보건학석사 학위논문

Suspect screening of emerging contaminants in granular activated carbon filter used for drinking water treatment

먹는 물 처리에 사용된 입상 활성탄 필터의 신규 오염물질 표적 스크리닝

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2018년 8월

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Abstract

Suspect screening of emerging contaminants in granular activated carbon filter used for drinking water treatment

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Drinking water has been contaminated with widespread distribution of various organic compounds. Recently, high-resolution mass spectrometry (HR-MS) has been used

increasingly for investigating emerging contaminants and transformation products in environmental samples. Universal screening and identification of novel micropollutants make it possible to overcome the limited information on occurrence and concentration of numerous micropollutants. Target, suspect and nontarget screening by using HR-MS have been developed and optimized continuously to identify unpredictable and unknown comtaminants at trace levels.

In this study, suspect screening method was applied on granular activated carbon filter samples installed in water purifiers collected in Korea. With those used GAC filter samples, unused GAC filter samples were analyzed as blank sample.

The first step, GAC sample extracted with methanol was screened for the 8 target perfluoroalkyl compounds (PFCs) using known retention times, accurate masses and fragment ions. All target compounds were detected and confirmed with reference standard. 6 out of 9 PFCs were detected in all GAC samples. Detected PFCs is Heptadecafluorooctane sulfonic acid(Perfluorooctane sulfonic acid), Perfluorodecanoic acid(Perfluorocapric acid), Perfluoroheptanoic acid, Perfluorohexanoic acid, Perfluorononanoic acid, Perfluorooctanesulfonic acid, Perfluorooctanoic acid, Perfluoropentanoic acid.

Next step was performed by suspect screening at full-scan mode

for accurate mass measurement with HR-MS, a post-target screening approach was undertaken, where searching and identification of other interesting compounds could be done at any time without performing additional analyses or without using reference standards. By GAC extracted sample analysis, tentative contaminants were identified. Data acquisition filter is applied for condition according to response value, mass error(ppm), the number of total fragment fount then we build up final comtaminant candidate list which is obtained as meaningful peak shape.

In the first extraction for 14 GAC filter using Acetonitrile solvent, 15 components are selected containing plant growth regulator (Heptopargil) in negative mode. Next extraction for 6 GAC filter detected Perfluoroakyl compounds using Methanol solvent, 25 components are selected containing veterinary antibiotic (Danofloxacin) in positive mode and 17 components are selected containing disinfection byproduct (Monobromoacetic acid) in negative mode. Finally, last extraction for 27 GAC filter using Dichloromethane solvent, 16 components are selected containing pesticide (Dipropetryne), hormone (Estradiol) in positive mode and 28 components are selected containing

insecticide(Sophamide) in negative mode.

When collecting for 19 tap water sample using solid phase extraction was performed, 11 components are selected containing acaricide(fluacrypyrim) in positive mode and 14 components are selected containing fungicide(piperalin) in negative mode.

In this study, suspect screening methods using HR-MS were shown to be a powerful tool for universal screening and identification of presence of micropollutants in drinking water. Its utility in this study is illustrated in our identification of several compounds that would not otherwise be monitored in drinking water. The need for a more comprehensive suspect screening approach is highlighted by the large number of features present in the samples, and the limited number of which that were confirmed or tentatively identified. We have demonstrated limited candidate contaminants list that prioritized frequency ranking by response data for which standards were not available on hand.

This results indicate that granular activated carbon used in drinking water filtration systems likely remove various micropollutants. As a result, extracted GAC filter enable to detect some micropolutants which is hardly detected in tap water with

trace level. Also, this study could overcome limitness of mornitoring method for long-term and time-lapse contaminants having concentration fluctuation in final water distribution system.

Keyword : Drinking Water, Micropollutant, Granular Activated Carbon, Filtration, Desorption, Suspect Screening, UPLC-QTOF

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I. Introduction

1.1. Emerging micropollutants in drinking water

Water pollution is perhaps the most prominent environmental concern for human health. Although anti-pollution measures taken over the past half-century have dramatically reduced the presence of many known contaminants in water, the number of potentially hazardous chemicals that can reach the environment is very large and new substances are constantly being developed and released (Gómeza et al., 2009).

The term “emerging pollutants” or “emerging contaminants” refers to compounds and their metabolites that are not currently covered by existing water-quality regulations, have not been studied often, are overlooked and are thought to be potential threats to environmental ecosystems and human health and safety since it would be compounds that are not included in routine environmental monitoring programs and may be candidates for future legislation due to their adverse effects and/or persistency (Bletsou et al., 2015).

Drinking water is produced from ground and surface water and conventional drinking water treatment was found inefficient for many micropollutants (Tröger et al., 2018). The contamination of source water containing numerous emerging micropollutants which is generated from various anthropogenic activities

increases with urbanization and population density affecting to water quality by their sources, occurrence, pathways, and health effects and wastewater treatment efficiency and natural attenuation processes that may take place in surface water and groundwater (Pal et al., 2014). Widely, over 340,000 chemicals are registered and regulated and used for many kinds of purposes such as pesticides, pharmaceuticals, flame retardants, food additives, cosmetics, and coatings (Sjerps et al., 2016).

