue, Danang, the Red River and SDR (except for fungicides and herbicides; Fig.3-2), because of differences in population density and economic activity. When comparing data from large cities and other sites; household chemicals, PAHs and sterols, had nearly identical numbers of detected compounds but vastly different total concentrations. The numbers and concentrations of fungicides and herbicides did not vary greatly between sites. PCBs, insecticides, and pharmaceutical and personal care products (PPCPs) were found in much higher numbers and concentrations in the large cities than at other sites (Table 3-4). When comparing the number and concentrations of detected organic compounds between urban and suburban area of cities, sampling sites in Hanoi urban area (HN1, HN2 and HN3) had high concentrations of household chemicals, and PPCPs compared to those in suburban areas (HN4 and HN5; Fig.3-2). This pattern was also observed among samples collected in urban area and suburban area of HCMC, Danang and Hue (Fig.3-2).



**Fig.3-2** Concentrations and number of compounds detected at each sampling site

We screened 13 plasticizers; seven of these [bis(2-ethylhexyl)phthalate (DEHP), bisphenol A, butyl benzyl phthalate, di(2-ethylhexyl)adipate (DEHA), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), triphenylphosphate (TPP)] were detected in very high concentrations ( $\mu\text{gL}^{-1}$  level) at each sampling site. Maximum

and average values of total detected concentrations were 38 and 13  $\mu\text{gL}^{-1}$  in HCMC, 22 and 14  $\mu\text{gL}^{-1}$  in Hanoi, and 17 and 4.3  $\mu\text{gL}^{-1}$  in the Red River, respectively. DEHP was predominant, with high concentrations accounting for 71% of the mean concentration of plasticizers detected in the Red River, 75% in Hanoi, 76% in SDR, and 65% in HCMC.

The highest concentration of PAHs was 1334  $\text{ngL}^{-1}$  (mean 64  $\text{ng/L}$ ), about three times lower than the value in a previous report from Vietnam (Duong et al. 2014) and about four times lower than in Tianjin, China (Kong et al. 2014). The number of detected PCBs (32) was similar to that reported by Duong et al. (2014), but their total concentrations were  $< 7.6 \text{ ngL}^{-1}$  (mean 0.54  $\text{ngL}^{-1}$ ), two times lower than previously reported values.

Only five out of the 12 sterols examined were observed and occurred at the highest concentration compared with the other compounds detected in this survey (Hanoi (194  $\mu\text{gL}^{-1}$ ), HCMC (159  $\mu\text{gL}^{-1}$ )). A ratio of coprostanol/cholesterol  $\geq 0.2$  indicates sewage contamination (Grimalt et al. 1990). Generally, values near or greater than 0.2 were found in populous locations such as Hanoi (site HN1 0.96, HN2 0.86, HN3 0.88, HN4 0.37, HN5 0.82), Red10 (0.32, downstream of Hanoi), urban areas of Hue (HU4 0.19) and Danang (DN3 0.46), and HCMC (HCM6 0.30, HCM7 0.67, HCM9 0.79, HCM10 0.3, HCM11 0.20) (Table S3-1). Galassmeyer et al. (2005) suggested that a ratio exceeding 0.3 indicates fecal contamination. This means that wastewater containing feces from households was directly discharged into rivers or canals in urban areas, and domestic wastewater treatment plants were not operating effectively.

**Table 3-4** Concentrations (mg/L) of the chemicals found and the numbers of chemicals found (in parentheses)

Group	Type of compound	Compound	N	Mean-max value of measured concentration (number of detected compound)					
				Red River (14 samples)	Hanoi (5 samples)	Hue (5 samples)	Danang (7 samples)	Saigon–Dongnai River (5 samples)	HCMC (6 samples)
Household chemicals	Leaching from tire	2(3H)-benzothiazolone, 2-(methylthio)-benzothiazol, acetophenone, benzyl alcohol, phenylethyl alcohol	5	nd	3.9–6.9 (4)	0.043–0.087 (2)	nd	0.0044 - 0.022 (1)	3.3–12 (5)
	Petroleum		25	2.4–8.8 (22)	23–37 (24)	1.1–4.3 (22)	4.1–8.0 (19)	2.9–4.7 (21)	33–100 (25)
	Plasticizers	Bis(2-ethylhexyl)phthalate, bisphenol A, butyl benzyl phtalate, di(2-ethylhexyl)adipate, diethyl phthalate, di-n-butyl phthalate, triphenylphosphate	7	4.3–17 (7)	14–22 (6)	0.11–0.47 (3)	1.3–5.1 (4)	2.3–4.0 (7)	13–38 (6)
	Disinfectants	2-methylphenol, 3-&4-methylphenol, phenol	3	0.011–0.040 (1)	15–28 (2)	nd	nd	nd	17–63 (3)
	Others	4-methyl-2,6-di-t-butylphenol; 4-tert-octylphenol; nonylphenol	3	0.051–0.11 (1)	3.7–7.0 (3)	0.017–0.086 (1)	0.020–0.044 (1)	0.056–0.11 (2)	7.2–28 (3)

**Table 3-4** Concentrations (mg/L) of the chemicals found and the numbers of chemicals found (in parentheses) (continued)

Group	Type of compound	Compound	N	Mean-max value of measured concentration (number of detected compound)					
				Red River (14 samples)	Hanoi (5 samples)	Hue (5 samples)	Danang (7 samples)	Saigon– Dongnai River (5 samples)	HCMC (6 samples)
Industrial chemicals	Intermediates	2,4-dichloroaniline; 2-ethyl-1-hexanol; 2-phenylphenol; 3,4-dichloroaniline; 3,5-dimethylphenol; biphenyl; dicyclohexylamine; quinoline	8	0.026–0.076 (1)	3.9–5.4 (7)	0.048–0.067 (1)	0.40–1.8 (2)	0.10–0.16 (1)	4.2–21 (6)
	PAHs	1,3-dimethylnaphthalene; 2,6-dimethylnaphthalene; 2-methylnaphthalene; fluoranthene; phenanthrene; pyrene	6	3.2–44 <sup>a</sup> (3)	0.090–0.17 (3)	nd	11–74 <sup>a</sup> (3)	nd	0.35–1.3 (4)
	PCBs		32	0.057–0.15 <sup>a</sup> (2)	1.8–5.3 <sup>a</sup> (14)	0.086–0.14 <sup>a</sup> (1)	0.18–0.35 <sup>a</sup> (3)	0.19–0.27 <sup>a</sup> (2)	1.7–7.6 <sup>a</sup> (28)
	Paint/solvent	Isophorone	1	0.010–0.14 (1)	0.23–5.2 (1)	0.069–0.26 (1)	nd	nd	0.35–1.4 (1)

**Table 3-4** Concentrations (mg/L) of the chemicals found and the numbers of chemicals found (in parentheses) (continued)

Group	Type of compound	Compound	N	Mean-max value of measured concentration (number of detected compound)					
				Red River (14 samples)	Hanoi (5 samples)	Hue (5 samples)	Danang (7 samples)	Saigon–Dongnai River (5 samples)	HCMC (6 samples)
Pesticides	Fungicides	Azoxystrobin, carbendazim, cyprodinil, epoxiconazole, ethoxyquin, hexachlorobenzene, isoprothiolane, tricyclazole	8	0.12–0.29 (2)	0.14–0.21 (3)	0.029–0.11 (3)	0.17–0.35 (2)	0.15–0.28 (4)	0.15–0.22 (5)
	Herbicides	Acetochlor, alachlor, ametryn, atrazine, bensulfuron-methyl, butachlor, diuron, flufenacet, naproanilide, prometryn, siduron, tebuthiuron	12	0.11–0.29 (4)	0.16–0.34 (5)	0.025–0.12 (3)	0.13–0.90 (2)	0.075–0.21 (4)	0.54–1.2 (4)
	Insecticides	Acetamiprid; a-HCH; aldrin; carbofuran; cis-chlordane; trans-chlordane; dimethoate; fenobucarb; fenoxycarb; imidacloprid; o,p'-DDD; p,p'-DDD +o,p'-DDT; p,p'-DDE; permethrin 1; permethrin 2; piperonyl butoxide; promecarb;	17	0.039–0.14 <sup>a</sup> (3)	1.8–2.9 (12)	0.036–0.10 (3)	0.034–0.22 (7)	0.054–0.10 (5)	1.0–3.0 (9)
	Sterols	Cholestanol, cholesterol, coprostanol, beta-sitosterol, stigmasterol	5	5.3–17 (4)	121–194 (5)	3.8–6.5 (4)	9.6–39 (4)	8.6–11 (4)	58–159 (4)

**Table 3-4** Concentrations (mg/L) of the chemicals found and the numbers of chemicals found (in parentheses) (continued)

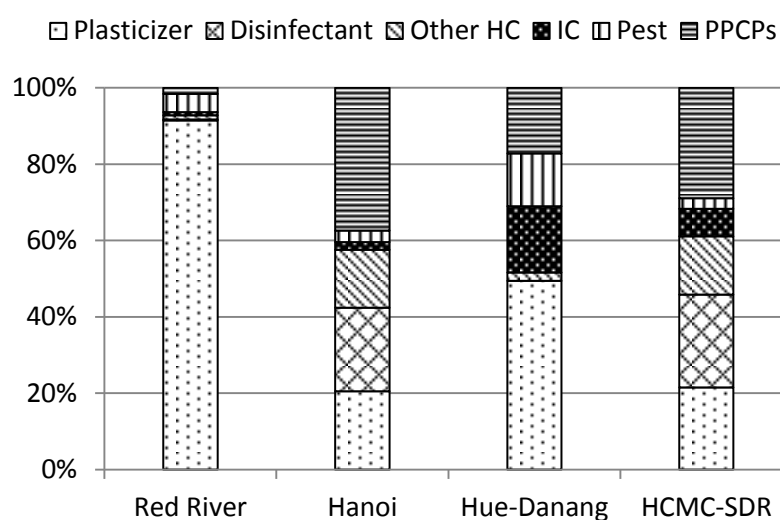
Group	Type of compound	Compound	N	Mean-max value of measured concentration (number of detected compound)					
				Red River (14 samples)	Hanoi (5 samples)	Hue (5 samples)	Danang (7 samples)	Saigon–Dongnai River (5 samples)	HCMC (6 samples)
	Antibiotics	Ampicillin, clarithromycin, erythromycin, griseofulvin, lincomycin, oleandomycin, roxithromycin, spiramycin, sulfadiazine, sulfanilamide, sulfamethoxazole, sulfapyridine, trimethoprim	13	0.017–0.24 (3)	3.7–5.5 (10)	nd	0.12–0.86 (2)	0.26–0.63 (2)	2.1–4.4 (10)
PPCPs	Other pharmaceuticals	Acetaminophen, atenolol, acetohexamide, antipyrine, caffeine, carbamazepin, cimetidine, cotinine, diethyltoluamide, lidocaine, hexamethylenetetramine, L-menthol, losartan, metformin, nicotine, phenacetin, propranolol, sulpiride, testosterone, theophylline	20	0.058–0.25 (4)	22–38 (14)	0.14–0.55 (2)	0.27–1.5 (7)	1.1–3.1 (8)	17–60 (16)
Total number of detected compounds			165	58	113	46	56	61	129

N: number of detected compounds detected in all 42 samples at least once; a: concentrations were calculated in the unit of ng/L; nd: not detected.

Thirty-three PPCPs were found in the survey, among which 13 compounds were antibiotics (ampicillin, clarithromycin, erythromycin, griseofulvin, lincomycin, oleandomycin, roxithromycin, spiramycin, sulfadiazine, sulfamethoxazole, sulfanilamide, sulfapyridine and trimethoprim). The total concentration of all detected antibiotics was highest in Hanoi ( $5.5 \mu\text{gL}^{-1}$ ; mean  $3.7 \mu\text{gL}^{-1}$ ), followed by  $4.4 \mu\text{gL}^{-1}$  in HCMC (mean  $2.1 \mu\text{gL}^{-1}$ ). In Vietnam, antibiotics are dispensed without a doctor's prescription (Nguyen et al. 2011), and may enter the environment through feces or urine. However, it is possible that important point sources of antibiotics are hospitals because hospital wastewater contains high levels of antibiotics, and removal values through wastewater treatment plants are smaller than those in developed countries (Duong et al. 2008).

### 3.5.2 Distribution of micro-pollutants in surface waters

More than 50% of total micropollutant concentrations detected in both urban and suburban areas were household chemicals (Red River 92%, Hanoi 58%, Hue-Danang 52%, HCMC-SDR 71%; Fig.3-3). The distributions of contaminants in the environment of Hanoi and HCMC-SDR were nearly identical, but were very different to those of Hue-Danang and the Red River (Fig.3-3).



**Fig. 3-3** Percentages of concentrations of compounds detected at each location  
(Other HC: other household chemicals; ICs: industrial chemicals)



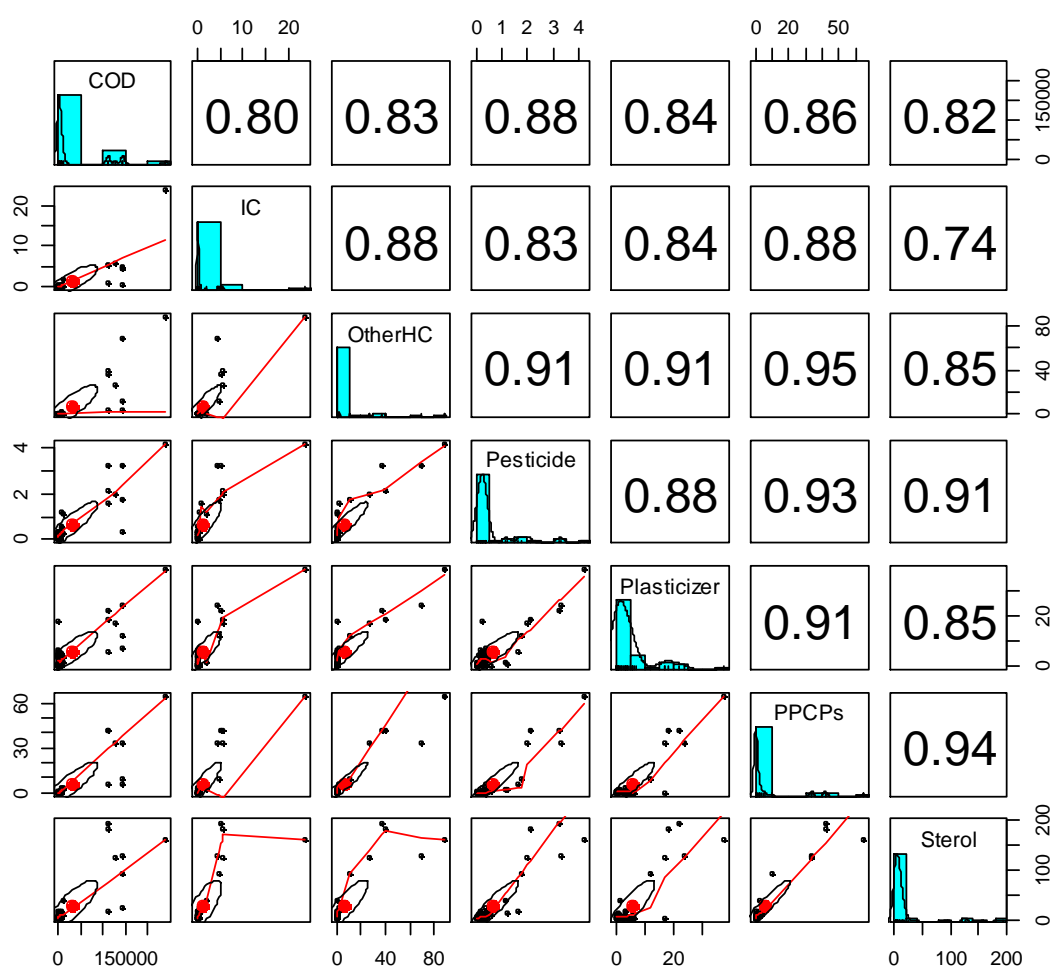
Plasticizers are commonly used, and with millions of tons produced worldwide annually (Koch et al. 2003) these chemicals have become widespread in the environment (Fromme et al. 2002; Fauser et al. 2003). In the present study, plasticizers were a large proportion of detected contaminants, accounting for 21–22% in Hanoi and HCMC-SDR, 50% in Hue-Danang, and up to 91% in the Red River. A likely source of plasticizers in the environment of large cities is storm water (Clara et al. 2010; Björklund et al. 2009). However, in the case of Hue-Danang and the Red River, untreated wastewater from craft villages is considered the main plasticizer source. Craft villages are classified into many different groups according to their products, such as textiles, construction materials, recycled metal, paper, or plastics. Most of these villages are in northern and central Vietnam, and the Red River basin has the largest number of craft villages, accounting for 60% of all such villages in the country (MONRE 2008). All these villages have been facing environmental pollution problems. Pollution in these villages has not decreased and, in fact, has tended to increase. This may explain why industrial chemicals constituted large proportions of the contaminant composition in Hue-Danang (17%).

Many pharmaceuticals and their metabolites have been detected in aquatic environments (Hereber 2002; Caliman et al. 2009). In the present study, PPCPs contributed greatly to the total distribution; 37% in Hanoi, 29% in HCMC-SDR, and 17% in Hue-Danang (Fig. 3-3). Because PPCPs are one of the major contaminants in surface samples of crowded cities, more research is needed on their fates and effects in the environment. Pesticides and industrial chemicals comprised only three and two percent in Hanoi; and three and seven percent in HCM-SDR, respectively; or 2–7 times lower than the rates found in Hue-Danang.

### **3.5.3 Correlations between organic compounds detected in surface waters**

The water quality parameters pH, total suspended solids (SS) and chemical oxygen demand (COD) were measured in this survey (Table S3-1). COD was observed in the range from 0.32 to 240 mg L<sup>-1</sup>. Seven sampling sites had COD values more than 5 times higher than Vietnam's 20 mg/L national surface water quality regulation (QCVN 08: 2008/BTNMT; HN1, HN2, HN3, HCM7, HCM9, HCM10

and HCM11). These sites are located in urban areas of Hanoi and HCMC. There were strong, positive correlations between COD and all groups of detected organic compounds (industrial chemicals, household chemicals, pesticides, plasticizers, and sterol; Fig. 3-4). Therefore, it can be said that there was no specific sources of contaminants, and surface water has become polluted by wastewater discharges from domestic, hospitals, factories and agricultural activities.



**Fig.3-4** Correlation between groups of detected organic compounds (COD: definition of chemical oxygen demand, IC: industrial chemical, Other HC: other household chemical)

### 3.5.4 Most frequently detected compounds in surface waters

Twenty four substances were found frequently ( $\geq 40\%$  samples, with detected concentrations  $>LOD$ ; Table 3-5), including 4 sterols [beta-sitosterol, cholesterol, stigmasterol (100%) and coprostanol (69%)], 6 plasticizers [DEHP (64%), DBP and TPP (62%), DEHA (57%), DEP (52%), bisphenol A (50%)], 6 pesticides

[pp'-DDE (60%), atrazine (57%), carbendazim (45%), ethoxyquin, tricyclazole (43%), fenobucarb (40%)], 4 PPCPs [cotinine (64%), lidocaine (55%), metformin (45%), caffeine (40%)], 2 industrial chemicals [PCB#1 (83%), dicyclohexylamine (81%)], and 2 household chemicals [4-methyl-2-6-di-t-butylphenol (67%), 4-tert-octylphenol (40%)]. The substances showing high concentrations ( $>1 \mu\text{g/L}$ ) were sterols such as cholesterol (81%), beta-sitosterol (74%), stigmasterol (71%), coprostanol (29%), phthalate plasticizer of DEHP (57%), DBP (17%), followed by caffeine and metformin (19%).