The increasing number of emerging contaminants, such as pharmaceuticals (both human and veterinary) and personal-care products (PPCPs), or illicit drugs, detected in the water cycle can be attributed to the growth of the human population, the shift towards the use of more hydrophilic compounds in consumer applications, and undoubtedly the improvements in selectivity and sensitivity of modern analytical techniques. Pharmaceuticals and illicit drugs are continuously excreted or discarded into the sewer systems as the unaltered parent compounds or their metabolites. Subsequently, they often end up in environmental waters, as a consequence of incomplete elimination by wastewater-treatment plants. There is justified concern over the possible impact of these pharmacologically-active compounds on the environment, especially over the long-term toxicological effects on living organisms and the combined effect of exposure to multiple compounds, articularly antibiotics. In addition, a large number of transformation products (TPs), in many cases unknown, can be formed in the water cycle and need to be taken into account to know the overall contribution of these contaminants in the environment (Hernández et al., 2014).

Nowadays, the presence of TPs in the environment is a matter

of concern because of their wide consumption and potential negative effects on water quality and living organisms. Although rather limited, reported data show that some TPs are as, if not more, hazardous than the parent compound, producing negative effects on humans and wildlife. However, the ecotoxic, mutagenic and other potential harmful effects of TPs are mostly unknown and need to be investigated. As many of the TPs are still unknown, the analytical task is a challenge as not only the reported TPs must be detected and identified, but also new/unreported TPs must be discovered (Ibá et al., 2017).

Due to the distrust in tap water generated by water treatment plants, there are usually three types of consuming drinking water in Korea: tap water, purified water (tap water that is filtered through point-of use water purifier), and bottled water. Koreans use more purfied water(49 % of the total drinking water consumption) than tap water(32%) or bottled water (19%) (Jang et al., 2014).

Recent study shows some micropollutants existing in drinking water of Korea. Park et al., (2018) investigated the occurrence level of perfluoroalkylsubstances(PFASs) and organophosphate fl ame retardants (OPFRs) in 44 tap water samples, collected from eight major cities in Korea. The total concentrations of PFASs and OPFRs ranged from 1.44 to 224 ng/L (median = 11.9 ng/L), and 74.0 to 342 ng/L (median = 151 ng/L), respectively. The predominant compounds in tap water were perfluorohexane sulfonate (PFHxS), perfluoropentanoic acid (PFPeA), perflorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), tris(2-chloroethyl) phosphate (TCEP), tris (chloroisopropyl) phosphate (TCIPP), and tris(2-butoxyethyl) phosphate (TBOEP).

Tap water originating from the Nakdong River with in an industrial complexs how edanotably higher PFHxS proportion to total PFASs.

In this study, we focus on the widespread distribution of various organic contaminants in drinking water system using granular activated carbon filter. Chemical contaminants that end up in tap water may pose a direct threat to human health. Investigating on the presence of contaminants in drinking water treatment filter by desorption technique gives a broad chance to identify a variety of emerging pollutants in tap water.

1.2. Suspect screening by LC-QTOF HRMS

Liquid chromatography is a suitable chromatographic technique for polar, thermolabile compounds, thus for the identification of various organic compounds. There are various workflows in the literature for the identification of micropollutants. In order to assess and maintain the quality of drinking water, target compound monitoring is often not sufficient. Many unknown micro-contaminants are present in water, originating in municipal, industrial or agricultural effluents. Some of these might pose a risk to drinking water production and consequently to human health (Bobeldijka et al., 2001).

It becomes more important to investigate numerous micropollutants that may be present in the water. Liquid chromatography-high resolution mass spectrometry (LC-HRMS) is increasingly used for detect various chemicals that are present in water than target analytical methods (Sjerps et al., 2016). Richardson et al. (2016) highlighted "High-resolution-mass spectrometry (HR-MS) continues growing exponentially as a hot trend for use with liquid chromatography (LC) for identifying unknown contaminants, especially environmental transformation products (TPs) and disinfection byproducts (DBPs). For these analyses, growing trend is the combination of TOF-MS screening for large multianalyte analyses followed by target quantification. This approach streamlines research efforts and minimizes the use of analytical standards".

There is a growing need in the field of exposure science for

monitoring methods that rapidly screen environmental media for suspect contaminants and measurement and analysis tools, based on high resolution mass spectrometry (HRMS) exist to meet this need (Rager et al., 2016). HRMS offers the possibility of detecting a large number of contaminants without pre-selection of analytes due to its accurate-mass full-spectrum acquisition at good sensitivity. Interestingly, large screening can be made even without reference standards, as the valuable information provided by HRMS allows the tentative identification of the compound detected. It is necessary to accomplish universal approaches in terms of comprehensive measurement for broad screening of organic contaminants within a large range of polarity and volatility in waters (Hernández et al., 2015). High-resolution mass spectrometry coupled to LC is a very powerful combination for screening and identification purposes (Hogenbooma et al., 2009).

To detect site-specific, suspected and formerly unknown contaminants in a wastewater treatment plant effluent, a screening procedure based on LC-HRMS with stepwise identification schemes established. Based on automated substructure searches a list of suspected site-specific and documented water contaminants was reduced to those amenable to LC-HRMS. After searching chromatograms for exact masses of suspects, presumably false positive detections were stepwise excluded by retention time prediction, the evaluation of isotope patterns, ionization behavior, and HRMS/MS spectra. In nontarget analysis, peaks for identification were selected based on distinctive isotope patterns and intensity. Suspected and nontarget chemicals were identified, of which two have not been

previously reported as environmental pollutants (Hug et al., 2014).

Screening of a large number of emerging pollutants is highly desirable for the control of water quality. LC coupled to HRMS is a promising analytical technique, especially as the full scan mode enables post-target and non-target analysis of chemical fingerprints. The next step will then be to assess the ability to highlight the presence of unexpected contaminants not present in compound database. Developing in-house library containing various information on the targeted compounds allows their proper annotation and identification. Liquid chromatography coupled to HRMS is a promising analytical technique, especially as the full scan mode enables post-target and non-target analysis of chemical fingerprints. The next step will then be to assess the ability of this method to highlight the presence of unexpected contaminants not present in prepared database (Zushi et al., 2016).

QTOF-MS has been used for unequivocal confirmation of the identity of pharmaceuticals previously detected and quantified by LCMS/MS using hybrid quadrupole linear ion trap (QTRAP) or QqQ. The possibility of performing retrospective analysis has allowed the revision of recorded chromatograms for new compounds, metabolites or TPs in the samples, increasing the scope of the method in monitoring programs. LC-MS/ MS and LC-(Q)TOF-MS can be seen as complementary techniques. On the one hand, LC-MS/MS is the first choice for quantification in pre-target analysis,due to its good sensitivity and precision. On the other hand, QTOF provides accurate-mass measurements, and is ideal forpost-target screening and confirmation.The most

suitable strategy seems to be automated screening and identifi cation by LC(Q)TOF, followed by quantification by LC-MS/MS (Hernández et al., 2014).

An additional concern is the transformation of micropollutants during drinking water production, particularly in oxidation or disinfection processes, where a variety of transformation products may be formed that may be more toxic than the parent chemical (Duirk et al., 2011; Prasse et al., 2012; Wang et al., 2016).

In some cases, an approach for sequential nontarget and target screening for the rapid and efficient analysis of multiple samples as an environmental monitoring had been conducted. A key feature of the approach was the construction of an accurate mass spectral database learned from the sample via nontarget screening. To enhance the detection power in the nontarget screening, a global spectral deconvolution procedure based on non-negative matrix factor ization was applied. The approach was applied to the monitoring of rivers in the Tokyo Bay basin. The developed GCxGC-HRTOFMS approach was efficient and effective for environmental monitoring and provided valuable new information on various aspects of monitoring in the context of environmental management (Gómeza et al., 2009).

There is a growing need in the field of exposure science for monitoring methods that rapidly screen environmental media for suspect contaminants. Measurement and analysis platforms, based on high resolution mass spectrometry (HRMS), now exist to meet this need. Vacuum dust samples were collected from 56 households across the U.S. as part of the American Healthy Homes Survey (AHHS). Sample extracts were analyzed using

liquid chromatography time of-flight mass spectrometry (LC-TOF/MS) with electrospray ionization. On average, approximately 2000 molecular features were identified per sample (based on accurate mass) in negative ion mode, and 3000 in positive ion mode. Exact mass, isotope distribution, and isotope spacing were used to match molecular features with a unique listing of chemical formulas extracted from EPA's Distributed Structure-Searchable Toxicity (DSSTox) database. A total of 33 chemicals were confirmed present in the dust samples by formula and retention time match; nearly half of these do not appear to have been associated with house dust in the published literature. Thousands of chemicals exist in house dust. Yet, to date, most studies of chemicals in dust have focused on a relatively small set of analytes. Considering these findings, it is likely that scaled-up efforts, involving a more inclusive reference database, a larger number of standards, and optimized analytical methods would aid in identifying (and potentially quantifying) hundreds of previously unstudied chemicals in dust and other media. Broad-scale approaches of this nature will be required to define the breadth of chemical exposures, characterize the impacts of chemical co-exposures on human and environmental health, and prioritize chemicals and chemical classes for which targeted research should be performed (Rager et al., 2016).