Of the plasticizers, DEHP was detected at the highest concentrations ( $>1 \mu\text{g L}^{-1}$  at each sampling location) of  $19 \mu\text{g L}^{-1}$  (HCMC),  $13.5 \mu\text{g L}^{-1}$  (Hanoi) and  $13.0 \mu\text{g L}^{-1}$  (Red River), followed by bisphenol A (HCMC 7.82), DEP (HCMC 7.49, Hanoi 6.41), DBP (Danang 4.92, Red River 4.22, HCMC 3.24, Hanoi 1.45). Other studies have also suggested high detection frequencies ( $>50\%$ ) of these substances in surface waters, but at higher concentrations. For example Clara et al. (2010) reported DEHP with a detection frequency of 100%, and maximum concentration of  $34 \mu\text{g L}^{-1}$ ; DEP: 100%,  $9.2 \mu\text{g L}^{-1}$ ; DBP: 53%,  $8.7 \mu\text{g L}^{-1}$ . Higher concentrations have also been reported in France, Germany and Canada [DEHP: maximum  $44 \mu\text{g L}^{-1}$ , DEP:  $25 \mu\text{g L}^{-1}$  (Dargnat et al. 2009); DEHP:  $97.8 \mu\text{g L}^{-1}$ , DBP:  $8.8 \mu\text{g L}^{-1}$  (Fromme et al. 2002); DEHP:  $70 \mu\text{g L}^{-1}$  (Barnabé et al. 2008), respectively].

**Table 3-5** List of most frequently detected compounds in 42 samples

Compound	Type of compound	LOD (ngL <sup>-1</sup> )	N > LOD	N > 0.1 µgL <sup>-1</sup>	N > 1 µgL <sup>-1</sup>	N > 10 µgL <sup>-1</sup>	Max (µgL <sup>-1</sup> )	Median (µgL <sup>-1</sup> )
Beta-Sitosterol	Sterol	100	42	42	31	7	25.2	1.98
Cholesterol	Sterol	100	42	42	34	8	70.6	1.66
Stigmasterol	Sterol	100	42	42	30	2	16.4	1.84
PCB #1	PCB	0.03	35	0	0	0	0.32 <sup>a</sup>	0.11 <sup>a</sup>
Dicyclohexylamine	Intermediate	8	34	14	3	0	3.32	0.07
Coprostanol	Sterol	10	29	22	12	6	57.8	0.12
4-Methyl-2,6-di-t-butylphenol	Antioxidant	25	28	7	0	0	0.41	0.04
Bis(2-ethylhexyl)phthalate	Plasticizer	10	27	26	24	6	19.0	2.25
Cotinine	Nicotine metabolite	8	27	10	5	0	2.84	0.01
Di-n-butyl phthalate	Plasticizer	10	26	19	7	0	4.92	0.08
Triphenylphosphate	Plasticizer	20	26	1	0	0	0.14	0.01
p,p'-DDE	Insecticide	0.03	25	0	0	0	4.14 <sup>a</sup>	0.04 <sup>a</sup>
Di(2-ethylhexyl)adipate	Plasticizer	10	24	14	0	0	0.44	0.03
Atrazine	Herbicide	10	24	0	0	0	0.03	0.01
Lidocaine	Anesthetic/ antiarrhythmic	8	23	4	0	0	0.23	0.02
Diethyl phthalate	Plasticizer	10	22	15	6	0	7.49	0.03
Bisphenol A	Plasticizer	10	21	9	2	0	7.82	0.01
Carbendazim	Fungicide	8	19	9	0	0	0.21	nd
Metformin	Antidiabetic	8	19	13	7	0	8.25	nd
Ethoxyquin	Fungicide	8	18	6	0	0	0.29	nd
Tricyclazole	Fungicide	8	18	0	0	0	0.10	nd
4-tert-Octylphenol	Nonionic detergent metabolite	10	17	3	0	0	0.85	nd
Fenobucarb	Insecticide	8	17	1	0	0	0.22	nd
Caffeine	Food product	10	17	16	8	1	13.0	nd

LOD: Limit of detection; a: calculated concentrations have unit ng L<sup>-1</sup>.

N: Number, Max: Maximum

In our study, we detected caffeine in surface waters at a maximum concentration of  $13.0 \mu\text{g L}^{-1}$ , much lower than the  $91.6 \mu\text{g L}^{-1}$  reported by Duong et al. (2014) but higher than in other studies [ $1.43 \mu\text{g L}^{-1}$  (Kong et al. 2014);  $6.9 \mu\text{g L}^{-1}$  (Edwards et al. 2015)]. Another PPCP, metformin (an antidiabetic), was detected at the highest concentration compared with other PPCPs found in this survey (Hanoi:  $8.23 \mu\text{g L}^{-1}$  at maximum, HCMC:  $2.25 \mu\text{g L}^{-1}$ ), albeit these concentrations were more than two times lower than the maximum concentration found in a study in China ( $20 \mu\text{g L}^{-1}$ ; Kong et al. 2014). Lower concentrations of metformin in surface waters have been observed in many developed countries, such as the maximum  $735 \text{ ng L}^{-1}$  in France (Vulliet et al. 2011) and  $1700 \text{ ng L}^{-1}$  in Germany (Scheurer et al. 2009).

### **3.5.5 Environmental risk assessment of micro-organic compounds**

The ratios of the measured environmental concentration (MEC, maximum concentration in surface water) and the predicted no effect concentration (PNEC) were used to assess the environmental risk of detected compounds. The MEC/PNEC values were  $< 1$  indicating no toxic potential (Quinn et al. 2008). Of 16 substances that were evaluated, six substances: nonylphenol (nonionic detergent metabolite), sulfamethoxazole, ampicillin, erythromycin, clarithromycin (antibiotic) and acetaminophen (analgesic) had  $\text{MEC} / \text{PNEC} > 1$  (Table 3-6). It indicates that these compounds are of concern and may warrant tier three toxicity assessment.

**Table 3-6** The MEC/PNEC ratios of detected compounds

Compound	MEC ( $\mu\text{g L}^{-1}$ )	PNEC, ( $\mu\text{g L}^{-1}$ )	MEC/PNEC
Nonylphenol	26.9	0.21 <sup>a</sup>	128
Sulfamethoxazole	2.16	0.027 <sup>b</sup>	80
Ampicillin	0.64	0.075 <sup>c</sup>	8.6
Acetaminophen	5.64	1 <sup>b</sup>	5.6
Erythromycin	0.09	0.02 <sup>b</sup>	4.3
Clarithromycin	0.17	0.07 <sup>b</sup>	2.4
Sulfadiazine	0.11	0.135 <sup>b</sup>	0.8
Bisphenol A	7.82	11 <sup>a</sup>	0.7
Propranolol	0.13	0.244 <sup>b</sup>	0.5
Trimethoprim	0.18	2.6 <sup>b</sup>	0.1
Lincomycin	2.66	82 <sup>b</sup>	0.03
Roxithromycin	0.05	4 <sup>b</sup>	0.01
Atenolol	0.27	30 <sup>b</sup>	0.01
Cimetidine	0.19	35 <sup>b</sup>	0.01
Carbamazepin	0.03	13.8 <sup>b</sup>	0.002
Sulfapyridine	0.03	21.61 <sup>b</sup>	0.002

a: MOE 2001; b: Verlicchi et al. 2012; c: Kümmerer et al. 2003

### 3.5.6 Polar organic pollutants in surface water and groundwater

#### 3.5.6.1 Detection of polar organic pollutants in surface water

The results of compounds detected in each study site were summarized in Table 3-7. Since only few compounds were found in Red River, Hue City and Danang City at low concentrations in the dry season, samples of these sites were not collected in the rainy season. In general, the number and concentrations of compounds detected in samples collected from Hanoi and HCMC were nearly the same, and were much larger than those detected in Danang and Hue (Table 3-7). Sampling sites in Hanoi urban area had high concentrations of PPCPs compared with those in suburban areas. This pattern was also observed among samples collected in urban area and suburban area of HCMC, Danang and Hue. The total concentration of PPCPs in all the samples from Hanoi and HCMC was also higher than in samples from Danang and Hue. It is clear that differences in population density and economic activities are one of the

main reasons leading to the disparity in the number and concentration of detected compounds. In the rainy season, the number of detected compounds increased, however, the concentrations of them decreased, probably due to dilution of rainwater.

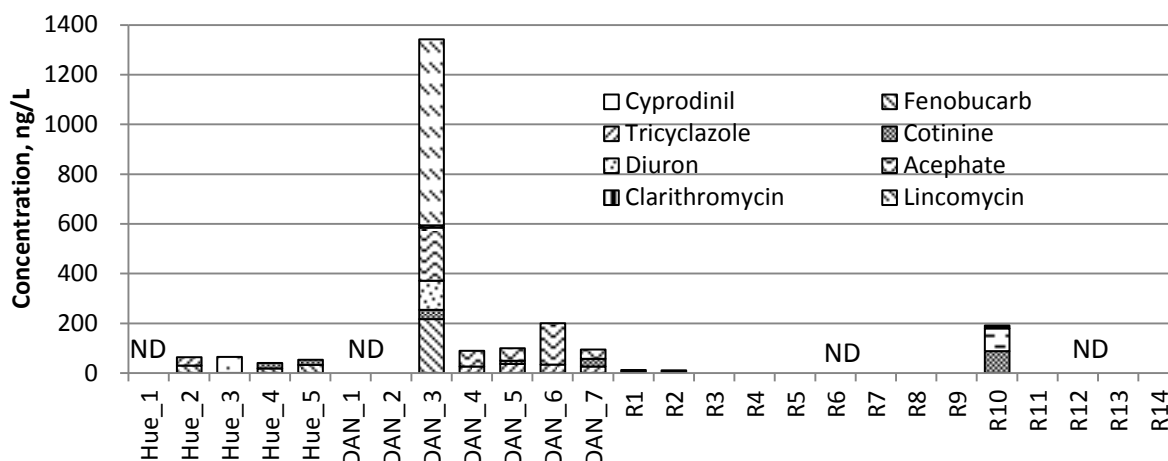
**Table 3-7** Summary of the number and total concentrations of compounds detected in study areas

	Ns	Dry season, 2013/2		Rainy season, 2013/9	
		TC, ng/L	Nc	TC, ng/L	Nc
Red river	14	ND - 190	3	-	-
Hue City	5	ND - 70	4	-	-
Danang	7	ND - 1340	11	-	-
Hanoi	5	3170 - 13 600	21	160 – 10 600	24
HCMC	6	860 – 11 900	22	590 – 14 600	30
Saigon-Dongnai River	5	280 - 1750	13	275 - 1390	40

Ns: Number of samples, TC: Total concentration, Nc: Number of detected compounds

#### 3.5.6.1.1 Red River

No compound was found in most of the 14 samples except for sampling site R1, R2 and R10 (Fig.3-5). Carbendazim (fungicide) was detected in R1 and R2, R10 with concentration of 10 – 12 ng L<sup>-1</sup>. Acetaminophen (analgesic) and cotinine (metabolite of nicotin) were only found at R10 at the concentrations of 91 ng L<sup>-1</sup> and 88 ng L<sup>-1</sup>, respectively. Total concentration of compounds found at R10 was 191 ng L<sup>-1</sup>. Sampling site R10 is the ferry terminal located in the south of Hanoi and about 30 km from the center of Hanoi. The down stream of Hanoi and high population density are the main reasons for the detection of PPCPs at this ferry terminal. In site R11, no compound was found, although it was only about 25 km from site R10. Probably, the reason was that compounds detected in site R10 at low concentrations, were diluted and decomposed before reaching the downstream.



**Fig.3-5:** Total concentrations of PPCPs and pesticides found in Hue, Danang and Red river

### 3.5.6.1.2 Hue city

Four compounds out of 310 target compounds were detected in Hue samples at low concentrations ( $<70 \text{ ng L}^{-1}$ ) including 1 PPCP (cotinine) and 1 insecticide (fenobucarb), 2 fungicides (tricyclazole, and cyprodinil) (Fig.3-5). Cotinine was only found at Hue\_4 and Hue\_5 in the urban area with nearly the same concentrations (21 and  $20 \text{ ng L}^{-1}$ ). Small numbers of PPCPs were found in Hue samples maybe because Hue city is sparsely populated (average,  $235 \text{ persons/km}^2$  (GSO 2016)) in most areas. Pesticides were detected in samples of the rural areas due to agricultural activities.

### 3.5.6.1.3 Danang city

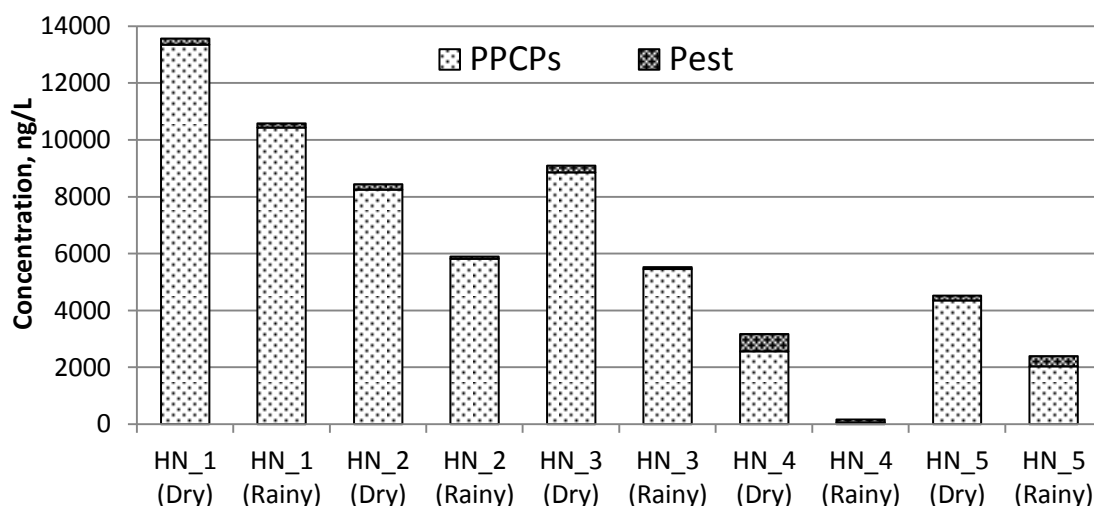
Seven compounds (3 PPCPs, 4 pesticides) were detected and their total concentrations ranged from ND to  $1340 \text{ ng L}^{-1}$  (Fig.3-5). DAN\_1 and DAN\_2 were collected in Lien Chieu River and Cu De River, which the water sources are seriously contaminated due to the wastes from industrial zones at Danang coastal area. However, in this study no water soluble chemicals were detected in these sites (Fig.3-5). Whereas DAN\_3 was collected from a small canal – Phu Loc River in the center of the city (the old urban area) showed a high concentration. Most of PPCPs were found in this sample at the total concentration of  $790 \text{ ng L}^{-1}$ . Lincomycin, one kind of antibiotics using for both human and animals, was detected with  $750 \text{ ng L}^{-1}$  accounting 94% of the total concentration of PPCPs found and 56% of total concentration of compounds found in DAN\_3. There are a lot of clinics and hospitals in this area including Thanh Khe health center, Lien Chieu health center, Da Nang



emergency center, etc. Wastewater from these hospitals and clinics is either already treated or not, discharged into global sewer collection systems of the city. This is probably the main reason that leads to high concentrations of PPCPs detected in site DAN\_3.

#### 3.5.6.1.4 Hanoi city

In the dry season, 22 compounds (14 PPCPs and 7 pesticides, 1 industrial chemical) were found with total concentrations of 3170 – 13 600 ng L<sup>-1</sup>. Twenty four compounds (14 PPCPs and 10 pesticides) were found with total concentrations of 160 – 10 600 ng L<sup>-1</sup> in the rainy season. Eleven compounds (7 PPCPs and 4 pesticides) were detected in both the dry and rainy season. In general, the concentrations of PPCPs detected in urban areas (HN\_1, HN\_2 and HN\_3) were 2 – 5 times higher than those in suburban areas (HN\_4 and HN\_5); and decreased in the rainy season, maybe because of dilution by rainwater (Fig.3-6). PPCPs accounted for more than 80% of the total concentration of each sampling site. The number and total concentrations of pesticides found in suburban areas increased in the rainy season due to agricultural activities.



**Fig.3-6:** Total concentrations of PPCPs and pesticides found in Hanoi samples

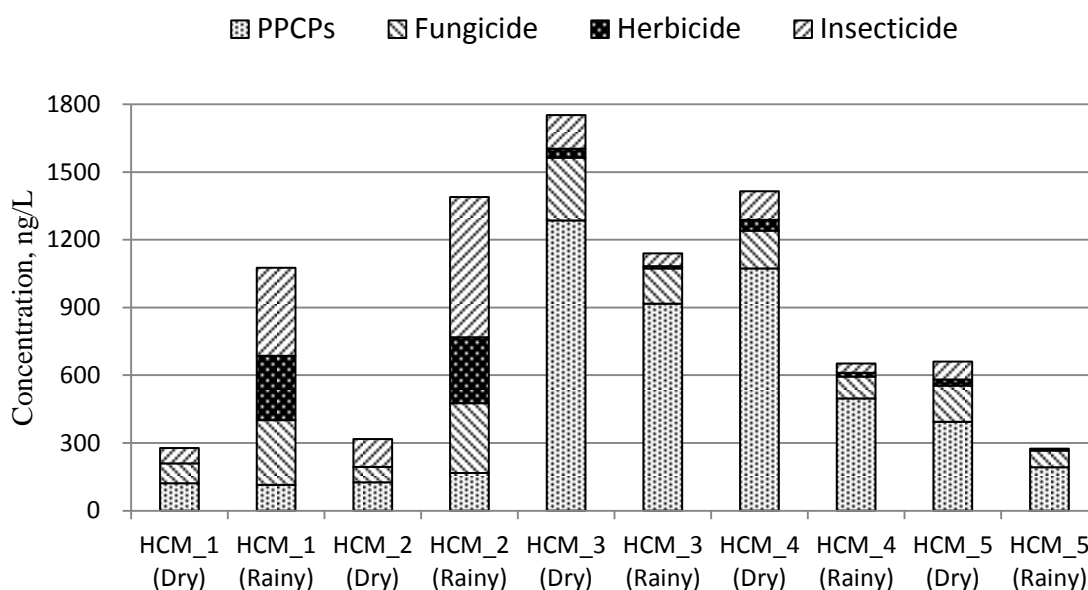
HN\_4 and HN\_5 were collected at the upstream and downstream of Nhue River, which is formed on the right bank of the Red River and receives Hanoi's wastewater.

The total concentrations of compounds found at the downstream site (4540 ng L<sup>-1</sup> and 2400 ng L<sup>-1</sup>) were higher than those at the upstream site (3190 ng/L and 160 ng/L) in both the dry and rainy season, respectively (Fig.3-6). The total concentration of compounds detected in HN\_4 decreased nearly 20 times in the rainy season, since Nhue River received a huge water volume from Red River. Fifteen compounds (7 PPCPs and 7 pesticides, 1 industrial chemical) and 19 compounds (9 PPCPs and 10 pesticides) were found at these sites in the dry and rainy season, respectively. Although water of the Nhue River is polluted, it is still used for agricultural and aquacultural activities in the watershed. Therefore, pesticides and veterinary medicines were found at these sites. The number of detected compounds in the rainy season, especially the number of pesticides, is higher than this in the dry season, however, the concentrations of detected compounds decreased in the rainy season due to rainwater.