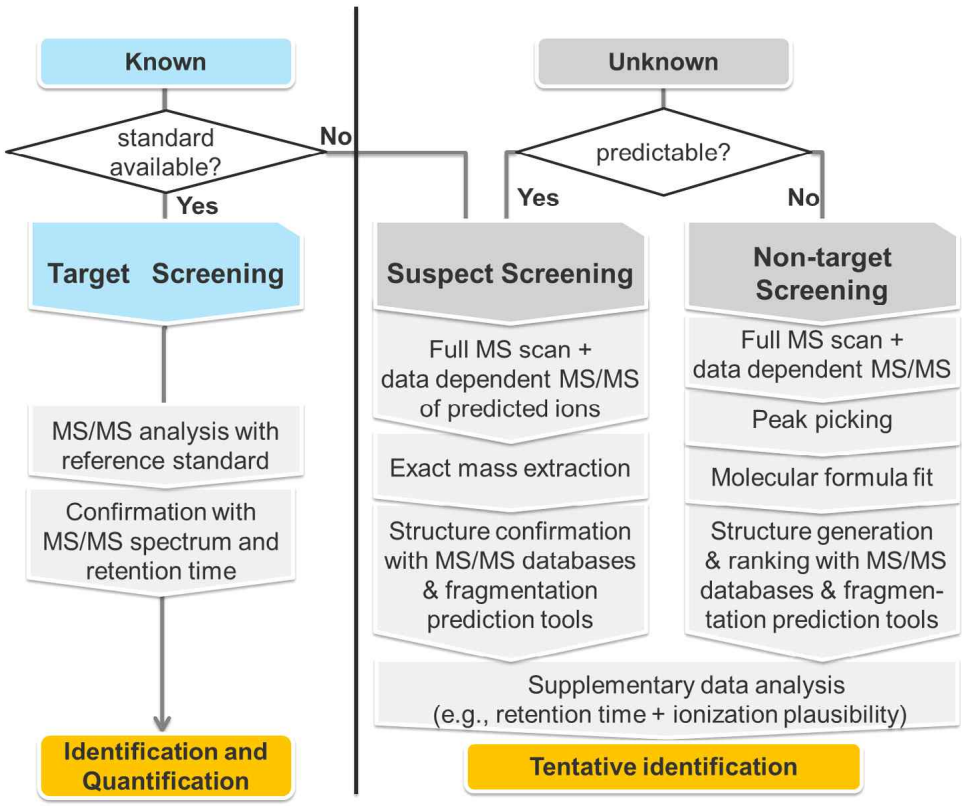
A target screening method using ultra high performance liquid chromatography-high resolution mass spectrometry (UPLC-HRMS) was developed. The method was applied to 14 groundwater and 11 surface water samples. The measured data are compared with mass spectrometric data of over 2000 organic micropollutants, including pharmaceuticals, personal care products, pesticides,

industrial chemicals and metabolites of these classes. A total number of 151 and 159 OMPs were detected in groundwater and surface water, respectively, of which 12 have not been reported before in these matrices. Among these 12 compounds were 11 pharmaceuticals and one personal care product (Wode et al., 2015).

Environmental risk assessment requires a vast amount of information and, among it, data on the occurrence of the contaminants in the environmental compartments. Instruments with high mass resolution, especially TOF and Q-TOF, have been increasingly used for the identification of pesticides degradation products and for confirmation purposes in waters (Kuster et al., 2009).

Fig. 1 shows the main outline: (a) target analysis, which is based on the determination of already known compounds, and identification is carried out with standard solutions; (b) suspect screening, with a list of possible contaminants assembled from the literature or from prediction models, and the samples are screened for those candidates; and, (c) non-target screening, with identification of novel contaminants being carried out with sophisticated post-acquisition data tools and supplementary analytical techniques. The development and the use of powerful HR-MS is the driving force in development of novel analytical methodologies for the identification of emerging contaminants. Due to its sensitivity in full-scan acquisition mode and high mass accuracy, HR-MS is suitable for target and nontarget analysis, pre- and post-acquisition processing, retrospective analysis and discovery of novel compounds (Bletsou et al., 2015).

Figure 1. Outline of target/suspect/non-target screening precedure (Bletsou et al., 2015).



1.3. Carbon filter desorption technic

Vrana et al., (2005) reviews the state of the art of different passive sampling methods that have been developed to measure both organic and inorganic pollutants in water and highlights their range of applicability. Most aquatic monitoring programmes rely on collecting discrete grab, spot or bottle samples of water at a given time. Often, where pollutants are present at only trace levels, large volumes of water need to be collected. The subsequent laboratory analysis of the sample provides only a snapshot of the levels of pollutants at the time of sampling. However, there are drawbacks to this approach in environments where contaminant concentrations vary over time, and episodic pollution events can be missed. One solution to this problem is to increase the frequency of sampling or to install automatic sampling systems that can take numerous water samples over a given time period. This is costly and in many cases impractical, since a secure site and significant pre-treatment of water are required. Such systems are rarely used in widespread monitoring campaigns. Spot sampling yields different apparent concentrations of pollutants depending on the pre-treatment applied (e.g., filtering) and does not provide information on the truly dissolved, bioavailable fraction of the contaminants. In some cases, alternatives have been sought to overcome some of these difficulties. Of these, passive sampling methods have shown much promise as tools for measuring aqueous concentrations of a wide range of priority pollutants. Passive samplers avoid many of the

problems outlined above, since they collect the target analyte in situ and without affecting the bulk solution. Depending on sampler design, the mass of pollutant accumulated by a sampler should reflect either the concentration with which the device is at equilibrium or the time-averaged concentration to which the sampler was exposed. Such devices have been available for monitoring air quality since the early 1970s. These diffusion-based dosimeters have been employed extensively by industry to measure toxic chemicals in workplace air. Later, the principles of passive dosimetry were applied in monitoring in aqueous environments.

Desorption of from a spent activated carbon using organic solvent extraction were investigated(Kwon et al., 2017; Newton et al., 2018). Under optimized the desorption conditon compared several extraction solvents, apropriate amount of solvent, and sonication time, micropolutants were detected in the spent powdered activated carbon(PAC) filter such as pharmaceuticals and personal care products(PPCPs) and endocrine disrupting compounds(EDCs). Among the micropolutants, cafeine, metoprolol, naproxen, and diclofenac had higher detection frequencies (>60%), and sulfamethazine, metoprolol and ibuprofen were only detected in the carbon filters, but not in the tap water, indicating that these micropolutants might exist less than detection level in the tap water, but acumulated in the carbon filter(Kwon et al., 2017).

Monitored contaminants in drinking water represent a small portion of the total compounds present, many of which may be relevant to human health. To understand the totality of human exposure to compounds in drinking water, broader monitoring

methods are necessary. In an effort to more fully characterize the drinking water exposome, point-of-use water filtration devices were employed to collect time-integrated drinking water samples in a pilot study of nine North Carolina homes(Newton et al., 2018). A suspect screening analysis was performed by matching high resolution mass spectra of unknown features to molecular formulas. Candidate compounds with those formulas were recently developed data hub for approximately 720,000 compounds. To prioritize compounds into those most relevant for human health, toxicity data as well as exposure estimates were used in conjunction with sample detection frequency and abundance to calculate a score for each candidate compound. From more than 15,000 molecular features in the raw data, 91 candidate compounds were ultimately grouped into the highest priority class for follow up study. Fifteen of these compounds were confirmed using analytical standards including the highest priority compound, 1,2-Benzisothiazolin-3-one, which appeared in 7 out of 9 samples. The majority of the other high priority compounds are not targets of routine monitoring, highlighting major gaps in our understanding of drinking water exposures. Although there have been abundant research efforts directed at identifying contaminants in drinking water, to the best of our knowledge, this study is the first to use a point-of-use home filter combined with an suspect and non-target screening analysis approach in korea. Surprisingly, this several compounds identified were novel compound that would not otherwise be monitored in drinking water. The need for a more comprehensive suspect and non-target analysis approach is highlighted by the large number of features present in the samples, and the limited

number of which that were confirmed or tentatively identified.

Desorption of from a spent activated carbon used in the water purifiers in Korea using organic solvent extraction were investigated (Kwon et al., 2017; Newton et al., 2018). Under optimized the desorption condition compared several extraction solvents, appropriate amount of solvent, and sonication time, micropollutants were detected in the spent powdered activated carbon(PAC) filter such as pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds(EDCs). Among the micropollutants, caffeine, metoprolol, naproxen, and diclofenac had higher detection frequencies (>60%), and sulfamethazine, metoprolol and ibuprofen were only detected in the carbon filters, but not in the tap water, indicating that these micropollutants might exist less than detection level in the tap water, but accumulated in the carbon filter (Kwon et al., 2017).

1.4. Objectives

The objectives of this study were: (1) to examine screening methods of the micropollutants sorbed in the activated carbon used in the water purifiers (2) to identify various micropollutants sorbed in the activated carbon by suspect screening performed by matching high resolution mass spectra of unknown features to molecular formulas from master and custom library; (3) to make a micropollutant candidate list of tap waters which filters were used.

II. Materials and Methods

2.1. Chemicals and materials

The standard reference samples (N95% in purity) of Heptadecafluorooctane sulfonic acid(Perfluorooctane sulfonic acid), Perfluorodecanoic acid(Perfluorocapric acid), Perfluoroheptanoic acid, Perfluorohexanoic acid, Perfluorononanoic acid, Perfluorooctanesulfonic acid, Perfluorooctanoic acid, Perfluoropentanoic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Individual stock solutions of these reference standards were prepared to a concentration of 1 mg mL−1 in methanol and stored at −20 ˚C until further use. Working standard mixtures of the test compounds were prepared in a solution of methanol at different concentrations by appropriate dilution of the individual stock solutions.

The characteristics of the 8 target micropollutants compounds are listed in Table 1. The LC-MS grade reagents used in this study include: water from J.T. Baker (Phillisburg, NJ, USA); methanol (MeOH) and Acetonitrile (ACN) and formic acid and ammonium acetate from Sigma-Aldrich (St. Louis, MO, USA). Deionized water was obtained from Milli-Q-Plus (Millipore, Bedford, MA, USA).

2.2. Experimental procedures

2.2.1. GAC filter and Tap water sampling

Granular activated carbon(GAC) were collected from water purifier filter which is installed in 42 and tap water in 19 house of Korea. Information about the region can be found in Table 1. This process took between 7 and 9 months for each sample with an average sampling time 8 months. We distinguished collected location region and source water river in Table1.