Seventeen compounds (14 PPCPs and 2 pesticides, 1 industrial chemical) and 17 compounds (14 PPCPs and 3 pesticides) were found at HN\_1, HN\_2 and HN\_3 with total concentrations of 8480 – 13 600 ng L<sup>-1</sup> and 5530 – 10 600 ng L<sup>-1</sup> in the dry and rainy season, respectively. Site HN\_1, HN\_2 and HN\_3 were collected in Kim Nguu River and Lu River, Tolich River which seem to be wastewater canals and received large amount of untreated domestic wastewater in Hanoi city. Therefore, most of detected compounds were PPCPs with high concentrations. The number of PPCPs detected in these urban sites was nearly the same and 2 times higher than this in suburban sites. In addition of pesticides, the number of detected compounds was 5 times less than this in suburban sites.

#### **3.5.6.1.5 Saigon River and Dongnai River**

At the 5 sites, 13 compounds (5 PPCPs, 7 pesticides and 1 industrial chemical) were detected with total concentrations of 320 - 1780 ng L<sup>-1</sup> in the dry season, and 40 compounds (7 PPCPs and 33 pesticides) were detected with total concentrations of 260 - 1390 ng L<sup>-1</sup> in the rainy season.



**Fig.3-7:** Total concentrations of PPCPs and pesticides found in Dongnai River samples and Saigon River samples of HCMC

Since these sampling sites are located in rural areas, the number and concentrations of PPCPs were few and low except for HCM\_3 and HCM\_4. Concentrations of PPCPs found in HCM\_3 were  $1290 \text{ ng L}^{-1}$  and  $890 \text{ ng L}^{-1}$ ; HCM\_4:  $1070 \text{ ng L}^{-1}$  and  $450 \text{ ng L}^{-1}$  in the dry and rainy season, respectively, 3-7 times higher than those in other sites as influenced by wastewater from the urban area of HCMC. At present, four water resources are used for water supply in HCMC. They are Dong Nai River, Sai Gon River, ground water and rain water. Saigon and Dong Nai Rivers obtained 67% of the total volume of water for domestic and industrial uses in HCMC (Nga 2006). This study showed that site HCM\_2 (Ben Suc Bridge) at the upstream of the Hoa Phu Pump Station of the Tan Hiep Water Treatment Plant and HCM\_1 (Dongnai Bridge) located at the middle of the Hoa An Pump Station and a the Binh An raw water pumping station; were detected with high level of pesticides. The number and concentrations of pesticides found at site HCM\_1 and HCM\_2 in the rainy season were 6 times higher than those in the dry season because of agricultural activities (Fig.3-7). However, there has not been any study to evaluate the effectiveness of STPs in the treatment of water-soluble chemicals such as pesticides.

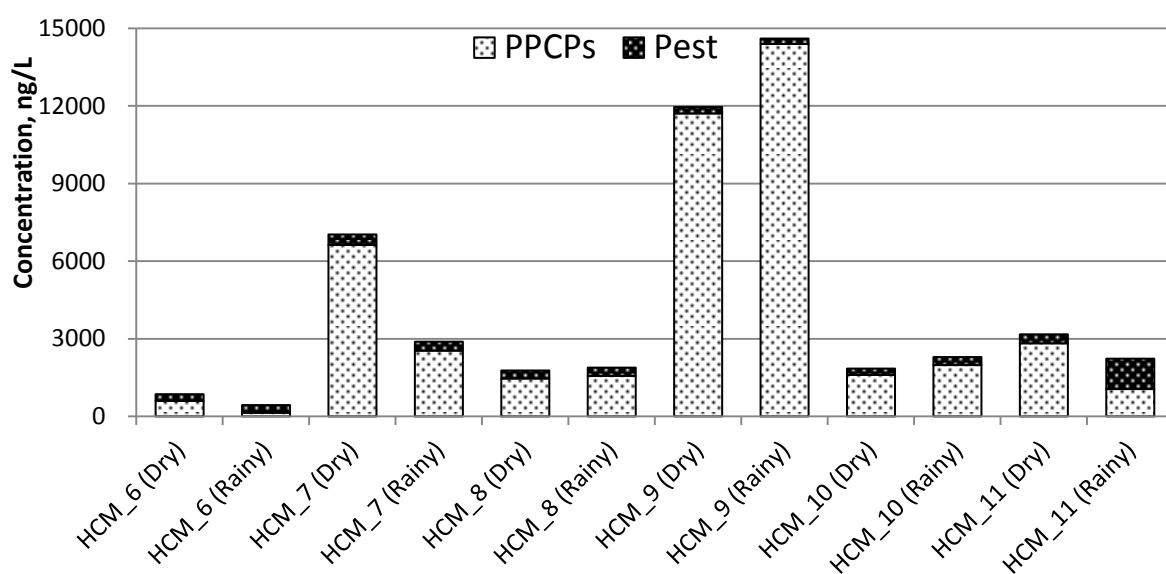
### 3.5.6.1.6 Ho Chi Minh city

In HCMC samples, 22 compounds (15 PPCPs, 6 pesticides and 1 industrial chemical) were detected with total concentrations of 860 – 11 900 ng L<sup>-1</sup> in the dry season, and 30 compounds (16 PPCPs and 14 pesticides) were detected with total concentrations of 590 – 14 600 ng L<sup>-1</sup> in the rainy season. Similar to Hanoi, most of detected compounds were PPCPs accounting over 80% of total concentrations. The total concentrations of PPCPs were high in urban areas and decreased in the rainy season. Seventeen compounds (11 PPCPs and 6 pesticides) were detected in both the dry and rainy season. Pesticides were found with high number and concentrations in suburban area.

In urban area, wastewater of Tham Luong-Vam Thuat canal (HCM\_7), Nhieu Loc-Thi Nghe canal (HCM\_8) was collected by wastewater collection system and diluted by Saigon Rive. Wastewater of Tau Hu-Ben Nghe canal (HCM\_10) was collected and treated at Binh Hung wastewater treatment plant with a capacity of 141000 m<sup>3</sup>/day. Therefore, quality of water of these canals has been significantly improved, however, still not met the environmental standards. This is probably a main result that total concentrations of compounds detected in urban area of HCMC were 2 – 3 times lower than those in Hanoi, excepting for Tan Hoa-Lo Gom canal (HCM\_9). Domestic wastewater from 120 000 households of Tan Hoa-Lo Gom area was collected and treated at Binh Hung Hoa wastewater treatment plant, however, this treatment plant was not operated properly capacity of 30 000 m<sup>3</sup>/day. Therefore, the water of Tan Hoa-Lo Gom canal did not satisfy column B2 of the environmental standards QCVN 08:2008/BTNMT (HCMC People's Committee, report 2014). This lead to high concentrations of compounds found at site HCM\_9, about 2 – 5 times higher than other urban sites of HCMC (Fig.3-8).

In suburban area, Thay Cai-An Ha canal (HCM\_6) polluted by pH, TSS, DO, BOD. It is said that this area affected by the Tan Phu Trung Industrial Zone, North West Industrial Zone in Cu Chi, industrial clusters - Xuan Nhi residential, industrial, handicraft Le Minh Xuan and Vinh Loc A, etc. and production facilities located outside industrial parks. There is also the landfills, waste treatment, such as solid

waste Northwest Cu Chi, garbage treatment plant and composting Viet Star treatment plant and recycle household waste Tam Sinh Nghia (DONRE 2012). Other suburban site, HCM\_11 taken at Binh Dien Bridge crossing Cho Dem River (the downstream of Tan Hoa-Lo Gom and Doi canal) was detected with high concentration of PPCPs, even higher than this in urban sites (HCM\_8, HCM\_10) in the dry season (Fig.3-8). In the rainy season, both number and total concentration of pesticides increased about 3 times, probably due to agricultural activities.



**Fig.3-8:** Total concentrations of PPCPs and pesticides found in HCMC samples

### 3.5.6.1.7 Description of the most frequently detected contaminants in big cities

In case of Hanoi and HCMC samples (total 22 samples collected in the dry and rainy seasons), the most common type of PPCPs detected in samples was antibiotic. As shown in Table 3-8, Lincomycin and sulfamethoxazole were found with a high frequency (91% and 86%, respectively). Maximum concentrations of lincomycin and sulfamethoxazole were found in urban rivers ( $3550 \text{ ng L}^{-1}$ ,  $2250 \text{ ng/L}$ , respectively), their concentrations were higher than in surface waters in Spain ( $47 \text{ ng L}^{-1}$  and  $30 \text{ ng L}^{-1}$ ) (Emma GL *et al*, 2011), and Germany ( $480 \text{ ng/L}$  of sulfamethoxazole) (Roma H *et al*, 1999).

**Table 3-8** Frequency of compounds detected in Hanoi and HCMC samples (both the dry and rainy seasons, n=22)

Compound	LOD ng L <sup>-1</sup>	Frequency %	Median ng L <sup>-1</sup>	Max ng L <sup>-1</sup>	Use
Cotinine	8	100	525	2855	Nicotine metabolite
Carbendazim	8	95	105	200	Fungicide
Lincomycin	80	91	1130	3550	Antibiotic
Sulfamethoxazole	20	86	455	2250	Antibiotic
Diuron	8	86	54	133	Herbicide
Lidocaine	8	77	82	229	Anesthetic
Fenobucarb	8	73	31	66	Insecticide
Clarithromycin	8	68	43	172	Antibiotic
Tricyclazole	8	64	48	531	Fungicide
Dicyclohexylamine	8	45	128	565	Enzyme inhibitors
Losartan	8	45	78	325	Anti-arrhythmia
Triphenyl phosphate	20	45	28	54	Flame retardant
Carbofuran	8	45	68	83	Insecticide
Acetaminophen	20	41	1560	4880	Analgesic
Sulpiride	20	36	60	537	Antidepressant
Atenolol	8	32	61	627	Anti-arrhythmia
Acetamiprid	8	32	18	42	Insecticide

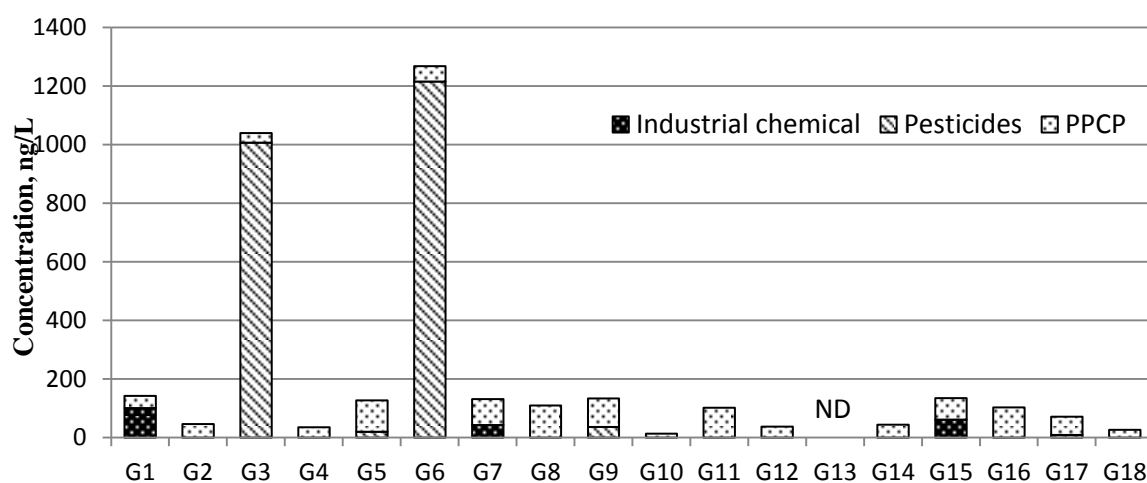
Cotinine was detected in all Hanoi and HCMC samples at an average concentration of  $942 \text{ ng L}^{-1}$ , and it is higher than the average concentration ( $40 \text{ ng L}^{-1}$ ) of cotinine in US surface waters (Ferrer I *et al*, 2012). One possible source of this cotinine is untreated wastewater from cigarette factories containing a high level of cotinine, being discharged directly into rivers. Acetaminophen was detected in urban river from Hanoi and HCMC at maximum concentrations of  $4780 \text{ ng L}^{-1}$  and  $4880 \text{ ng L}^{-1}$ , respectively; these concentrations are higher than the maximum value ( $1970 \text{ ng L}^{-1}$ ) in surface water reported in Spain (Emma GL *et al*, 2011).

About detected pesticides, some compounds were detected frequently in samples of Hanoi and HCMC. These included carbendazim and diuron, fenobucarb (Table 3-8). Carbendazim was detected in 95 % of Hanoi and HCMC samples with the maximum and mean values of  $200 \text{ ng L}^{-1}$  and  $105 \text{ ng L}^{-1}$ , respectively. Duron was detected in 86% of Hanoi and HCMC samples with  $133 \text{ ng L}^{-1}$  of maximum concentration. Some compounds were detected frequently in HCMC samples but infrequently in Hanoi samples such as fenobucarb (insecticide) and tricyclazole (fungicide). Fenobucarb was detected in 90% of HCMC samples and 60% of Hue samples with maximum concentration of  $43 \text{ ng L}^{-1}$  (HCMC) and  $33 \text{ ng L}^{-1}$  (Hue). Tricyclazone was detected in 100% of HCMC samples with maximum concentration of  $98 \text{ ng L}^{-1}$  and median value of  $56 \text{ ng L}^{-1}$ . However, it was detected in only one Hanoi sample with  $9 \text{ ng L}^{-1}$  of concentration. Tricyclazone was also detected in 57% of Danang samples with  $36 \text{ ng L}^{-1}$  of maximum concentration and  $26 \text{ ng L}^{-1}$  of median value. These compounds are used commonly in agricultural of Vietnam. But in each area, the amount of consumption of these compounds is different. Therefore, the kind of detected pesticides and detected concentration were different in river samples of the studied cities.

### **3.5.6.2 Detection of polar organic pollutants in groundwater**

A summary of the analytical results for the water-soluble chemicals measured in the 18 groundwater samples is given in Table 3-9. In total 36 compounds (1 industrial chemical, 4 PPCPs and 31 pesticides) were detected with total concentrations of ND~ $1270 \text{ ng L}^{-1}$  (Fig. 3-9). The average frequency of detection for all compounds

was 15%. A comparison with the results from the Hanoi river water, where the average frequency of detection was 55%, shows a higher chemical contamination of surface water in comparison to groundwater. Since groundwater samples were collected in the urban zones of Hanoi, PPCPs were detected in most of samples (Fig.3-8). Especially, the total concentrations of PPCPs in site G5 (107 ng L<sup>-1</sup>), G7 (88 ng L<sup>-1</sup>), G8 (109 ng L<sup>-1</sup>), G9 (98 ng L<sup>-1</sup>), G11 (102 ng L<sup>-1</sup>) and G16 (103 ng L<sup>-1</sup>) were 2-3 times higher these in other sites. These sites had high levels of PPCPs, probably because of leakage of the heavily polluted river water (site G5 nearby Kimnguu River; G7 and G11 nearby Tolich River; and G8, G9 nearby Lu River). Most of pesticides were found in site G3 (29 compounds) and G6 (32 compounds) with total concentrations of 1000 and 1210 ng L<sup>-1</sup>, respectively (Fig.3-9). The sources of these pesticides were still unknown. Therefore, it is necessary to survey on water-soluble chemicals in groundwater around these sites.



**Fig.3-9:** Total concentrations of PPCPs and pesticides found in Hanoi groundwater

The most frequently detected compounds were lidocaine (89%) and dicyclohexylamine (67%) with the maximum concentrations of 81 and 39 ng L<sup>-1</sup>, respectively (Table 3-9). Their concentrations were higher than the maximum concentrations reported in the research on pharmaceuticals in groundwater of Tama river basin, Japan (61 ng L<sup>-1</sup> of lidocaine, Akifumi Abe 2010), and in the results from the Swedish National Screening Program 2007 (4 ng L<sup>-1</sup> of dicyclohexylamine, Andreas et al. 2008). Other 2 PPCPs of sulfamethoxazole and lincomycin were



detected in 3 out of 18 Hanoi groundwater samples with the maximum levels of 32 and 47 ng L<sup>-1</sup>, respectively. Sulfamethoxazole was the most frequently detected compound in EU groundwater (24.4% of frequency and a maximum concentration of 38 ng L<sup>-1</sup>, Robert Loos et al. 2010) and in the United States groundwater (23.4%, 1.11µg L<sup>-1</sup>, Kimberlee K.B et al. 2008). Lincomycin was found with 5.4% of the frequency of detection in the United States groundwater and the maximum concentration is 320 ng L<sup>-1</sup> (Kimberlee K.B et al. 2008), 6 times higher than this level in Hanoi groundwater.

**Table 3-9** Analytical results for water-soluble chemicals in Hanoi groundwater

Compound	LOD, ng/l	Frequency %	Max, ng/L	Median, ng/L	Use
Lidocaine	8	89	81	33	Anesthetic
Dicyclohexylamine	8	67	39	19	Enzyme Inhibitor
Fenthion sulfone	8	22	105	0	Insecticide
Triphenylphosphate	20	17	101	0	Flame retardant
Carbofuran	8	17	24	0	Insecticide
Fenthion sulfoxide	8	17	82	0	Insecticide
Tebuthiuron	8	11	45	0	Herbicide
Carbaryl	8	11	19	0	Insecticide
Diuron	8	11	89	0	Herbicide
Fluridone	8	11	12	0	Herbicide
Flufenacet	8	11	36	0	Herbicide
Tebufenozide	8	11	17	0	Insecticide
Thiabendazole	8	11	39	0	Fungicide
Dimethirimol	8	11	19	0	Fungicide
Ferimzone(E)	40	11	47	0	Fungicide
Ferimzone(Z)	8	11	60	0	Fungicide
Chromafenozide	8	11	14	0	Insecticide
Butafenacil	8	11	23	0	Herbicide
Iprovalicarb	8	11	44	0	Fungicide
Pirimicarb	8	11	32	0	Insecticide
Furametpyr	8	11	38	0	Fungicide
Methabenzthiazuron	8	11	41	0	Herbicide
Azoxystrobin	8	11	47	0	Fungicide
Dymron	8	11	48	0	Herbicide
Cumyluron	8	11	25	0	Herbicide
Chloroxuron	8	11	24	0	Herbicide
Mepanipyrim	8	11	26	0	Fungicide
Triticonazole	8	11	48	0	Fungicide
Fenthion oxon sulfone	8	11	57	0	Insecticide
Fenthion oxon sulfoxide	8	11	70	0	Insecticide
Tricyclazole	8	11	53	0	Fungicide
Sulfamethoxazole	20	11	32	0	Antibiotic
Lincomycin	80	11	47	0	Antibiotic
Boscalid	40	6	84	0	Fungicide
Pyrifthalid	20	6	22	0	Herbicide
Methoxyfenozide	8	6	19	0	Insecticide

### 3.6 Conclusions

In the present study, 165 out of 1153 micro-pollutants examined were detected in surface waters, and of which more than 100 contaminants occurred at  $\mu\text{g L}^{-1}$  level of concentrations in Hanoi and HCMC. Rivers in large cities were heavily polluted by a large number of organic micro contaminants, mainly from domestic sources such as PPCPs, plasticizers and other household chemicals. Compared with large cities, Hue-Danang, the Red River and Saigon-Dongnai River were less contaminated, and their pollutant sources were not just domestic but also agricultural and small-scale industries. The most frequently detected contaminants were plasticizers (DEHP, DEP, DBP, bisphenol A), dicyclohexylamine, and PPCPs (caffeine, metformin, cotinine). Their concentrations were high ( $> 1\mu\text{g L}^{-1}$ ) higher than those found in international studies. Nonylphenol, sulfamethoxazole, ampicillin, acetaminophen, erythromycin, clarithromycin had risk quotients (MEC/PNEC)  $>1$ , suggesting these chemicals may be causing ecological harm, although further detailed field study is required to confirm this hypothesis.