Table 1. Sampling list in Korea

1) 1st, 2nd GAC sample list

No.		location	River
1st -1	2nd -1	Busan	Nak-dong
1st -2		Seoul	Han
1st -3		Chung-buk	Keum
1st -4	2nd -2	Ulsan	Nak-dong
1st -5	2nd -3	Seoul	Han
1st -6		Kyung-buk	Nak-dong
1st -7		Cheon-buk	Geum
1st -8		Seoul	Han
1st -9	2nd -4	Kyung-ki	Han
1st -10		Busan	Nak-dong
1st -11		Kyung-buk	Nak-dong
1st -12	2nd -5	Kyung-buk	Nak-dong
1st -13	2nd -6	Seoul	Han
1st -14		Busan	Nak-dong

2) total GAC sample list distribution with 1st, 2nd , 3rd

River	Province/City	N	sum
Han	Kang-won	2	16
	Kyung-ki	1	
	Seoul	13	
Keum	Cheon-buk	4	13
	Chung-buk	3	
	Chung-nam	6	
Nak-dong	Busan	6	12
	Kyung-buk	3	
	Ulsan	3	
Young-san	Gwang-ju	1	1
Total			42

* 1st : Desorption solvent (Acetonitrile)

** 2nd : Desorption solvent (Methanol)

*** 3rd : Desorption solvent (Dichloromethane)

3) Tap water sample list

River	City	N
Han	Seoul	2
Nak-dong	Daegu	4
	Busan	13
Total		19

Figure 2. GAC filter Sampling point in Korea

1) 1ST, 2ND sampling distribution(14, 6)

2) 3RD sampling distribution (27)

3) Tap water sampling distribution (19)

2.2.2. GAC filter extraction

The filters was removed from the plastic casing using a band saw with a clean blade and dried in hood for two days to remove any water which remained in the filter pores then placed into a plastic bag for storage until extraction. The GAC 100 g samples in 500 mL glass bottle were extracted via ultrasound sonication using 250 mL of two different solvent (first time with acetonitrile and second time 6 out of 14 filter with methanol) for 4 hours. Upon completion, the vials were centrifuged at 12,500 x g for 60 min to remove particles from suspension. The extract of 120 mL was re-dissolved in an autosampler vial with 1 mL of methanol for analysis.

Final condition is processed with dichloromethane solvent for 27 sampling site. The GAC 5 g samples in 50 m polyethylene tube were extracted via ultrasound sonication using 40 mL solvent with same physical condition (sonication and centrifuging). The extract of 30 mL was re-dissolved in an autosampler vial with 1 mL of methanol for analysis.

2.2.3. Tap water sample pretreatment

Samples were analyzed by UPLC-ESI-QTOF MS,after a generic solid-phase extraction (SPE). Briefly, 1 L of water samples were passed through 1 g Oasis HLB cartridges at a flow rate of 10 mL/min using a vacuum manifold, previously conditioned with 10 mL methanol and 10 mL HPLC-grade water. After drying under vacuum, analytes were eluted with 10 mL methanol. The extract was evaporated to dryness under a gentle nitrogen stream at 35 ℃ and reconstituted with 1 mL methanol (final pre-concentration factor : 1000).

Figure 3. GAC filter extraction process

Process	Image	Condition
GAC Filter		Housing Cut-off
GAC drying		dried in hood for 2 days
Sonication		GAC 100 g in 250 mL Organic Solvent for 4 hours
Concentration		30 or 120 mL Evaporation Concentrator
LC-QTOF		1 mL

2.3. Instrumental analysis

The extracts were analyzed by ultra high performance liquid chromatography (ACQUITY UPLC H-class, Waters Corp., Milford, MA.), interfaced with an quadrupole time-of-flight mass spectrometry (Synapt G2-Si MS, Waters Corp., Milford, MA.).

Operating the instrument under MS^E acquisition mode it is feasible to simultaneously obtain full-spectrum accurate-mass data at low and high collision energy. The combination of these two datasets is very useful for identification and elucidation purposes, as LE MS spectra usually showthe (de)protonated molecule, while HE MS spectra are richer in fragment ions. With all the information provided by this technique (accurate mass, isotopic distribution, and MS data at LE and HE), and the efficient chromatographic separation offered by UHPLC, it is feasible to identify compounds in complex environmental matrices, by searching for target analytes on the basis of a compound database. Ultimate confirmation would require the injection of reference standards, which should be acquired only in those cases where QTOF experimental data strongly support their presence in the samples(Ibánez et al., 2017).