About groundwater, 36 out of 311 target compounds were detected at  $\text{ng L}^{-1}$  level of concentration. The sources of contaminants were largely unknown. Therefore, more systematic regional scale studies are needed to fully assess the spatial and temporal occurrence of water-soluble chemicals in groundwater.

## Chapter 4 GENERAL CONCLUSIONS

In this study, we developed a comprehensive analytical method consisting of SPE, using PS2-AC2 and HLB-AC2, and LC-TOF/MS analysis equipped with an accurate-mass database of 311 LOCs with accurate masses of protonated molecule and fragment ions, retention times, method detection limits and calibration curves. The experimental results clearly showed the effectiveness of the combination of the tandem SPE and LC-TOF/MS-TIM methods for the screening analysis of LOCs in real environmental samples. The developed screening analytical method saves on the cost of labor required to run multiple tests, and decreases both the consumption of solvent and the emission of toxic wastes, while making it possible to quickly determine a huge number of pollutants in one analysis. This proposed method is expected to be very efficient for primary screening surveys of previously uninvestigated waters, for a more complete grasp of a pollution picture, particularly by the combination with the comprehensive methods using an Automated Identification and Quantification System, and for emergency surveys after natural disasters such as earthquakes as well as the accidental release of pollutants. In addition, data obtained by this method can be used for non-target analysis and retrospective analysis. Since full-mass spectrum with accurate masses is obtained by LC-TOF/MS, the number of compounds found and confirmed can be increased unlimitedly, even after analysis.

By applying the developed screening method, the occurrence, contamination levels, pollution characteristic, and the potential sources of contaminants in Vietnamese aquatic environment were clarified. In addition, the toxicological effects of detected contaminants on human and aquatic organisms were assessed. This study showed that Vietnamese rivers in big cities (Hanoi and HCMC) were heavily polluted with a large number of LOCs; particularly, concentrations of PPCPs (cotinine, lincomycin, sulfamethoxazole and acetaminophen) were higher than those of international studies. The number and concentrations of compounds detected in samples collected from Hanoi and HCMC were nearly the same, and were much larger than those detected in small cities and rural areas (Danang and Hue).

Regarding the seasonal difference of detected compounds, the concentrations of PPCPs decreased in the rainy season because of dilution by rainwater. The number and total concentration of pesticides found in suburban areas were increased in the rainy season due to agricultural activities. The number of detected contaminants and concentration levels in groundwater were much lower than those of surface water. One of the main causes of serious pollution is that construction speed of sewage treatment plants does not catch up economic growth and urbanization. Therefore accelerated construction of sewage treatment plants and enlightenment about chemicals are necessary to prevent expansion of pollution.

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Appendices

**APPENDICES**

**Table S2-1** List of target compounds

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion		Isotopic ion, m/z	Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound		
					Ion	m/z		Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV			
1	Household chemicals	Dicyclohexylamine	8	18.03	(M+H)+	182.1899		83.0856	250		100.1122	200										Intermediate			
2	Household chemicals	Triphenylphosphate	20	29.69	(M+H)+	327.0782																Plasticizer			
3	Industrial chemicals	2-(Di-n-butylamino)ethanol	8	14.00	(M+H)+	174.1851																Intermediate for dyes			
4	Industrial chemicals	3,3-Dimethoxybenzidine	8	20.59	(M+H)+	245.1275																Dyes/intermediate			
5	Industrial chemicals	4,4'-Diaminodiphenyl-methane	20	19.06	(M+H)+	199.1226																Dyes/intermediate			
6	Industrial chemicals	4,4'-Methylenebis(N,N-dimethylaniline)	40	31.81	(M+H)+	255.1855																Dyes/intermediate			
7	Industrial chemicals	4,4'-Oxybis-benzenamine	80	16.55	(M+H)+	201.1014																Azo dyes			
8	Pesticide	2,3,5-Trimethacarb	8	24.07	(M+H)+	194.1174																Insecticide			
9	Pesticide	Acephate	20	6.51	(M+H)+	184.0189	186.0150	CH <sub>2</sub> O <sub>2</sub> PS	110.9670	250		94.9894	250	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS	124.9826	250							Insecticide		
10	Pesticide	Acetamiprid	8	16.35	(M+H)+	223.0750	225.0716	C <sub>6</sub> H <sub>5</sub> CIN	126.0105	250	C <sub>3</sub> H <sub>2</sub> Cl	72.9845	250										Insecticide		
11	Pesticide	Adenochrome semicarbazone/Carbazochrome	20	10.99	(M+H)+	237.0974																Other pesticide			
12	Pesticide	Alachlor	40	27.81	(M+H)+	270.1252	272.1226		238.0993		C <sub>11</sub> H <sub>16</sub> N	162.1277											Herbicide		
13	Pesticide	Aldicarb	8	18.90	(M+NH <sub>4</sub> )+	208.1111	210.1072	C <sub>5</sub> H <sub>10</sub> NS	116.0534	100	C <sub>4</sub> H <sub>6</sub> NS	100.0221		C <sub>4</sub> H <sub>6</sub> S	89.0425	100								Insecticide	
14	Pesticide	Aldicarb sulfone	8	10.56	(M+H)+	223.0744	225.0705	C <sub>4</sub> H <sub>8</sub> NO	86.0606	200	C <sub>5</sub> H <sub>10</sub> NO <sub>2</sub> S	148.0432	200	C <sub>3</sub> H <sub>12</sub> NO <sub>3</sub> S	166.0538	200	C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub>	76.0399	200					Insecticide	
15	Pesticide	Ametryn	8	25.94	(M+H)+	228.1275	230.1235	C <sub>6</sub> H <sub>12</sub> N <sub>3</sub> S	186.0813	250	C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> S	116.0282	250	C <sub>5</sub> H <sub>10</sub> N <sub>3</sub> S	144.0595									Herbicide	
16	Pesticide	Anilofos	40	29.16	(M+H)+	368.0312	370.0276	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS	124.9826	250	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> PS <sub>2</sub>	198.9652	250	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> PS <sub>2</sub>	170.9703	250								Herbicide	
17	Pesticide	Aramite	400	31.61	(M+NH <sub>4</sub> )+	352.1343	354.1314	C <sub>13</sub> H <sub>19</sub> O	191.1436	200	C <sub>9</sub> H <sub>11</sub> O	135.0810	250	C <sub>7</sub> H <sub>7</sub>	91.0548	250	C <sub>7</sub> H <sub>7</sub> O	107.0497	250					Insecticide	
18	Pesticide	Asulam	8	2.03	(M+NH <sub>4</sub> )+	248.0698	250.0657	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S	156.0119	200	C <sub>6</sub> H <sub>6</sub> N	92.0500	250	C <sub>5</sub> H <sub>6</sub> N	80.0500	250								Herbicide	
19	Pesticide	Atrazine	8	23.68	(M+H)+	216.1011	218.0981	C <sub>5</sub> H <sub>9</sub> CIN <sub>5</sub>	174.0546	250	C <sub>2</sub> H <sub>3</sub> CIN <sub>3</sub>	104.0015	250										Herbicide		
20	Pesticide	Avermectin B1a	80	33.83	(M+Na)+	895.4803			528.2443	250		570.4583	250		746.5623	250		305.2117	250				Anthelmintics		
21	Pesticide	Azamethiphos	8	20.89	(M+H)+	324.9811	326.9780	C <sub>7</sub> H <sub>4</sub> CIN <sub>2</sub> O <sub>2</sub>	182.9961	200		111.9951	250	C <sub>6</sub> H <sub>4</sub> CIN <sub>2</sub>	139.0063	250								Insecticide	
22	Pesticide	Azimsulfuron	80	14.72	(M+H)+	425.1102	427.1057	C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>	182.0566	250	C <sub>6</sub> H <sub>10</sub> N <sub>7</sub> O <sub>2</sub> S	244.0617	250										Herbicide		
23	Pesticide	Azinphos-methyl	40	25.83	(M+H)+	318.0132	320.0088	C <sub>8</sub> H <sub>6</sub> NO	132.0449	250	C <sub>6</sub> H <sub>5</sub> N <sub>2</sub>	105.0453	200	C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> O	160.0511	150	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS	124.9826	200					Insecticide	
24	Pesticide	Azoxystrobin	8	26.07	(M+H)+	404.1243		C <sub>21</sub> H <sub>14</sub> N <sub>3</sub> O <sub>4</sub>	372.0984	250	C <sub>20</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub>	344.1035	250										Fungicide		
25	Pesticide	Bendiocarb	40	21.21	(M+H)+	224.0914		C <sub>9</sub> H <sub>11</sub> O <sub>3</sub>	167.0708	150	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub>	109.0290	200	C <sub>5</sub> H <sub>5</sub> O	81.0340	250								Insecticide	
26	Pesticide	Benfuracarb	40	31.05	(M+H)+	411.1960	413.1906	C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S	195.0440	250	C <sub>12</sub> H <sub>14</sub> NO <sub>3</sub> S	252.0694	250	C <sub>8</sub> H <sub>16</sub> NO <sub>3</sub> S	190.0902	200								Insecticide	
27	Pesticide	Bensulfuron-methyl	80	22.13	(M+H)+	411.0974	413.0927	C <sub>9</sub> H <sub>9</sub> O <sub>2</sub>	149.0603	250	C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>	182.0566	250	C <sub>7</sub> H <sub>7</sub>	91.0548	250			181.1054	250				Herbicide	
28	Pesticide	Bensulide	8	28.29	(M+H)+	398.0683	400.0636	C <sub>8</sub> H <sub>13</sub> NO <sub>4</sub> PS <sub>3</sub>	313.9744	200	C <sub>11</sub> H <sub>19</sub> NO <sub>4</sub> PS <sub>3</sub>	356.0214	150	C <sub>6</sub> H <sub>8</sub> NO <sub>2</sub> S	158.0276	250	C <sub>8</sub> H <sub>12</sub> NO <sub>2</sub> S <sub>2</sub>	218.0309	200						Herbicide
29	Pesticide	Benzobicyclon	8	26.96	(M+H)+	447.0493	449.0457	C <sub>15</sub> H <sub>13</sub> O <sub>2</sub> S	257.0636	250	C <sub>22</sub> H <sub>19</sub> O <sub>4</sub> S <sub>2</sub>	411.0725	250										Herbicide		
30	Pesticide	Benzobicyclon metabolite	8	12.20	(M+NH <sub>4</sub> )+	372.0662	374.0637	C <sub>6</sub> H <sub>13</sub> O <sub>3</sub> S	165.0585	250	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> S	319.0640	250										Other pesticide		
31	Pesticide	Benzofenap	40	31.32	(M+H)+	431.0928	433.0894	C <sub>8</sub> H <sub>9</sub>	105.0704	250	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	320.0119	250										Herbicide		
32	Pesticide	Boscalid	40	26.31	(M+H)+	343.0395	345.0370	C <sub>18</sub> H <sub>12</sub> CIN <sub>2</sub> O	307.0638	250	C <sub>6</sub> H <sub>3</sub> CINO	139.9903	250	C <sub>3</sub> H <sub>3</sub> CIN	111.9954	250								Fungicide	
33	Pesticide	Bromacil	40	20.77	(M+H)+	261.0233	263.0213	C <sub>5</sub> H <sub>3</sub> BrN <sub>2</sub> O <sub>2</sub>	204.9613	250	C <sub>3</sub> H <sub>3</sub> BrNO <sub>2</sub>	187.9347	250	C <sub>4</sub> H <sub>3</sub> BrNO	161.9555	250								Herbicide	
34	Pesticide	Butafenacil	8	27.70	(M+NH <sub>4</sub> )+	492.1149	494.1114	C <sub>13</sub> H <sub>7</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>3</sub>	331.0097	250	C <sub>13</sub> H <sub>9</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>4</sub>	349.0203	250	C <sub>8</sub> H <sub>3</sub> CINO <sub>2</sub>	179.9852	250								Herbicide	

Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion			Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound	
					Ion	m/z	Isotopic ion, m/z	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV		
35	Pesticide	Butocarboxim	20	18.56	(M+NH <sub>4</sub> ) <sup>+</sup>	208.1110	210.1072	C <sub>4</sub> H <sub>6</sub> NS	100.0221	250		118.0492	250										Insecticide	
36	Pesticide	Butocarboxim sulfoxide	8	8.87	(M+H) <sup>+</sup>	207.0796	209.0756	C <sub>5</sub> H <sub>10</sub> NOS	132.0477	200		C <sub>3</sub> H <sub>7</sub> S	75.0268	250	C <sub>3</sub> H <sub>8</sub> NS	90.0377	250							Other pesticide
37	Pesticide	Cafenstrole	8	27.20	(M+H) <sup>+</sup>	351.1485	353.1443																Herbicide	
38	Pesticide	Carbaryl	8	22.41	(M+NH <sub>4</sub> ) <sup>+</sup>	219.1127		C <sub>10</sub> H <sub>9</sub> O	145.0653	100, 150, 200		C <sub>9</sub> H <sub>9</sub>	117.0704	250		155.0602	250						Insecticide	
39	Pesticide	Carbendazim	8	17.70	(M+H) <sup>+</sup>	192.0769		C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> O	160.0511	250		C <sub>7</sub> H <sub>6</sub> N <sub>3</sub>	132.0562	250	C <sub>6</sub> H <sub>5</sub> N <sub>2</sub>	105.0453	250							Fungicide
40	Pesticide	Carbofuran	8	21.42	(M+H) <sup>+</sup>	222.1126		C <sub>10</sub> H <sub>13</sub> O <sub>2</sub>	165.0916	200		C <sub>7</sub> H <sub>7</sub> O <sub>2</sub>	123.0446	200, 250	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub>	109.0290	200							Insecticide
41	Pesticide	Carbosulfan	40	33.95	(M+H) <sup>+</sup>	381.2219	383.2164	C <sub>5</sub> H <sub>12</sub> NS	118.0690	250		C <sub>8</sub> H <sub>18</sub> NS	160.1160	250	C <sub>10</sub> H <sub>13</sub> O <sub>2</sub>	165.0916	250							Insecticide
42	Pesticide	Carpropamid	200	28.91	(M+H) <sup>+</sup>	334.0520	336.0497	C <sub>8</sub> H <sub>8</sub> Cl	139.0315	250													Fungicide	
43	Pesticide	Chlorfluzuron	40	32.97	(M+H) <sup>+</sup>	539.9703	541.9673	C <sub>7</sub> H <sub>6</sub> F <sub>2</sub> NO	158.0417	250	C <sub>13</sub> H <sub>5</sub> Cl <sub>3</sub> F <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	382.9369	250	C <sub>7</sub> H <sub>3</sub> F <sub>2</sub> O	141.0152	250								Insecticide
44	Pesticide	Chloridazon	8	16.71	(M+H) <sup>+</sup>	222.0429	224.0399	C <sub>7</sub> H <sub>6</sub> N	104.0500	250		C <sub>6</sub> H <sub>6</sub> N	92.0500	250	C <sub>4</sub> H <sub>5</sub> CIN <sub>3</sub> O	146.0121	250							Herbicide
45	Pesticide	Chlorimuron-ethyl	80	19.86	(M+H) <sup>+</sup>	415.0474	417.0444	C <sub>6</sub> H <sub>5</sub> CIN <sub>3</sub> O <sub>2</sub>	186.0070	200	C <sub>13</sub> H <sub>10</sub> CIN <sub>4</sub> O <sub>5</sub> S	369.0060	200										Herbicide	
46	Pesticide	Chloroxuron	8	26.98	(M+H) <sup>+</sup>	291.0892	293.0865	C <sub>3</sub> H <sub>6</sub> NO	72.0449	250		C <sub>12</sub> H <sub>9</sub> CINO	218.0373	250	C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> O	164.0950	250							Herbicide
47	Pesticide	Chlorsulfuron	80	15.09	(M+H) <sup>+</sup>	358.0373	360.0342	C <sub>3</sub> H <sub>9</sub> N <sub>4</sub> O	141.0776	250													Herbicide	
48	Pesticide	Chromafenozide	8	27.92	(M+H) <sup>+</sup>	395.2337		C <sub>11</sub> H <sub>11</sub> O <sub>2</sub>	175.0759	250	C <sub>20</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub>	339.1709	200	C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> O	147.0558	250								Insecticide
49	Pesticide	Cinosulfuron	80	15.53	(M+H) <sup>+</sup>	414.1083	416.1036	C <sub>6</sub> H <sub>7</sub> N <sub>4</sub> O <sub>3</sub>	183.0518	250		C <sub>3</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>	157.0726	250									Herbicide	
50	Pesticide	Clodinafop	80	21.32	(M+H) <sup>+</sup>	312.0432	314.0404	C <sub>13</sub> H <sub>10</sub> ClFNO <sub>2</sub>	266.0384	250		C <sub>11</sub> H <sub>7</sub> ClFNO <sub>2</sub>	239.0149	250									Herbicide	
51	Pesticide	Clofencet	80	15.43	(M+H) <sup>+</sup>	279.0531	281.0501	C <sub>13</sub> H <sub>10</sub> CIN <sub>2</sub> O <sub>2</sub>	261.0431	200		C <sub>9</sub> H <sub>9</sub> CIN	166.0424	250									Herbicide	
52	Pesticide	Clofentezine	400	30.68	(M+H) <sup>+</sup>	303.0195	305.0169	C <sub>7</sub> H <sub>5</sub> CIN	138.0111	200, 250													Insecticide	
53	Pesticide	Clomeprop	40	31.61	(M+H) <sup>+</sup>	324.0551	326.0523	C <sub>8</sub> H <sub>10</sub> N	120.0813	250		C <sub>7</sub> H <sub>7</sub> N	105.0578	250									Herbicide	
54	Pesticide	Cloquintocet-mexyl	40	31.90	(M+H) <sup>+</sup>	336.1371	338.1331	C <sub>11</sub> H <sub>9</sub> CINO <sub>3</sub>	238.0271	250		C <sub>9</sub> H <sub>6</sub> CINO	179.0138	250	C <sub>10</sub> H <sub>7</sub> CINO	192.0216	250							Herbicide
55	Pesticide	Clothianidin	20	15.13	(M+H) <sup>+</sup>	250.0158	252.0130	C <sub>6</sub> H <sub>9</sub> N <sub>4</sub> S	169.0548	200		C <sub>4</sub> H <sub>3</sub> CINS	131.9675	200	C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> S	113.0173	250							Insecticide
56	Pesticide	Cumyluron	8	26.95	(M+H) <sup>+</sup>	303.1256	305.1229	C <sub>8</sub> H <sub>10</sub> CIN <sub>2</sub> O	185.0482	200													Herbicide	
57	Pesticide	Cyanazine	8	20.47	(M+H) <sup>+</sup>	241.0963	243.0933	C <sub>8</sub> H <sub>13</sub> CIN <sub>5</sub>	214.0859	200		C <sub>3</sub> H <sub>9</sub> CIN <sub>5</sub>	174.0546	200									Herbicide	
58	Pesticide	Cyazofamid	8	27.69	(M+H) <sup>+</sup>	325.0519	327.0491	C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub> S	108.0119	200		C <sub>11</sub> H <sub>8</sub> CIN <sub>3</sub>	217.0407	200	C <sub>13</sub> H <sub>14</sub> CIN <sub>4</sub>	261.0907	250							Fungicide
59	Pesticide	Cycloprothrin	400	32.77	(M+NH <sub>4</sub> ) <sup>+</sup>	499.1180	501.1156	C <sub>14</sub> H <sub>10</sub> NO	208.0762	250		C <sub>13</sub> H <sub>9</sub> O	181.0653	250									Insecticide	
60	Pesticide	Cyclosulfamuron	80	23.64	(M+H) <sup>+</sup>	422.1132	424.1087	C <sub>7</sub> H <sub>9</sub> N <sub>4</sub> O <sub>5</sub> S	261.0294	250		C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>	182.0566	250									Herbicide	
61	Pesticide	Cyflufenamid	40	30.06	(M+H) <sup>+</sup>	413.1286		C <sub>12</sub> H <sub>12</sub> F <sub>3</sub> N <sub>2</sub> O	295.0870	250		C <sub>8</sub> H <sub>6</sub> F <sub>3</sub> N <sub>2</sub> O	241.0400	250	C <sub>8</sub> H <sub>3</sub> F <sub>4</sub> N <sub>2</sub>	203.0232	250							Fungicide
62	Pesticide	Cyprodinil	40	29.84	(M+H) <sup>+</sup>	226.1342		C <sub>7</sub> H <sub>10</sub> N	108.0813	250		C <sub>6</sub> H <sub>7</sub> N	93.0578	250	C <sub>13</sub> H <sub>12</sub> N <sub>3</sub>	210.1031	250							Fungicide
63	Pesticide	Diclosulam	40	20.33	(M+H) <sup>+</sup>	405.9937	407.9909	C <sub>6</sub> H <sub>5</sub> C <sub>12</sub> N	160.9799	250	C <sub>11</sub> H <sub>7</sub> Cl <sub>2</sub> FN <sub>5</sub> O <sub>3</sub> S	377.9632	250	C <sub>11</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>5</sub> S	314.0034	250								Herbicide
64	Pesticide	Difenoconazole	20	29.81	(M+H) <sup>+</sup>	406.0725	408.0690	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> O	251.0030	250		C <sub>17</sub> H <sub>15</sub> Cl <sub>2</sub> O <sub>3</sub>	337.0398	250									Fungicide	
65	Pesticide	Diflubenzuron	8	28.31	(M+H) <sup>+</sup>	311.0388	313.0364	C <sub>7</sub> H <sub>6</sub> NOF <sub>2</sub>	158.0417	200		C <sub>7</sub> H <sub>3</sub> F <sub>2</sub> O	141.0152	250									Insecticide	
66	Pesticide	Dimethirimol	8	23.39	(M+H) <sup>+</sup>	210.1607		C <sub>8</sub> H <sub>14</sub> NO	140.1075	250		C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O	167.1059	250	C <sub>7</sub> H <sub>10</sub> N <sub>3</sub> O	152.0824	250							Fungicide
67	Pesticide	Dimethoate	8	15.61	(M+H) <sup>+</sup>	230.0068	232.0027	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS	124.9826	200		C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> PS <sub>2</sub>	170.9703	200	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS <sub>2</sub>	156.9547	200							Insecticide
68	Pesticide	Dimethomorph(E)	8	26.17	(M+H) <sup>+</sup>	388.1319	390.1281	C <sub>17</sub> H <sub>14</sub> O <sub>3</sub> Cl	301.0631	250													Fungicide	
69	Pesticide	Dimethomorph(Z)	8	26.67	(M+H) <sup>+</sup>	388.1310	390.1281	C <sub>17</sub> H <sub>14</sub> O <sub>3</sub> Cl	301.0631	250													Fungicide	

Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion		Isotopic ion, m/z	Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound	
					Ion	m/z		Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV		
70	Pesticide	Dinotefuran	8	9.89	(M+H) <sup>+</sup>	203.1142		C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> O	129.0902	200	C <sub>5</sub> H <sub>12</sub> N <sub>3</sub>	114.1031	200	C <sub>5</sub> H <sub>10</sub> N <sub>3</sub>	112.0875	200							Insecticide	
71	Pesticide	Dioxacarb	20	15.96	(M+H) <sup>+</sup>	224.0916		C <sub>7</sub> H <sub>7</sub> O <sub>2</sub>	123.0446	200	C <sub>6</sub> H <sub>7</sub> O	95.0499	250										Insecticide	
72	Pesticide	Diuron	8	24.23	(M+H) <sup>+</sup>	233.0242	235.0213	C <sub>3</sub> H <sub>6</sub> NO	72.0449	250													Herbicide	
73	Pesticide	Dymron	8	26.69	(M+H) <sup>+</sup>	269.1650		C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O	151.0871	200													Herbicide	
74	Pesticide	Epoxiconazole	8	27.94	(M+H) <sup>+</sup>	330.0804	332.0774		123.0330	250		129.0482	250		75.0264	250		141.0144	250		101.0415	250	Fungicide	
75	Pesticide	Esprocarb	40	31.36	(M+H) <sup>+</sup>	266.1572	268.1531																Herbicide	
76	Pesticide	Ethametsulfuron-methyl	80	17.71	(M+H) <sup>+</sup>	411.1087	413.1039	C <sub>7</sub> H <sub>10</sub> N <sub>5</sub> O <sub>2</sub>	196.0834	250	C <sub>5</sub> H <sub>8</sub> N <sub>5</sub> O <sub>2</sub>	168.0521	250	C <sub>4</sub> H <sub>8</sub> N <sub>5</sub> O	142.0729	250								Herbicide
77	Pesticide	Ethiofencarb	8	22.43	(M+H) <sup>+</sup>	226.0894	228.0854	C <sub>7</sub> H <sub>7</sub> O	107.0497	250	C <sub>9</sub> H <sub>10</sub> NO <sub>2</sub>	164.0712	250										Insecticide	
78	Pesticide	Ethoxyquin	8	27.56	(M+H) <sup>+</sup>	218.1539		C <sub>13</sub> H <sub>16</sub> NO	202.1232	200	C <sub>11</sub> H <sub>12</sub> NO	174.0919	250	C <sub>12</sub> H <sub>14</sub> NO	188.1075	250								Fungicide
79	Pesticide	Ethoxysulfuron	80	16.37	(M+NH <sub>4</sub> ) <sup>+</sup>	416.1236	401.0992																Herbicide	
80	Pesticide	Etobenzanid	8	29.03	(M+H) <sup>+</sup>	340.0508	342.0472																Herbicide	
81	Pesticide	Fenamidon	8	26.27	(M+H) <sup>+</sup>	312.1169	314.1123	C <sub>15</sub> H <sub>14</sub> N <sub>3</sub>	236.1188	250													Fungicide	
82	Pesticide	Fenarimol	20	27.53	(M+H) <sup>+</sup>	331.0392	333.0370																Fungicide	
83	Pesticide	Fenhexamid	80	26.91	(M+H) <sup>+</sup>	302.0710	304.0680	C <sub>7</sub> H <sub>13</sub>	97.1017	250	C <sub>6</sub> H <sub>6</sub> Cl <sub>2</sub> NO	177.9826	250										Fungicide	
84	Pesticide	Fenobucarb	8	25.23	(M+H) <sup>+</sup>	208.1328		C <sub>6</sub> H <sub>7</sub> O	95.0497	200, 250	C <sub>8</sub> H <sub>10</sub> NO <sub>2</sub>	152.0712	150	C <sub>6</sub> H <sub>5</sub>	77.0391	250								Insecticide
85	Pesticide	Fenoxaprop-ethyl	40	30.90	(M+H) <sup>+</sup>	362.0788	364.0760	C <sub>15</sub> H <sub>11</sub> ClNO <sub>3</sub>	288.0427	250													Herbicide	
86	Pesticide	Fenoxycarb	8	28.81	(M+H) <sup>+</sup>	302.1388		C <sub>3</sub> H <sub>6</sub> NO <sub>2</sub>	88.0399	200	C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub>	256.0974	250	C <sub>5</sub> H <sub>10</sub> NO <sub>2</sub>	116.0712	200								Insecticide
87	Pesticide	Fenpyroximate	80	33.52	(M+H) <sup>+</sup>	422.2083		C <sub>20</sub> H <sub>20</sub> N <sub>3</sub> O <sub>4</sub>	366.1454	250													Insecticide	
88	Pesticide	Fenthion oxon sulfone	8	17.48	(M+NH <sub>4</sub> ) <sup>+</sup>	312.0671	314.0623	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub> PS	217.0452	250													Other pesticide	
89	Pesticide	Fenthion oxon sulfoxide	8	16.90	(M+H) <sup>+</sup>	279.0458	281.0409	C <sub>9</sub> H <sub>13</sub> O <sub>3</sub> PS	264.0221	250	C <sub>9</sub> H <sub>13</sub> O <sub>4</sub> P	216.0551	250	C <sub>9</sub> H <sub>12</sub> O <sub>4</sub> PS	247.0194	250								Other pesticide
90	Pesticide	Fenthion sulfone	8	22.76	(M+NH <sub>4</sub> ) <sup>+</sup>	328.0441	330.0395	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS	124.9826	250													Other pesticide	
91	Pesticide	Fenthion sulfoxide	8	22.21	(M+H) <sup>+</sup>	295.0231	297.0180	C <sub>9</sub> H <sub>13</sub> O <sub>4</sub> PS <sub>2</sub>	279.9993	250	C <sub>2</sub> H <sub>6</sub> O <sub>3</sub> P	109.0055	250	C <sub>9</sub> H <sub>13</sub> O <sub>3</sub> PS	232.0323	250								Other pesticide
92	Pesticide	Fentrazamide	8	28.80	(M+H) <sup>+</sup>	350.1384	352.1349	C <sub>10</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub>	197.1290	150	C <sub>9</sub> H <sub>16</sub> NO	154.1232	150	C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	115.0508	200	C <sub>6</sub> H <sub>11</sub>	83.0861	200					Herbicide
93	Pesticide	Fenvalerate	40	33.22	(M+NH <sub>4</sub> ) <sup>+</sup>	437.1628	439.1597	C <sub>10</sub> H <sub>9</sub>	129.0704	250	C <sub>17</sub> H <sub>23</sub> O <sub>2</sub>	259.1698	200										Insecticide	
94	Pesticide	Ferimzone(E)	40	26.81	(M+H) <sup>+</sup>	255.1611		C <sub>9</sub> H <sub>10</sub> N	132.0813	250	C <sub>8</sub> H <sub>11</sub> N <sub>4</sub>	163.0984	250	C <sub>15</sub> H <sub>16</sub> N <sub>3</sub>	238.1344	250								Fungicide
95	Pesticide	Ferimzone(Z)	8	27.07	(M+H) <sup>+</sup>	255.1616		C <sub>9</sub> H <sub>10</sub> N	132.0813	250	C <sub>8</sub> H <sub>11</sub> N <sub>4</sub>	163.0984	250	C <sub>15</sub> H <sub>16</sub> N <sub>3</sub>	238.1344	250								Fungicide
96	Pesticide	Fipronil	40	27.91	(M+NH <sub>4</sub> ) <sup>+</sup>	453.9726	455.9696																Insecticide	
97	Pesticide	Flazasulfuron	80	16.11	(M+H) <sup>+</sup>	408.0584	410.0542	C <sub>5</sub> H <sub>10</sub> F <sub>2</sub> N <sub>3</sub> S	182.0563	250	C <sub>12</sub> H <sub>12</sub> F <sub>3</sub> N <sub>4</sub> O <sub>2</sub>	301.0912	250		182.0558	250							Herbicide	
98	Pesticide	Florasulam	80	14.70	(M+H) <sup>+</sup>	360.0374	362.0331	C <sub>6</sub> H <sub>5</sub> F <sub>2</sub> N	129.0390	250	C <sub>12</sub> H <sub>9</sub> F <sub>3</sub> N <sub>5</sub> O	296.0759	250										Herbicide	
99	Pesticide	Fluazifop	80	21.50	(M+H) <sup>+</sup>	328.0793		C <sub>14</sub> H <sub>11</sub> F <sub>3</sub> NO <sub>2</sub>	282.0742	250		255.0499	250										Herbicide	
100	Pesticide	Flufenacet	8	27.67	(M+H) <sup>+</sup>	364.0740	366.0695	C <sub>8</sub> H <sub>7</sub> FNO	152.0512	200, 250													Herbicide	
101	Pesticide	Flumetsulam	8	11.64	(M+H) <sup>+</sup>	326.0519	328.0476	C <sub>12</sub> H <sub>10</sub> F <sub>2</sub> N <sub>5</sub>	262.0904	250													Herbicide	
102	Pesticide	Fluridone	8	26.00	(M+H) <sup>+</sup>	330.1110		C <sub>19</sub> H <sub>14</sub> F <sub>2</sub> NO	310.1043	250	C <sub>19</sub> H <sub>13</sub> FNO	290.0981	250										Herbicide	
103	Pesticide	Fomesafen	40	23.92	(M+NH <sub>4</sub> ) <sup>+</sup>	456.0239	458.0209	C <sub>14</sub> H <sub>6</sub> ClF <sub>3</sub> NO <sub>4</sub>	343.9937	250		379.0308	250										Herbicide	
104	Pesticide	Foramsulfuron	80	15.89	(M+H) <sup>+</sup>	453.1187	455.1145	C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>	182.0566	250	C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> O <sub>4</sub> S	272.0705	200	C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S	255.0440	250								Herbicide
105	Pesticide	Forchlorfenuron	8	23.98	(M+H) <sup>+</sup>	248.0586	250.0556	C <sub>3</sub> H <sub>6</sub> ClN <sub>2</sub>	129.0220	250	C <sub>6</sub> H <sub>4</sub> ClN <sub>2</sub> O	155.0012	250	C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> O	111.0558	250								Plant growth regulator
106	Pesticide	Furametpyr	8	23.63	(M+H) <sup>+</sup>	334.1313	336.1287	C <sub>17</sub> H <sub>19</sub> ClN <sub>3</sub> O	316.1217	250													Fungicide	

Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion			Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound
					Ion	m/z	Isotopic ion, m/z	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	
107	Pesticide	Furathiocarb	40	31.54	(M+H)+	383.1648	385.1593	C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> S	195.0440	250	C <sub>4</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> S	167.0490	250	C <sub>12</sub> H <sub>14</sub> NO <sub>3</sub> S	252.0694	250						Insecticide	
108	Pesticide	Halosulfuron-methyl	80	18.57	(M+H)+	435.0486	437.0455	C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>	182.0566	250	C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	139.0508	250	C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O	83.0245	250						Herbicide	
109	Pesticide	Hexaconazole	20	29.11	(M+H)+	314.0814	316.0729														Fungicide		
110	Pesticide	Hexythiazox	400	32.24	(M+H)+	353.1082	355.1056	C <sub>10</sub> H <sub>11</sub> CINOS	228.0250	200, 250	C <sub>9</sub> H <sub>11</sub> CIN	168.0580	250	C <sub>11</sub> H <sub>12</sub> CIN <sub>2</sub> O <sub>2</sub> S	271.0308	200						Insecticide	
111	Pesticide	Imazalil	200	28.83	(M+H)+	297.0556	299.0526	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub>	158.9768	250	C <sub>6</sub> H <sub>9</sub> N <sub>2</sub>	109.0766	250	C <sub>11</sub> H <sub>9</sub> Cl <sub>2</sub> N <sub>2</sub> O	255.0092	250						Fungicide	
112	Pesticide	Imazaquin	8	14.65	(M+H)+	312.1347		C <sub>16</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub>	284.1399	250	C <sub>16</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub>	267.1134	250	C <sub>11</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	199.0508	250	C <sub>16</sub> H <sub>16</sub> N <sub>3</sub> O	266.1293	250			Herbicide	
113	Pesticide	Imazosulfuron	8	17.11	(M+H)+	413.0432	415.0400	C <sub>6</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub>	156.0773	250	C <sub>8</sub> H <sub>5</sub> CIN <sub>3</sub> O <sub>3</sub> S	257.9740	250	C <sub>7</sub> H <sub>7</sub> CIN <sub>3</sub> O <sub>2</sub> S	231.9947	250						Herbicide	
114	Pesticide	Imibenconazole	40	31.30	(M+H)+	411.0000	412.9970	C <sub>7</sub> H <sub>6</sub> Cl	125.0158	250	C <sub>15</sub> H <sub>11</sub> C <sub>13</sub> NS	341.9678	250	C <sub>9</sub> H <sub>9</sub> CIN <sub>3</sub>	194.0485	200						Other pesticide	
115	Pesticide	Imidacloprid	40	15.21	(M+H)+	256.0595	258.0566	C <sub>9</sub> H <sub>11</sub> N <sub>4</sub>	175.0984	250	C <sub>9</sub> H <sub>10</sub> CIN <sub>4</sub>	209.0594	250	C <sub>3</sub> H <sub>6</sub> N <sub>3</sub>	84.0562	200						Insecticide	
116	Pesticide	Inabenfide	20	25.52	(M+H)+	339.0897	341.0865	C <sub>19</sub> H <sub>14</sub> CIN <sub>2</sub> O	321.0795	250												Other pesticide	
117	Pesticide	Indanofan	200	27.92	(M+H)+	341.0932	343.0909	C <sub>11</sub> H <sub>11</sub> O <sub>2</sub>	175.0759	200	C <sub>10</sub> H <sub>11</sub>	131.0861	250									Herbicide	
118	Pesticide	Indoxacarb	80	30.57	(M+H)+	528.0781	530.0750	C <sub>13</sub> H <sub>10</sub> CIN <sub>2</sub> O <sub>4</sub>	293.0329	250	C <sub>12</sub> H <sub>10</sub> CIN <sub>2</sub> O <sub>2</sub>	249.0431	250	C <sub>12</sub> H <sub>8</sub> CIN <sub>2</sub> O <sub>3</sub>	263.0223	250			203.0195	250		Insecticide	
119	Pesticide	Iodosulfuron-methyl-sodium	80	18.45	(M+H)+	529.9596	531.9560	C <sub>6</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>	167.0569	250												Herbicide	
120	Pesticide	Iprodione	20	22.79	(M+H)+	330.0410	332.0377															Fungicide	
121	Pesticide	Iprovalicarb	8	27.60	(M+H)+	321.2183		C <sub>9</sub> H <sub>11</sub>	119.0861	200, 250	C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>	203.1396	200	C <sub>3</sub> H <sub>8</sub> NO	98.0606	200	C <sub>6</sub> H <sub>10</sub> NO <sub>3</sub>	144.0661	200			Fungicide	
122	Pesticide	Isoprocarb	8	23.24	(M+H)+	194.1173		C <sub>6</sub> H <sub>7</sub> O	95.0497	250	C <sub>9</sub> H <sub>13</sub> O	137.0966	200									Insecticide	
123	Pesticide	Isouron	20	21.60	(M+H)+	212.1404		C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub>	167.0821	250	C <sub>10</sub> H <sub>16</sub> N <sub>3</sub> O	194.1293	250									Herbicide	
124	Pesticide	Isoxaflutole	200	24.42	(M+H)+	360.0513	362.0470	C <sub>9</sub> H <sub>6</sub> O <sub>3</sub> F <sub>3</sub> S	250.9990			377.0777	250									Herbicide	
125	Pesticide	Lactofen	80	31.59	(M+NH <sub>4</sub> )+	479.0829	481.0798	C <sub>14</sub> H <sub>6</sub> ClF <sub>3</sub> NO <sub>4</sub>	343.9937													Herbicide	
126	Pesticide	Linuron	40	26.00	(M+H)+	249.0188	251.0163	C <sub>8</sub> H <sub>7</sub> CIN <sub>2</sub> O	182.0247	250												Herbicide	
127	Pesticide	Mefenacet	8	27.15	(M+H)+	299.0843	301.0807	C <sub>9</sub> H <sub>10</sub> NO	148.0762	200	C <sub>8</sub> H <sub>10</sub> N	120.0813	250									Herbicide	
128	Pesticide	Mepanipyrim	8	28.12	(M+H)+	224.1186		C <sub>8</sub> H <sub>7</sub> N <sub>2</sub>	131.0609	250		106.0646										Fungicide	
129	Pesticide	Mepanipyrim metabolite	8	23.97	(M+H)+	244.1450		C <sub>14</sub> H <sub>16</sub> N <sub>3</sub>	226.1344	250	C <sub>12</sub> H <sub>14</sub> N <sub>3</sub>	200.1188	250	C <sub>5</sub> H <sub>8</sub> N	82.0657	250						Other pesticide	
130	Pesticide	Mesosulfuron-methyl	80	17.45	(M+H)+	504.0854	506.0811	C <sub>10</sub> H <sub>12</sub> NO <sub>6</sub> S <sub>2</sub>	306.0106	250												Herbicide	
131	Pesticide	Methabenzthiazuron	8	23.82	(M+H)+	222.0690	224.0654	C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> S	165.0486	200	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> S	150.0252	250	C <sub>6</sub> H <sub>6</sub> NS	124.0221	250	C <sub>3</sub> H <sub>6</sub> N	80.0500	200			Herbicide	
132	Pesticide	Methamidophos	8	4.35	(M+H)+	142.0087	144.0044	CH <sub>3</sub> NO <sub>2</sub> P	94.0058	200	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> PS	124.9826	200	CH <sub>2</sub> O <sub>2</sub> P	78.9949	200						Insecticide	
133	Pesticide	Methiocarb	20	25.80	(M+H)+	226.0890	228.0854	C <sub>8</sub> H <sub>11</sub> NOS	169.0561	200	C <sub>7</sub> H <sub>5</sub> O	105.0340	250	C <sub>7</sub> H <sub>8</sub> NOS	154.0327	250						Insecticide	
134	Pesticide	Methomyl	8	12.22	(M+H)+	163.0534	165.0494	C <sub>3</sub> H <sub>6</sub> NS	88.0221	150	C <sub>3</sub> H <sub>8</sub> NOS	106.0327	150	C <sub>2</sub> H <sub>3</sub> NS	72.9986	200						Insecticide	
135	Pesticide	Methoxyfenozide	8	27.32	(M+H)+	369.2179		C <sub>18</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub>	313.1552	200	C <sub>9</sub> H <sub>9</sub> O <sub>2</sub>	149.0603	200	C <sub>7</sub> H <sub>7</sub>	91.0548	250						Other pesticide	
136	Pesticide	Metolcarb	20	19.66	(M+H)+	166.0860		C <sub>7</sub> H <sub>9</sub> O	109.0653	200	C <sub>6</sub> H <sub>6</sub> O	94.0419	250	C <sub>7</sub> H <sub>7</sub>	91.0548	250						Insecticide	
137	Pesticide	Metominostrobin(E)	8	24.58	(M+H)+	285.1235		C <sub>13</sub> H <sub>8</sub> NO	194.0606	200	C <sub>13</sub> H <sub>10</sub> NO	196.0762	250	C <sub>15</sub> H <sub>12</sub> NO <sub>2</sub>	238.0868	250						Fungicide	
138	Pesticide	Metosulam	80	19.39	(M+H)+	418.0141	420.0109	C <sub>2</sub> H <sub>8</sub> CIN <sub>2</sub> O <sub>3</sub> S	174.9944	250	C <sub>14</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>2</sub>	354.0525	250	C <sub>10</sub> H <sub>4</sub> O	140.0262	250						Herbicide	
139	Pesticide	Metribuzin	8	20.58	(M+H)+	215.0964	217.0919	C <sub>7</sub> H <sub>13</sub> N <sub>4</sub> S	187.1017	200	C <sub>5</sub> H <sub>10</sub> N	84.0813	200									Herbicide	
140	Pesticide	Metsulfuron-methyl	80	13.89	(M+H)+	382.0818	384.0774	C <sub>8</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>	167.0569	250	C <sub>8</sub> H <sub>7</sub> O <sub>4</sub> S	199.0065	250									Herbicide	
141	Pesticide	Monocrotophos	80	13.35	(M+NH <sub>4</sub> )+	241.0946		C <sub>6</sub> H <sub>10</sub> O <sub>3</sub> P	193.0260		C <sub>2</sub> H <sub>6</sub> O <sub>4</sub> P	127.0155		C <sub>2</sub> H <sub>6</sub> O <sub>3</sub> P	109.0049		C <sub>5</sub> H <sub>8</sub> NO	98.0600				Insecticide	
142	Pesticide	Monolinuron	80	22.94	(M+H)+	215.0579	217.0552	C <sub>6</sub> H <sub>5</sub> CIN	126.0111	200	C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O	148.0637	200									Herbicide	
143	Pesticide	Naproanilide	20	28.81	(M+H)+	292.1334		C <sub>12</sub> H <sub>11</sub> O	171.0810	250	C <sub>8</sub> H <sub>10</sub> N	120.0813	250									Herbicide	
144	Pesticide	Naptalam	80	17.78	(M+H)+	292.0967		C <sub>10</sub> H <sub>10</sub> N	144.0813	250	C <sub>18</sub> H <sub>12</sub> NO <sub>2</sub>	274.0868	200									Herbicide	

Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion			Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound
					Ion	m/z	Isotopic ion, m/z	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	
145	Pesticide	Nitenpyram	8	10.89	(M+H) <sup>+</sup>	271.0954	273.0927	C <sub>11</sub> H <sub>16</sub> ClN <sub>3</sub>	225.1033	250	C <sub>11</sub> H <sub>14</sub> ClN <sub>4</sub>	237.0907	250	C <sub>6</sub> H <sub>5</sub> ClN	126.0111	250	C <sub>9</sub> H <sub>11</sub> ClN <sub>3</sub>	196.0642	250				Insecticide
146	Pesticide	Oryzalin	400	27.80	(M+H) <sup>+</sup>	347.1022	349.0978															Herbicide	
147	Pesticide	Oxadiargyl	20	29.33	(M+NH <sub>4</sub> ) <sup>+</sup>	358.0724	360.0690	C <sub>10</sub> H <sub>6</sub> Cl <sub>2</sub> NO <sub>3</sub>	257.9725	250	C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>	151.0144	250	C <sub>7</sub> H <sub>3</sub> ClNO <sub>3</sub>	183.9801	250							Herbicide
148	Pesticide	Oxamyl	8	11.50	(M+NH <sub>4</sub> ) <sup>+</sup>	237.1016	239.0974	C <sub>3</sub> H <sub>8</sub> NO <sub>2</sub>	90.0555	150, 200	C <sub>3</sub> H <sub>6</sub> NO	72.0449	150, 200										Insecticide
149	Pesticide	Oxaziclomfene	40	30.99	(M+H) <sup>+</sup>	376.0864	378.0836	C <sub>11</sub> H <sub>12</sub> NO <sub>2</sub>	190.0868	200	C <sub>7</sub> H <sub>12</sub> ClNO	161.0607	250										Herbicide
150	Pesticide	Oxycarboxin	8	17.50	(M+H) <sup>+</sup>	268.0639	270.0596	C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> S	175.0065	200	C <sub>4</sub> H <sub>3</sub> O <sub>4</sub> S	146.9752	200										Fungicide
151	Pesticide	Pencycuron	40	29.82	(M+H) <sup>+</sup>	329.1414	331.1386	C <sub>7</sub> H <sub>6</sub> Cl	125.0158	250	C <sub>14</sub> H <sub>14</sub> ClN <sub>2</sub> O	261.0795	250	C <sub>7</sub> H <sub>5</sub>	89.0391	250	C <sub>13</sub> H <sub>13</sub> ClN	218.0737	250				Fungicide
152	Pesticide	Penoxsulam	80	19.54	(M+H) <sup>+</sup>	484.0715	486.0667															Herbicide	
153	Pesticide	Phoxim	200	29.89	(M+H) <sup>+</sup>	299.0615	301.0572	H <sub>2</sub> O <sub>2</sub> PS	96.9513	250	C <sub>8</sub> H <sub>5</sub> N <sub>2</sub>	129.0453	250	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> PS	153.0139	200							Insecticide
154	Pesticide	Pirimicarb	8	23.40	(M+H) <sup>+</sup>	239.1502		C <sub>9</sub> H <sub>16</sub> N <sub>3</sub> O	182.1293	250				C <sub>4</sub> H <sub>9</sub> N <sub>2</sub>	85.0766	250	C <sub>7</sub> H <sub>9</sub> N <sub>2</sub> O	137.0715	250				Insecticide
155	Pesticide	Pirimiphos-methyl	20	29.82	(M+H) <sup>+</sup>	306.1042	308.0994															Insecticide	
156	Pesticide	Prochloraz	8	29.42	(M+H) <sup>+</sup>	376.0383	378.0351	C <sub>12</sub> H <sub>13</sub> NO <sub>2</sub> Cl <sub>3</sub>	308.0012	250	C <sub>9</sub> H <sub>7</sub> Cl <sub>3</sub> NO <sub>2</sub>	265.9542	200	C <sub>3</sub> H <sub>4</sub> NO	70.0293	250							Fungicide
157	Pesticide	Promecarb	8	26.07	(M+H) <sup>+</sup>	208.1330		C <sub>7</sub> H <sub>9</sub> O	109.0653	250	C <sub>10</sub> H <sub>15</sub> O	151.1123	200	C <sub>7</sub> H <sub>7</sub>	91.0548	250							Insecticide
158	Pesticide	Prometryn	8	27.59	(M+H) <sup>+</sup>	242.1431	244.1392	C <sub>7</sub> H <sub>14</sub> N <sub>3</sub> S	200.0970	250	C <sub>4</sub> H <sub>8</sub> N <sub>3</sub> S	158.0500	250	C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> S	116.0282	250							Herbicide
159	Pesticide	Propamocarb	8	11.51	(M+H) <sup>+</sup>	189.1604		C <sub>4</sub> H <sub>8</sub> NO <sub>2</sub>	102.0555	200	C <sub>7</sub> H <sub>14</sub> NO <sub>2</sub>	144.1025	200	C <sub>2</sub> H <sub>4</sub> NO <sub>2</sub>	74.0242	200							Fungicide
160	Pesticide	Propanil	8	25.40	(M+H) <sup>+</sup>	218.0136	220.0104	C <sub>6</sub> H <sub>6</sub> ClN	127.0189	250	C <sub>6</sub> H <sub>6</sub> Cl <sub>2</sub> N	161.9877	250									Herbicide	
161	Pesticide	Propaquizafop	400	31.65	(M+H) <sup>+</sup>	444.1323	446.1291	C <sub>16</sub> H <sub>12</sub> ClN <sub>2</sub> O <sub>2</sub>	299.0587	250	C <sub>19</sub> H <sub>16</sub> ClN <sub>2</sub> O <sub>4</sub>	371.0799	250									Herbicide	
162	Pesticide	Propoxur	8	20.83	(M+H) <sup>+</sup>	210.1123		C <sub>6</sub> H <sub>7</sub> O <sub>2</sub>	111.0446	200	C <sub>8</sub> H <sub>10</sub> NO <sub>3</sub>	168.0661	250	C <sub>6</sub> H <sub>5</sub> O	93.0340	250							Insecticide
163	Pesticide	Propoxycarbazono-sodium	200	16.37	(M+H) <sup>+</sup>	421.0788	423.0746															Herbicide	
164	Pesticide	Pymetrozin	8	12.98	(M+H) <sup>+</sup>	218.1040		C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	105.0453	250	C <sub>5</sub> H <sub>4</sub> N	78.0344	250	C <sub>3</sub> H <sub>3</sub> N	79.0422	250							Anti-feedant
165	Pesticide	Pyraclostrobin	40	30.00	(M+H) <sup>+</sup>	388.1068	390.1029	C <sub>9</sub> H <sub>9</sub> NO <sub>2</sub>	163.0633	250	C <sub>10</sub> H <sub>12</sub> NO <sub>3</sub>	194.0817	200	C <sub>9</sub> H <sub>10</sub> NO <sub>2</sub>	164.0712	200	C <sub>16</sub> H <sub>11</sub> ClN <sub>3</sub> O	296.0591	250				Fungicide
166	Pesticide	Pyrazolynate/Pyrazolate	40	30.33	(M+H) <sup>+</sup>	439.0284	441.0251	C <sub>7</sub> H <sub>3</sub> Cl <sub>2</sub> O	172.9561	250	C <sub>12</sub> H <sub>10</sub> ClN <sub>2</sub> O <sub>2</sub>	249.0431	250										Other pesticide
167	Pesticide	Pyrazosulfuron-ethyl	80	18.24	(M+H) <sup>+</sup>	415.1035	417.0988	C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>	182.0566	250	C <sub>12</sub> H <sub>13</sub> N <sub>6</sub> O <sub>6</sub> S	369.0617	250	C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	139.0508	250							Herbicide
168	Pesticide	Pyrifthalid	20	26.13	(M+H) <sup>+</sup>	319.0758	321.0705	C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> S	301.0647	250	C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	139.0508	250	C <sub>11</sub> H <sub>10</sub> NO <sub>2</sub> S	220.0432	250							Herbicide
169	Pesticide	Pyriminobac-methyl(E)	8	26.62	(M+H) <sup>+</sup>	362.1352																Herbicide	
170	Pesticide	Pyriminobac-methyl(Z)	4	26.46	(M+H) <sup>+</sup>	362.1350		C <sub>16</sub> H <sub>16</sub> N <sub>3</sub> O <sub>5</sub>	330.1090	250	C <sub>14</sub> H <sub>10</sub> N <sub>3</sub> O <sub>4</sub>	284.0671	250									Herbicide	
171	Pesticide	Quizalofop-ethyl	40	31.32	(M+H) <sup>+</sup>	373.0954	375.0920	C <sub>16</sub> H <sub>12</sub> ClN <sub>2</sub> O <sub>2</sub>	299.0587	250	C <sub>14</sub> H <sub>8</sub> ClN <sub>2</sub> O	255.0325	250	C <sub>17</sub> H <sub>14</sub> ClN <sub>2</sub> O <sub>4</sub>	345.0642	250							Herbicide
172	Pesticide	Sethoxydim	8	25.61	(M+H) <sup>+</sup>	328.1948	330.1899	C <sub>15</sub> H <sub>24</sub> NO <sub>2</sub> S	282.1528	200	C <sub>10</sub> H <sub>12</sub> NO <sub>2</sub>	178.0868	250	C <sub>10</sub> H <sub>14</sub> NO <sub>2</sub>	180.1025	250							Herbicide
173	Pesticide	Siduron	8	25.58	(M+H) <sup>+</sup>	233.1654		C <sub>6</sub> H <sub>8</sub> N	94.0657	250	C <sub>7</sub> H <sub>9</sub> N <sub>2</sub> O	137.0715	250	C <sub>7</sub> H <sub>6</sub> NO	120.0449	250							Herbicide
174	Pesticide	Simazine	8	21.30	(M+H) <sup>+</sup>	202.0852	204.0825	C <sub>2</sub> H <sub>3</sub> ClN <sub>3</sub>	104.0015	250	C <sub>4</sub> H <sub>7</sub> ClN <sub>3</sub>	132.0328	250	C <sub>4</sub> H <sub>6</sub> N <sub>3</sub>	96.0562	250							Herbicide
175	Pesticide	Simeconazole	8	27.56	(M+H) <sup>+</sup>	294.1437		C <sub>9</sub> H <sub>8</sub> F	135.0610	250	C <sub>2</sub> H <sub>4</sub> N <sub>3</sub>	70.0405	250	C <sub>9</sub> H <sub>7</sub>	115.0548	250							Fungicide
176	Pesticide	Spinosyn A	4	34.29	(M+H) <sup>+</sup>	732.4698		C <sub>33</sub> H <sub>46</sub> NO	142.1232	250	C <sub>33</sub> H <sub>52</sub> NO <sub>6</sub>	558.3795	200									Insecticide	
177	Pesticide	Spinosyn D	4	34.92	(M+H) <sup>+</sup>	746.4861		C <sub>33</sub> H <sub>46</sub> NO	142.1232	250	C <sub>33</sub> H <sub>52</sub> NO <sub>6</sub>	558.3795	250									Insecticide	
178	Pesticide	Sulfentrazone	80	20.79	(M+NH <sub>4</sub> ) <sup>+</sup>	404.0159	406.0127	C <sub>10</sub> H <sub>7</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>4</sub> O	306.9965	250													Herbicide
179	Pesticide	Sulfosulfuron	80	16.29	(M+H) <sup>+</sup>	471.0753	473.0709	C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S	211.0541	250	C <sub>6</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub>	156.0773	250	C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> OS	165.0123	250							Herbicide
180	Pesticide	Tebuconazole	8	28.31	(M+H) <sup>+</sup>	308.1526	310.1495	C <sub>2</sub> H <sub>4</sub> N <sub>3</sub>	70.0405	250	C <sub>7</sub> H <sub>6</sub> Cl	125.0158	250	C <sub>9</sub> H <sub>8</sub> Cl	151.0315	250							Fungicide
181	Pesticide	Tebufenozide	8	28.53	(M+H) <sup>+</sup>	353.2225		C <sub>18</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub>	297.1603	100, 150	C <sub>9</sub> H <sub>9</sub> O	133.0653	200, 250										Insecticide
182	Pesticide	Tebufenpyrad	8	30.96	(M+H) <sup>+</sup>	334.1688	336.1651																Insecticide

Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion			Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound
					Ion	m/z	Isotopic ion, m/z	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	
183	Pesticide	Tebuthiuron	8	21.72	(M+H) <sup>+</sup>	229.1121	231.1076	C <sub>7</sub> H <sub>14</sub> N <sub>3</sub> S	172.0908	200	C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> S	116.0282	250									Herbicide	
184	Pesticide	Tepraloxymid	20	19.58	(M+H) <sup>+</sup>	342.1464	344.1437	C <sub>7</sub> H <sub>15</sub> ClO <sub>2</sub>	166.0761	250												Herbicide	
185	Pesticide	Terbucarb	8	29.99	(M+NH <sub>4</sub> ) <sup>+</sup>	295.2380		C <sub>13</sub> H <sub>20</sub> NO <sub>2</sub>	222.1494	200	C <sub>7</sub> H <sub>6</sub> O	109.0653	250	C <sub>9</sub> H <sub>12</sub> NO <sub>2</sub>	166.0868	200						Insecticide	
186	Pesticide	Tetrachlorvinphos	20	28.35	(M+NH <sub>4</sub> ) <sup>+</sup>	381.9322	383.9301	C <sub>2</sub> H <sub>8</sub> O <sub>4</sub> P	127.0160	250	C <sub>2</sub> H <sub>6</sub> O <sub>3</sub> P	109.0055	250	C <sub>8</sub> H <sub>3</sub> Cl <sub>3</sub>	203.9300	250						Insecticide	
187	Pesticide	Tetraconazole	8	27.21	(M+H) <sup>+</sup>	372.0290	374.0259	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub>	158.9768	250												Fungicide	
188	Pesticide	Thiabendazole	8	21.02	(M+H) <sup>+</sup>	202.0436	204.0391	C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> S	175.0330	250	C <sub>8</sub> H <sub>7</sub> N <sub>2</sub>	131.0609	250	C <sub>6</sub> H <sub>6</sub> N	92.0500	250						Fungicide	
189	Pesticide	Thiabendazole metabolite	8	16.06	(M+H) <sup>+</sup>	218.0388	220.0341	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> OS	191.0279	250												Insecticide	
190	Pesticide	Thiacloprid	8	18.38	(M+H) <sup>+</sup>	253.0309	255.0280	C <sub>6</sub> H <sub>5</sub> CIN	126.0111	250	C <sub>6</sub> H <sub>4</sub> N	90.0344	250	CHN <sub>2</sub> S	72.9860	250						Insecticide	
191	Pesticide	Thiamethoxam	8	12.76	(M+H) <sup>+</sup>	292.0265	294.0236	C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> OS	211.0654	200	C <sub>6</sub> H <sub>6</sub> N <sub>3</sub> S	152.0282	250	C <sub>7</sub> H <sub>9</sub> N <sub>4</sub> S	181.0548	200250						Insecticide	
192	Pesticide	Thidiazuron	8	20.83	(M+H) <sup>+</sup>	221.0491		C <sub>2</sub> H <sub>4</sub> N <sub>3</sub> S	102.0126	200	C <sub>3</sub> H <sub>2</sub> N <sub>3</sub> OS	127.9919	250									Plant growth regulator	
193	Pesticide	Thifensulfuron-methyl	80	13.88	(M+H) <sup>+</sup>	388.0383	390.0338	C <sub>7</sub> H <sub>2</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	269.9493	200		167.0563	250									Herbicide	
194	Pesticide	Thifluzamide	8	27.64	(M+H) <sup>+</sup>	526.8494	528.8473	C <sub>5</sub> H <sub>3</sub> F <sub>3</sub> NS	168.0095	250												Fungicide	
195	Pesticide	Thiodicarb	20	23.69	(M+H) <sup>+</sup>	355.0558	357.0521	C <sub>3</sub> H <sub>6</sub> NS	88.0221	200			250	C <sub>5</sub> H <sub>2</sub> NS	107.9908	200	CH <sub>3</sub> S <sub>2</sub>	78.9676	200				Insecticide
196	Pesticide	Thiofanox sulfone	8	15.28	(M+NH <sub>4</sub> ) <sup>+</sup>	268.1324	270.1283	C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub>	76.0399	200	C <sub>7</sub> H <sub>16</sub> NO <sub>2</sub> S	194.0851	200									Other pesticide	
197	Pesticide	Thiofanox sulfoxide	8	14.68	(M+NH <sub>4</sub> ) <sup>+</sup>	252.1375	254.1334	C <sub>3</sub> H <sub>6</sub> NOS	104.0170	200	C <sub>7</sub> H <sub>16</sub> NO <sub>2</sub> S	178.0902	200	C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub>	76.0399	200							Other pesticide
198	Pesticide	Tiadinil	200	26.55	(M+H) <sup>+</sup>	268.0307	270.0276															Fungicide	
199	Pesticide	Tralkoxydim-1	8	23.20	(M+H) <sup>+</sup>	330.2064		C <sub>18</sub> H <sub>22</sub> NO <sub>2</sub>	284.1651	200	C <sub>7</sub> H <sub>8</sub> NO <sub>2</sub>	138.0555	250									Herbicide	
200	Pesticide	Tralkoxydim-2	8	26.24	(M+H) <sup>+</sup>	330.2067		C <sub>18</sub> H <sub>22</sub> NO <sub>2</sub>	284.1651	200	C <sub>7</sub> H <sub>8</sub> NO <sub>2</sub>	138.0555	250									Other pesticide	
201	Pesticide	Triasulfuron	80	16.59	(M+H) <sup>+</sup>	402.0635	404.0604	C <sub>5</sub> H <sub>9</sub> N <sub>4</sub> O	141.0776	250	C <sub>6</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>	167.0569	250									Herbicide	
202	Pesticide	Tribenuron-methyl	40	16.89	(M+H) <sup>+</sup>	396.0977	398.0930	C <sub>6</sub> H <sub>11</sub> N <sub>4</sub> O	155.0933	250	C <sub>7</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>	181.0726	250	C <sub>14</sub> H <sub>14</sub> N <sub>5</sub> O <sub>5</sub> S	364.0716	200						Herbicide	
203	Pesticide	Tricyclazole	8	18.91	(M+H) <sup>+</sup>	190.0438	192.0391	C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> S	163.0330	250	C <sub>7</sub> H <sub>6</sub> NS	136.0221	250									Fungicide	
204	Pesticide	Trifloxysulfuron-sodium	8	18.27	(M+H) <sup>+</sup>	460.0507	462.0467															Herbicide	
205	Pesticide	Triflumizole	8	30.41	(M+H) <sup>+</sup>	346.0935	348.0899	C <sub>12</sub> H <sub>12</sub> ClF <sub>3</sub> NO	278.0560	200	C <sub>8</sub> H <sub>4</sub> ClF <sub>3</sub> N	205.9984	200	C <sub>10</sub> H <sub>11</sub> ClF <sub>2</sub> N <sub>2</sub> O	248.0528	250						Fungicide	
206	Pesticide	Triflumizole metabolite	8	27.18	(M+H) <sup>+</sup>	295.0824	297.0790	C <sub>9</sub> H <sub>9</sub> ClF <sub>3</sub> N <sub>2</sub> O	253.0356	250												Other pesticide	
207	Pesticide	Triflumuron	40	29.71	(M+H) <sup>+</sup>	359.0402	361.0375	C <sub>7</sub> H <sub>7</sub> CINO	156.0216	200												Insecticide	
208	Pesticide	Trinexapac-ethyl	40	14.85	(M+H) <sup>+</sup>	253.1071		C <sub>11</sub> H <sub>11</sub> O <sub>4</sub>	207.0657	250	C <sub>10</sub> H <sub>11</sub> O <sub>3</sub>	179.0708	250	C <sub>8</sub> H <sub>5</sub> O <sub>4</sub>	165.0188	250						Other pesticide	
209	Pesticide	Triticonazole	8	27.16	(M+H) <sup>+</sup>	318.1361	320.1338	C <sub>2</sub> H <sub>4</sub> N <sub>3</sub>	70.0405	250												Fungicide	
210	Pesticide	Vamidothion	8	16.02	(M+H) <sup>+</sup>	288.0495	290.0446	C <sub>6</sub> H <sub>12</sub> NOS	146.0640	200	C <sub>4</sub> H <sub>8</sub> NOS	118.0370	200	C <sub>4</sub> H <sub>8</sub> NO	86.0606	200						Insecticide	
211	Pesticide	XMC	8	22.08	(M+H) <sup>+</sup>	180.1017		C <sub>8</sub> H <sub>11</sub> O	123.0810	250	C <sub>7</sub> H <sub>8</sub> O	108.0575	250									Insecticide	
212	Pesticide	Xylylcarb	8	22.43	(M+H) <sup>+</sup>	180.1016		C <sub>8</sub> H <sub>11</sub> O	123.0810	250	C <sub>7</sub> H <sub>8</sub> O	108.0575	250									Insecticide	

Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion		Isotopic ion, m/z	Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound
					Ion	m/z		Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	
213	PPCPs	2-Quinoxalinecarboxylic acid	8	7.74	(M+H)+	192.0762																Carbadox metabolite	
214	PPCPs	Acetaminophen	20	8.31	(M+H)+	152.0704				C <sub>6</sub> H <sub>8</sub> NO	110.0600	250										Analgesic	
215	PPCPs	Acetazolamide	80	7.94	(M+H)+	222.9950	224.9912				180.9842	200										Diuretic	
216	PPCPs	Acetohexamide	20	18.32	(M+H)+	325.1221	327.1175				138.0552	200										Diabetes mellitus	
217	PPCPs	Amitriptyline	8	28.07	(M+H)+	278.1903					233.1330	250										Nonnarcotic analgesic./antidepressant	
218	PPCPs	Ampicillin	20	13.48	(M+H)+	350.1172	352.1127				160.0427	200										Antibiotic	
219	PPCPs	Antipyrine	8	15.41	(M+H)+	189.1018					147.0919							130.0650				Anti-inflammatory	
220	PPCPs	Atenolol	8	9.80	(M+H)+	267.1702					190.0863											Antiarrhythmic/Antihypertensive	
221	PPCPs	Azithromycin	8	25.82	(M+H)+	749.5157				C <sub>30</sub> H <sub>59</sub> N <sub>2</sub> O <sub>9</sub>	591.4215											Antibiotic	
222	PPCPs	Betaxolol	8	21.57	(M+H)+	308.2221					290.2097	250										Medicine	
223	PPCPs	Bezafibrate	8	21.35	(M+H)+		364.1124				316.1109	250										Hypoglycemic	
224	PPCPs	Bisoprolol	8	19.97	(M+H)+	326.2327					116.1067	250										Anti-arrhythmia	
225	PPCPs	Candesartan	8	16.92	(M+H)+	441.1617					263.1295	250										Antihypertensive	
226	PPCPs	Carazolol	8	19.96	(M+H)+	299.1761					222.0914	250										Antihypertensive/antianginal/antiarrhythmic	
227	PPCPs	Carbadox	80	15.04	(M+H)+																	Antibiotic	
228	PPCPs	Carbamazepin	8	21.90	(M+H)+						194.0967	250										Psychotropic	
229	PPCPs	Cefuroxime	80	11.54	(M+NH <sub>4</sub> )+	442.1024	444.0985															Antibiotic	
230	PPCPs	Chloramphenicol	200	16.62	(M+H)+		325.0167				305.0088	250										Antibiotic	
231	PPCPs	Chlorpheniramine maleate	8	22.80	(C <sub>16</sub> H <sub>19</sub> ClN <sub>2</sub> +H)+	275.1311	277.1280				230.0731	250										Antihistamine	
232	PPCPs	Chlorpromazine	8	29.80	(M+H)+	319.1028	321.1001				86.1031								248.0060				Antiemetic/antipsychotic
233	PPCPs	Cimetidine	8	13.34	(M+H)+	253.1224	255.1188				159.0699											Anti-ulcer	
234	PPCPs	Clarithromycin	8	27.23	(M+H)+	748.4848					718.4735	200										Antibiotic	
235	PPCPs	Clenbuterol	80	17.16	(M+H)+	277.0866	279.0839				203.0142											Adrenergic	
236	PPCPs	Cotinine	8	12.21	(M+H)+	177.1018					146.0600											Nicotine metabolite	
237	PPCPs	Cyclophosphamide	8	18.35	(M+H)+	261.0327	263.0291				C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> N	140.0028	250										Antineoplastic
238	PPCPs	Dexamethasone	8	23.64	(M+H)+	393.2074					373.1999	200										Anti-inflammatory	
239	PPCPs	Dextromethorphan	20	24.22	(M+H)+	272.2006					213.1274	250										Antitussive	
240	PPCPs	Diazepam	8	26.04	(M+H)+	285.0787	287.0760				257.0843	250										Anti-anxiety	
241	PPCPs	Diltiazem	8	27.35	(M+H)+	415.1685	417.1644				178.0321	250										Antihypertensive	
242	PPCPs	Diphenidol	8	23.25	(M+H)+	310.2170					292.2060	250										Antiemetic/antivertigo	
243	PPCPs	Dipyridamole	8	28.42	(M+H)+	505.3246					504.3176	250										Platelet aggregation/vasodilator	
244	PPCPs	Disopyramide	8	17.55	(M+H)+	340.2387					239.1179	250										Antiarrhythmic	
245	PPCPs	Enrofloxacin	200	24.67	(M+H)+	360.1716					342.1612											Antineoplastic	
246	PPCPs	Epinastine	8	20.14	(M+H)+	250.1345					131.0609	250										Antihistamine	
247	PPCPs	Erythromycin	8	25.50	(M+H)+	734.4685					576.3742	250										Antibiotic	
248	PPCPs	Ethenzamide	8	18.27	(M+H)+	166.0866					149.0599	200										Analgesic/anti-inflammatory	
249	PPCPs	Etodolac	8	24.20	(M+H)+	288.1597					172.1128	200										Antipyretic/analgesic	
250	PPCPs	Fenofibrate	8	31.45	(M+H)+	361.1197	363.1172				C <sub>13</sub> H <sub>10</sub> ClO <sub>2</sub>	233.0369	250									Antilipemic	
251	PPCPs	Flumequine	40	20.65	(M+H)+						244.0838	250										Anti-infective	
252	PPCPs	Fluoxetine	8	25.76	(M+H)+	310.1410					148.1121	250										antidepressant	
253	PPCPs	Fluvoxamine	8	25.18	(M+H)+	319.1635					258.1100	200										Antidepressant	
254	PPCPs	Griseofulvin	8	24.11	(M+H)+	353.0781	355.0757				285.0493	250										Antibiotic	
255	PPCPs	Haloperidol	8	25.08	(M+H)+	376.1483	378.1445				165.0709	250										Antiemetic/antipsychotic	
256	PPCPs	Hexamethylenetetramine	8	1.97	(M+H)+	141.1132					112.0871	250										Medicine	



Appendices

Table S2-1 List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion		Isotopic ion, m/z	Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound	
					Ion	m/z		Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV		
257	PPCPs	Ifenprodil	8	20.97	(M+H)+	326.2122																	NMDA receptor antagonist	
258	PPCPs	Ifosfamide	8	17.52	(M+H)+	261.0317	263.0291	C <sub>2</sub> H <sub>7</sub> NOP	92.0265	250	C <sub>5</sub> H <sub>10</sub> ClNO <sub>2</sub> P	182.0138	250				153.9821	250					Antineoplastic	
259	PPCPs	Imipramine	8	26.04	(M+H)+	281.2012																	Antidepressant	
260	PPCPs	Ketoprofen	8	20.16	(M+NH <sub>4</sub> )+	272.1281					C <sub>15</sub> H <sub>13</sub> O	209.0961	250										Anti-inflammatory	
261	PPCPs	Lidocaine	8	24.37	(M+H)+	235.1804																	Anesthetic/antiarrhythmic	
262	PPCPs	Lincomycin	80	21.01	(M+H)+	407.2207	409.2168	C <sub>11</sub> H <sub>27</sub> N <sub>12</sub> S	359.2196					C <sub>8</sub> H <sub>16</sub> N	126.1277									Antibiotic
263	PPCPs	Losartan	8	23.13	(M+H)+	423.1694	425.1665		207.0919														Antiarrhythmic/Antihypertensive	
264	PPCPs	Mepirizole	8	21.30	(M+H)+	235.1192			220.0952	250													Antipyretic/analgesic	
265	PPCPs	Metformin	8	2.32	(M+H)+	130.1086			113.0822														Antidiabetic	
266	PPCPs	Metoclopramide	8	16.85	(M+H)+	300.1480	302.1444		227.0588	250													Antiemetic	
267	PPCPs	Metoprolol	8	17.76	(M+H)+	268.1903		C <sub>6</sub> H <sub>14</sub> NO	116.1070	250	C <sub>9</sub> H <sub>9</sub> O	133.0648	250	C <sub>11</sub> H <sub>11</sub> O	159.0804	250		56.0495						Anti-arrhythmia/antihypertensive
268	PPCPs	Naproxen	40	19.91	(M+NH <sub>4</sub> )+	248.1279		C <sub>13</sub> H <sub>13</sub> O	185.0961	250														Anti-inflammatory
269	PPCPs	Norgestimate	8	30.32	(M+H)+	370.2375			149.0240	250														Hormonal contraceptives
270	PPCPs	Oleandomycin	8	23.35	(M+H)+	688.4263																		Antibiotic
271	PPCPs	Ormetoprim	20	17.62	(M+H)+	275.1503			259.1189															Antibiotic
272	PPCPs	Paroxetine	8	24.54	(M+H)+	330.1506		C <sub>12</sub> H <sub>15</sub> FN	192.1183	250	C <sub>8</sub> H <sub>8</sub> F	123.0605	250	C <sub>8</sub> H <sub>7</sub> O <sub>3</sub>	151.0390	250								Antidepressant
273	PPCPs	Penicillin G	20	17.68	(M+H)+	335.1059	337.1018		160.0427	250														Antibiotic
274	PPCPs	Pentoxifylline	20	17.44	(M+H)+	279.1456		C <sub>7</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>	181.0720	250														Phosphodiesterase
275	PPCPs	Phenacetin	8	18.54	(M+H)+	180.1014			110.0610	250								93.0558	250			109.0531	250	Analgesic
276	PPCPs	Phenytoin	80	21.30	(M+H)+	253.0967			182.0964	250														Anticonvulsant
277	PPCPs	Pirenzepine	8	15.75	(M+H)+	352.1774			113.1077	250														Anti-ulcer
278	PPCPs	Prednisolone	8	22.16	(M+H)+	361.2014			343.1870	200														Anti-inflammatory
279	PPCPs	Primidone	20	15.91	(M+H)+	219.1123			91.0542	250	C <sub>10</sub> H <sub>12</sub> NO	162.0913	200											Anticonvulsant
280	PPCPs	Promethazine	8	28.90	(M+H)+	285.1417			86.0967	250														Antiallergic
281	PPCPs	Propranolol	8	21.76	(M+H)+	260.1645			183.0804															Antiarrhythmic/Antihypertensive
282	PPCPs	Propyphenazone	8	22.77	(M+H)+	231.1492		C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> O	189.1022	250	C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O	201.1022	250											Anti-inflammatory
283	PPCPs	Ranitidine	20	12.52	(M+H)+	315.1486	317.1443	C <sub>11</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> S	270.0907										130.0559					Anti-ulcer
284	PPCPs	Roxithromycin	8	28.18	(M+H)+	837.5319			679.4376															Antibiotic
285	PPCPs	Salbutamol	80	9.30	(M+H)+	240.1593		C <sub>13</sub> H <sub>20</sub> NO <sub>2</sub>	222.1489		C <sub>9</sub> H <sub>12</sub> NO <sub>2</sub>	166.0863		C <sub>9</sub> H <sub>10</sub> NO	148.0757									Adrenergic
286	PPCPs	Salinomycin	40	35.51	(M+NH <sub>4</sub> )+	768.5266			733.4901															Antibiotic
287	PPCPs	Scopolamine	8	16.43	(M+H)+	304.1550			138.0812	250														Adjuvant/Anesthesia
288	PPCPs	Sotalol	8	9.08	(M+H)+	273.1264	275.1225	C <sub>12</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> S	255.1167	200														Anti-arrhythmia/sympatholytic
289	PPCPs	Spiramycin	40	27.48	(M+H)+	438.2785			174.1126	250									142.1225	250		438.2785	250	Antibiotic
290	PPCPs	Sulfadiazine	20	8.05	(M+H)+	251.0593	253.0555	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S	156.0114															Antibiotic
291	PPCPs	Sulfadimethoxine	8	15.47	(M+H)+	311.0815	313.0766		156.0768	250														Anti-infective
292	PPCPs	Sulfamerazine	8	11.55	(M+H)+	265.0750	267.0712		156.0114										92.0495					Antibiotic
293	PPCPs	Sulfamethizole	8	9.03	(M+H)+	271.0311	273.0276		156.0114															Anti-infective
294	PPCPs	Sulfamethoxazole	20	10.40	(M+H)+	254.0585	256.0552	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> S	156.0114															Antibiotic
295	PPCPs	Sulfamonomethoxine	8	11.78	(M+H)+	281.0700	283.0661																	Anti-infective
296	PPCPs	Sulfanilamide	40	3.65	(M+NH <sub>4</sub> )+	190.0638	192.0603		156.0114															Antibiotic
297	PPCPs	Sulfapyridine	8	11.41	(M+H)+	250.0649	252.0603		95.0599	250														Antibiotic
298	PPCPs	Sulfathiazole	20	10.62	(M+H)+		258.0167		156.0117	200														Antibiotic

Appendices

**Table S2-1** List of target compounds (continued)

No.	Group	Compound	Limit of Detection, ng/L	RT, min	Quantitation ion			Fragment ion 1			Fragment ion 2			Fragment ion 3			Fragment ion 4			Fragment ion 5			Type of compound
					Ion	m/z	Isotopic ion, m/z	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	Elemental composition	m/z	FV	
299	PPCPs	Sulpiride	20	12.21	(M+H)+	342.1481	344.1440		112.1122	250		214.0169	250		84.0810	250						Antidepressant	
300	PPCPs	Terbutaline	8	8.97	(M+H)+	226.1435		C <sub>8</sub> H <sub>10</sub> NO <sub>2</sub>	152.0706			107.0494			125.0595							Bronchodilator	
301	PPCPs	Testosterone	40	26.62	(M+H)+	289.2155			97.0647			109.0647			271.2054		253.1949					Androgen	
302	PPCPs	Theophylline	400	10.78	(M+Na)+	181.0715		C <sub>5</sub> H <sub>6</sub> N <sub>3</sub> O	124.0506			181.0721										Bronchodilator	
303	PPCPs	Thiamphenicol	400	11.67	(M+NH <sub>4</sub> )+	373.0381	375.0357		307.9913			338.0021										Antibiotic	
304	PPCPs	Tilmicosin	80	25.93	(M+H)+	869.5726																Antibiotic	
305	PPCPs	Tolbutamide	20	19.62	(M+H)+	271.1115	273.1069		91.0540	250		172.0428	200		155.0162	200						Hypoglycemic	
306	PPCPs	Tolperisone	8	23.38	(M+H)+	246.1858			98.0964	250												Muscle relaxant	
307	PPCPs	Trimethoprim	8	16.66	(M+H)+				261.0992	250		275.1134	250		230.1158	250	123.0662	250				Antibiotic	
308	PPCPs	Tylosin	80	27.01	(M+H)+	916.5245			772.4478			174.1125										Antibiotic	
309	PPCPs	Verapamil	8	26.71	(M+H)+	455.2908			165.0898	250		303.2061	250									Antiarrhythmic/vasodilator	
310	PPCPs	Virginiamycin M1	20	24.40	(M+H)+	526.2553			508.2452	250		355.1305	250		395.1975	250						Antibiotic	
311	PPCPs	Warfarin	8	19.10	(M+H)+				251.0699	250		163.0392	250									Anticoagulant/rodenticide	

**Table S2-2** Pesticides used in examination for selection of suitable solid-phase extraction cartridges and their recoveries

Compound	log <i>P<sub>ow</sub></i>	Recovery, %				
		AC-2	C18	HLB	PLS-3	PS-2
Clofencet	-2.20	24	14	81	61	76
Florasulam	-1.22	7	25	85	80	77
Chlorsulfuron	-0.99	4	76	90	86	84
Flumetsulam	-0.68	14	9	73	60	53
Oxamyl	-0.44	72	0	3	0	6
Penoxsulam	-0.35	29	83	82	90	82
Thiamethoxam	-0.13	52	13	81	76	76
Halosulfuron-methyl	-0.02	5	30	47	50	62
Metsulfuron-methyl	0.02	18	79	90	85	84
Methomyl	0.09	62	37	84	85	64
Naptalam	0.10	0	70	85	88	83
Chlorimuron-ethyl	0.11	24	80	80	92	79
Imazaquin	0.34	20	20	80	66	75
Imidacloprid	0.57	47	48	86	83	77
Clothianidin	0.70	15	27	93	86	79
Oxycarboxin	0.77	54	0	5	1	9
Diclosulam	0.85	9	64	78	69	83
Azamethiphos	1.05	74	0	0	0	2
Thifensulfuron-methyl	1.06	14	67	83	80	81
Iodosulfuron-methyl-sodium	1.07	2	85	87	116	88
Triasulfuron	1.10	29	84	84	94	83
Chloridazon	1.19	6	28	88	65	74
Trifloxysulfuron-sodium	1.40	30	69	75	84	75
Tricyclazole	1.42	12	60	75	64	64
Sulfentrazone	1.48	32	72	78	88	73
Carbofuran	1.52	58	8	19	20	34
Cyclosulfamuron	1.58	19	85	82	85	81
Thiodicarb	1.62	58	1	16	7	34
Pirimicarb	1.70	46	43	52	57	51
Bendiocarb	1.72	58	0	0	0	0
Thidiazuron	1.77	0	106	94	80	86
Tebuthiuron	1.82	54	52	60	61	58
Carbary	1.85	18	0	5	2	11
Fluridone	1.87	36	85	88	76	79
Cinosulfuron	2.04	35	91	90	89	85
Monolinuron	2.20	34	38	49	56	47
Isoxaflutole	2.32	47	0	4	2	12
Furametpyr	2.36	52	52	63	64	60
Thiabendazole	2.39	2	47	64	66	60
Azoxystrobin	2.50	60	75	80	71	74
Hexythiazox	2.53	43	34	34	47	47
Pyrazolynate/Pyrazolate	2.58	72	1	2	4	18
Pyriftalid	2.60	43	54	66	62	64
Cumyluron	2.61	51	76	73	73	73
Dimethomorph(E)	2.63	66	74	82	74	76
Methabenzthiazuron	2.64	7	44	54	57	52
Dymon	2.70	44	80	79	75	76

**Table S2-2** Pesticides used in examination for selection of suitable solid-phase extraction cartridges and their recoveries (continued)

Compound	log <i>P<sub>ow</sub></i>	Recovery, %				
		AC-2	C18	HLB	PLS-3	PS-2
Chromafenozide	2.70	73	84	81	79	79
Dimethomorph(Z)	2.73	65	79	83	74	76
Fenobucarb	2.79	60	31	43	52	47
Fenamidone	2.80	35	67	71	66	67
Diuron	2.85	11	53	64	64	61
Ethoxysulfuron	2.89	10	82	83	88	83
Fomesafen	2.90	0	112	102	84	90
Azinphos-methyl	2.96	29	34	45	55	50
Boscalid	2.96	25	68	73	69	67
Linuron	3.00	28	57	63	64	61
Methiocarb	3.08	53	0	4	2	10
Pyrazosulfuron-ethyl	3.16	18	76	77	83	76
Forchlorfenuron	3.20	0	97	87	68	85
Simeconazole	3.20	71	71	73	72	68
Iprovalicarb	3.20	61	64	69	67	64
Flufenacet	3.20	58	58	59	65	59
Butafenacil	3.20	58	27	40	43	55
Mepanipyrim	3.28	7	45	43	53	51
Triticonazole	3.29	59	74	78	74	73
Epoxiconazole	3.44	50	60	66	68	64
Fenhexamid	3.51	47	83	87	77	75
Indanofan	3.59	57	51	55	62	57
Methoxyfenozide	3.70	75	85	85	79	78
Oryzalin	3.73	51	84	74	75	75
Siduron	3.80	43	80	78	71	75
Anilofos	3.81	57	51	53	61	58
Imazalil	3.82	30	42	49	61	54
Diflubenzuron	3.89	0	63	69	73	71
Cyprodinil	3.90	11	34	32	45	44
Pyraclostrobin	3.99	26	48	47	56	57
Fipronil	4.00	67	64	67	73	72
Oxaziclomefone	4.01	53	44	42	54	54
Fenoxycarb	4.07	58	46	47	58	54
Clofentezine	4.10	0	0	0	0	0
Bensulide	4.20	56	60	59	64	65
Carpropamid	4.20	66	60	59	66	63
Tebufenozide	4.25	68	78	77	76	76
Quizalofop-ethyl	4.28	12	22	25	38	42
Avermectin B1a	4.40	33	43	38	35	41
Spinosad A	4.50	4	12	16	11	14
Fenoxaprop-ethyl	4.58	11	18	21	34	38
Furathiocarb	4.60	45	23	26	35	39
Indoxacarb	4.65	50	18	26	35	45
Pencycuron	4.68	42	45	46	51	50
Benzofenap	4.69	43	43	41	50	51
Cyflufenamid	4.70	62	50	49	60	58

**Table S2-2** Pesticides used in examination for selection of suitable solid-phase extraction cartridges and their recoveries (continued)

Compound	log <i>P<sub>ow</sub></i>	Recovery, %				
		AC-2	C18	HLB	PLS-3	PS-2
Propaquizafop	4.78	15	13	17	27	37
Clomeprop	4.80	23	39	38	54	51
Triflumuron	4.91	12	48	51	63	57
Fenpyroximate	5.01	38	34	29	36	41
Cloquintocet-methyl	5.03	20	24	22	32	34
Aldicarb		53	28	44	40	40
Aldicarb sulfone		63	1	33	25	33
Aramite		53	23	27	41	44
Asulam		14	0	0	0	0
Azimsulfuron		16	87	90	89	84
Bensulfuron-methyl		30	81	81	88	79
Chloroxuron		24	67	70	68	67
Clodinafop		0	83	86	94	80
Dimethirimol		29	49	55	57	54
Ethametsulfuron-methyl		33	84	84	90	81
Fenthion Oxon Sulfone		57	61	72	67	67
Fenthion Oxon Sulfoxide		61	73	82	72	73
Fenthion Sulfone		62	73	80	69	70
Fenthion Sulfoxide		60	86	89	73	75
Ferimzone(E)		11	54	58	63	57
Ferimzone(Z)		17	60	64	63	59
Flazasulfuron		14	53	68	64	63
Fluazifop		2	83	83	92	80
Foramsulfuron		35	89	87	93	82
Iprodione		63	74	82	70	70
Lactofen		52	33	34	46	50
Mesosulfuron-methyl		32	84	83	89	82
Metosulam		24	81	82	90	80
Naproanilide		13	50	51	62	59
Propoxycarbazone-sodium		8	85	83	85	82
Sulfosulfuron		8	83	82	92	82
Tetrachlorvinphos		51	44	50	57	53
Thiacloprid		45	72	80	81	74
Tralkoxydim1		23	44	43	50	51
Tralkoxydim2		19	74	71	70	64

# Appendices

**Table 3-1** Concentrations of compounds detected in Vietnamese rivers, ng/L

Group	Compound	Type of compound	Detector	Red River												Hue City					Danang							Hanoi					Saigon-Dongnai River					Hochiminh City								
				Red_1	Red_2	Red_3	Red_4	Red_5	Red_6	Red_7	Red_8	Red_9	Red_10	Red_11	Red_12	Red_13	Red_14	HU1	HU2	HU3	HU4	HU5	DN1	DN2	DN3	DN4	DN5	DN6	DN7	HN1	HN2	HN3	HN4	HN5	HCM1	HCM2	HCM3	HCM4	HCM5	HCM6	HCM7	HCM8	HCM9	HCM10	HCM11	
Water quality parameter	pH			7.75	7.82	7.76	7.65	7.67	7.84	7.53	7.47	7.66	7.45	7.78	7.91	7.75	7.72	7.16	7.14	7.11	7.78	7.18	6.59	6.43	6.88	6.44	6.32	7.07	7.1	7.02	7.52	7.24	7.18	7.21	7.51	7.35	7.06	6.95	6.9	7.42	7.55	7.06	7.11	7.07	6.99	
	TSS (mg/L)			9	18	25	34	13	16	21	10	14	10	15	12	10	8	39	35	28	14	22	12	9	7	8	14	10	11	35	8	4	7	9	9	14	10	6	14	14	68	20	67	23	46	
	COD (mg/L)			1.8	0.8	1.3	2.6	6.8	1.6	1.76	1.8	1.1	4.5	1.1	1.3	1.12	9.9	112	128	112	6.6	144	0.48	0.32	2.72	0.8	0.16	3.2	0.8	12.2	1.6	9.5	7	4	2.1	6.2	7.2	6.4	11	4	144	9.8	240	144	112	
Household chemicals	4-Methyl-2,6-di-t-butylphenol	Antioxidant	GC/MS	30	21	20	112	68	66	76	29	34	48	69	62	45	30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	237	284	315	18	54	103	60	nd	nd	89	39	368	72	413	97	45	
	2-Methylphenol	Disinfectant	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1986	55	24
	3-&4-Methylphenol	Disinfectant	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	25246	17442	21012	nd	5778	nd	nd	nd	nd	nd	62	35974	95	53873	999	603		
	Phenol	Disinfectant	GC/MS	11	20	17	nd	nd	nd	nd	nd	nd	16	40	22	21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2260	1269	1635	31	791	nd	nd	nd	nd	nd	nd	nd	35	6964	179	115		
	2,4-Dichloroaniline	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	19	1152	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd		
	2-Ethyl-1-hexanol	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2657	1463	3035	nd	325	nd	nd	nd	nd	nd	nd	2285	157	4186	141	84			
	2-Phenylphenol	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	461	56	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	575	nd	53			
	3,4-Dichloroaniline	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1768	505	nd	nd	254	nd	nd	nd	nd	nd	409	61	1940	nd	103				
	3,5-Dimethylphenol	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	16	31	17	nd	16	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd		
	Biphenyl	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	26	14	24	nd	18	nd	nd	nd	nd	nd	136	nd	418	11	nd				
	Dicyclohexylamine	Intermediate	LC/TOF-MS	nd	46	45	29	nd	nd	nd	50	43	76	nd	nd	nd	72	48	51	43	67	32	43	155	1806	58	403	121	156	80	3316	1973	126	81	145	nd	114	156	99	46	75	108	99	106	196	
	Quinoline	Intermediate	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	21	2293	nd	nd	nd	nd	nd	nd	197	23	13740	78	90			
	2(3H)-Benzothiazolone	Leaching from tire	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3928	nd	2881	nd	632			
	2-(Methylthio)-benzothiazol	Leaching from tire	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	384	341	976	179	388	nd	nd	nd	nd	nd	nd	868	97	483	210	427		
	Acetophenone	Leaching from tire/fregrance	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	87	nd	nd	nd	nd	nd	nd	nd	nd	nd	107	nd	215	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	892	139	nd		
	Benzyl alcohol	Leaching from tire	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	71	58	nd	nd	nd	nd	nd	nd	nd	1568	911	1762	nd	683	nd	nd	nd	nd	22	nd	503	nd	2354	101	nd			
	Phenylethyl alcohol	Leaching from tire	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	4783	2177	3907	nd	1214	nd	nd	nd	nd	nd	nd	203	nd	5848	70	45			
	4-tert-Octylphenol	Nonionic detergent metabolite	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	86	nd	nd	25	nd	44	25	21	nd	26	89	47	104	11	46	nd	nd	nd	nd	25	nd	847	28	334	36	21		
	Nonylphenol	Nonionic detergent metabolite	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	4951	4114	6607	73	1468	nd	nd	nd	nd	nd	184	26939	155	12993	402	381			
	n-C10H22	Petroleum	GC/MS	nd	nd	nd	nd	nd	nd	nd	91	399	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	7265	1162	4800	289	nd	nd	nd	nd	304	697	488	nd	nd	2910	3916	3198			
	n-C11H24	Petroleum	GC/MS	nd	nd	nd	nd	nd	119	nd	nd	nd	149	nd	nd	nd	nd	nd	399	nd	nd	nd	nd	nd	nd	nd	143	1119	560	810	nd	188	nd	nd	nd	89	105	72	49	nd	673	866	306			
	n-C12H26	Petroleum	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	348	nd	nd	nd	nd	nd	32	nd	nd	nd	nd	nd	nd	nd	343	91	261	nd	nd	nd	nd	nd	34	nd	nd	44	nd	556	201	63				
	n-C13H28	Petroleum	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	307	245	317	59	88	nd	nd	nd	nd	nd	528	147	750	nd	115					
	n-C14H30	Petroleum	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	15	nd	nd	nd	nd	nd	100	nd	nd	nd	nd	nd	nd	nd	nd	468	500	752	nd	43	22	nd	nd	58	47	nd	750	64	685	141	15				
	n-C15H32	Petroleum	GC/MS	nd	nd	nd	1551	175	nd	1113	nd	nd	nd	195	108	nd	nd	nd	222	nd	nd	1295	nd	270	580	nd	nd	566	426	509	nd	nd	1367	52	32	615	647	81	2363	19	830	752	35			
	n-C16H34	Petroleum	GC/MS	nd	nd	nd	1645	279	nd	1071	nd	nd	nd	nd	33	nd	nd	nd	449	140	nd	1900	nd	nd	676	nd	nd	951	494	837	nd	11	1721	65	nd	781	766	40	4606	137	1318	1072	nd			
	n-C17H36	Petroleum	GC/MS	nd	nd	nd	455	125	nd	217	nd	nd	nd	33	61	nd	nd	nd	78	254	nd	458	nd	641	203	nd	202	435	651	674	nd	189	265	nd	76	511	610	nd	4241	657	1476	567	nd			
	n-C18H38	Petroleum	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	458	nd	nd	106	nd	nd	nd	nd	96	nd	693	837	933	nd	422	nd	nd	nd	172	163	nd	3963	22	1467	120	nd			
	n-C19H40	Petroleum	GC/MS	nd	nd	nd	nd	nd	nd	nd	nd	20	nd	nd	nd	nd	nd	102	46	nd	nd	nd	nd	nd	nd	301	722	348	nd	607	nd	nd	nd	nd	nd	5515	nd	886	56	45						
	n-C20H42	Petroleum	GC/MS	80	nd	nd	12	nd	29	nd	nd	nd	208	nd	nd	nd	nd	303	nd	nd	235	nd	39	235	290	297	231	78	538	217	nd	763	nd	nd	nd	111	151	nd	6274	nd	742	nd	nd			
n-C21H44	Petroleum	GC/MS	nd	33	nd	nd	nd	nd	nd	nd	nd	279	nd	nd	nd	nd	78	nd	nd	136	nd	33	22	235	53	nd	303	806	401	nd	1093	nd	nd	nd	20	nd	nd	7820	nd	953	nd	nd				
n-C22H46	Petroleum	GC/MS	181	115	49	71	11	141	70	44	42	45	460	80	40	60	nd	nd	419	nd	nd	508	120	205	322	564	366	363	494	961	719	nd	1266	nd	nd	83	nd	nd	5854	nd	1340	nd	nd			
n-C23H48	Petroleum	GC/MS	14	107	nd	14	nd	54	nd	nd	31	52	551	15	nd	15	nd	nd	144	nd	nd	215	nd	181	128	543	189	121	1328	1322	1243	37	1406	nd	nd	nd	55	43	nd	9607	27	2775	80	nd		
n-C24H50	Petroleum	GC/MS	63	156	15	35	nd	19	21	12	nd	nd	736	25	nd	20	nd	nd	351	nd	nd	385	50	190	344	781	390	419	589	940	1118	nd	1272	nd	nd	nd	nd	nd	5830	nd	2967	nd	nd			
n-C25H52	Petroleum	GC/MS	135	170	44	nd	nd	nd	99	173	139	862	69	23	94	nd	nd	255	nd	nd	266	nd	160	174	767	196	85	1945	1362	2087	nd	1327	49	80	197	23	23	nd	8629	nd	5067	109	24			
n-C26H54																																														































