The entire operation of this apparatus as well as processing of data was done by MassLynx V4.1. Chromatographic separation was carried out on an Acquity UPLC BEH C18 column (2.1 mm × 100 mm, 1.7 μm). The column temperature was set to 30 ℃, and the flow rate of mobile phase was 300 μL/min. The mobile phases has two condition. Fist condition is for analyzing for

Perfluoroalkyl substances. It is made of A=H2O containing Methanol (98:2) with 2 mM ammonium acetate and B=MeOH with 2 mM ammonium acetate. The percentage of organic modifier (B) was changed linearly as follows: 0 min, 10%; 10 min, 100%; 13 min, 100%; 16.01 min, 10%; 18 min, 10%. Second condition is for analyzing for pesticides and phamaceuticals screening. A=H2O with 0.01% formic acid and B=MeOH with 0.01% formic acid. The percentage of organic modifier (B) was changed linearly as follows: 0 min, 10%; 14 min, 90%; 16 min, 90%; 16.01 min, 10%; 18 min, 10%. Nitrogen (from a nitrogen generator) was used as the drying gas and nebulizing gas. The desolvation gas flow was set at 1,000 L/h and the cone gas at 80 L/h. Capillary voltages of 0.7 and 3.0 kV were used in positive and negative ionisation modes, respectively. A cone voltage of 20 V was selected for both ionisation modes. Collision gas was argon 99.995%. The interface temperature was set to 650°C and the source temperature to 130 ℃. The column temperature was set to 40 ℃. TOF MS resolution was approximately 20,000 at full width half maximum (FWHM) at m/z 556. MS data were acquired over an m/z range of 50-1,000. A scan time of 0.4 s was selected.

Calibration of mass axis was conducted from m/z 50 to 1,000 with a 2:1 mixture of 50 mM NaF with 2-Propanol:water (90:10, v/v):10 % HCOOH diluted in ultrapure water 20 mL(3:200, v/v). For automated accurate mass measurement, the lock-spray probe was used, using as lockmass a solution of leucine enkephalin (1 ng/μL) in acetonitrile:water (50:50) at 0.1 % HCOOH pumped at 20 μL/min through the lock-spray needle. For recalibrating the mass axis and ensuring a robust accurate mass measurement along time, the (de)protonated molecule of leucine enkephalin was used

(m/z 556.2771 in ESI+, m/z 554.2615 in ESI-).

The QTOF-MS data was collected in continum mode, using the lock spray to ensure accuracy and reproducibility. The lock spray frequency was set an 10s, and the lock mass data were averaged over 10 scans for correction. All of the data acquisition was controlled using Waters MassLynx software (Waters Corp. Milford, MA) with the MS^E program.

2.4. Data Processing

The software UNIFI Waters Scientific Information System (Waters Corp., Milford, USA) was used for identification and quantification of compounds and for instrumental control. All MS^E data were processed within UNIFI program. In this study, customized library of over 3,000 species for each ionization mode of environmental contaminants from master library (Water Toxicology) and reference materials. Based on this user library, all MS^E data peaks were identified through UNIFI program. Among the identified peaks compared the mass error, the number of fragments, and the mass error of the fragment to determine a meaningful peak. The identified compound list were compared with the unused blank filter extracts sample which is control group to avoid first contamination which is originated from unused filter and second contamination while operated.

The software UNIFI Waters Scientific Information System was used for identification and quantification of compounds and for instrumental control.

The target compounds were identified by UNIFI using accurate mass screening (maximum 10 ppm mass error). UNIFI was also used to group all isotopes and adducts together as one identified compound when processing the data.If such isotopes or adducts are available, this kind of approach strengthens the reliability of the positive identifications. The molecular structures for all target compounds were added to the database when setting up the method. With this information provided, the software is able to

compare the mass spectra from the high collision energy scans and match any detected ions to possible theoretical fragments originating from the parention. This is particularly useful for compounds for which database information on expected fragments is lacking, since it provides another identification criterion.

Suspect screening analysis in environmental samples is a complex task and identification of unknown compounds relies on the availability of chemical databases for finding candidates. The higher the number of compounds included in the library, the wider the possibilities to detect as many contaminants as possible in the samples(Hernández et al., 2014). The results obtained from the automatic screening should be carefully evaluated in order to rule out any false positive hit(Cotton et al., 2016).

In this study, we build home-made libraries to simplify searching by using both master library of WATERS UNIFI program library and reference materials from previous study(Sjerps et al., 2016; Wode et al., 2015; Cotton et al., 2016). The mass accuracy of the system was better than 10 ppm.

Table 2. Number of compound from master and custom (reference) library.

class	Library	Number of chemicals
	positive mode	
Master	Waters Screening Library [UNIFI 1.8]	2302
Master	Waters Toxicology Library [UNIFI 1.8 Pos]	1246
Custom	Reference[1,2,3]	640
	sum	4188
	negative mode	
Master	Waters Screening Library [UNIFI 1.8]	2302
Master	Waters Toxicology Library [UNIFI 1.8 Neg]	71
Custom	Reference[1), 2), 3)]	431
	sum	2804

1) Sjerps et al., 2016

2) Wode et al., 2015

3) Cotton et al., 2016

III. Results

3.1. Target screening

Perfluorochemicals (PFCs) are a family of man-made compounds with strong C-F bonds widely detected in drinking water(Hoffman et al., 2011; Post et al., 2009; Thompson et al. 2011). Due to their unique properties, they are commonly used in consumer products and industrial processes, such as protective coatings of carpets and furniture, paper and cloth coatings,Polytetrafl uoroethylene products, and fire-fighting foams(Jian et al., 2017).

The 6 GAC out of 14 extracted sample with methanol was screened for the 8 target perfluoroalkyl compounds (PFCs) using known retention times, accurate masses and fragment ions. All target compounds were detected and confirmed with reference standard. Table 3 presents the detected components in the sample and the number of contaminated samples.

6 out of 9 PFCs components were detected in all GAC samples, which is Heptadecafluorooctane sulfonic acid(Perfluorooctane sulfonic acid), Perfluorodecanoic acid(Perfluorocapric acid), Perfluoroheptanoic acid, Perfluorohexanoic acid, Perfluorononanoic acid, Perfluorooctanesulfonic acid, Perfluorooctanoic acid, Perfluoropentanoic acid, Perfluorohexane sulfonic acid.

Figure 4. LC-QTOF overall chromatogram (6 GAC fIlters extracted by methanol)

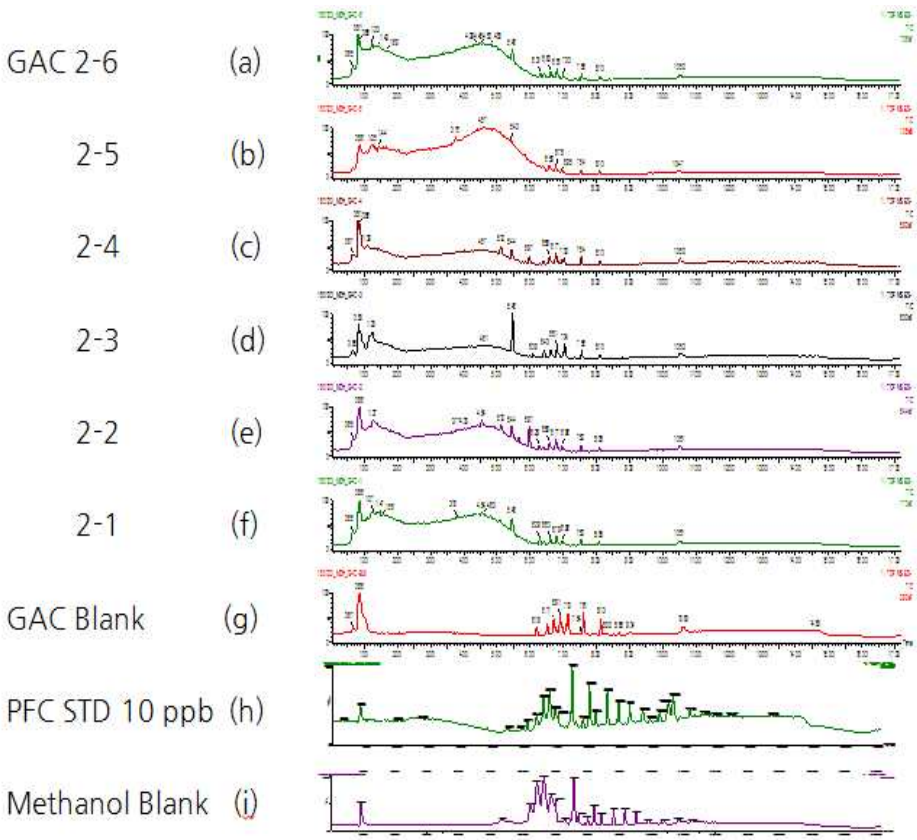
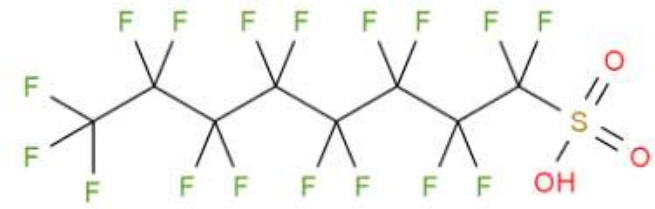


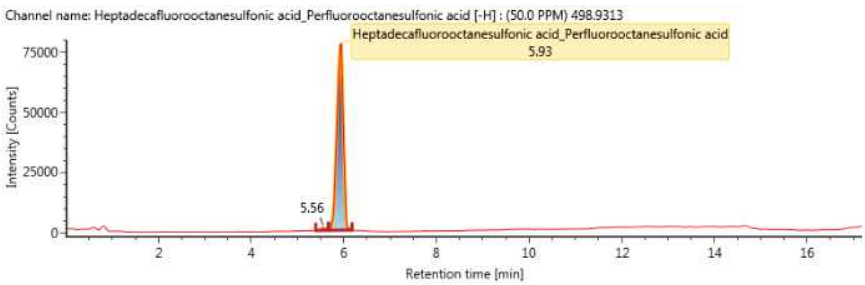
Table 3. Confirmed PFC list in negative mode of GAC(#5) extracted by methanol.

Component name	Observed m/z	Mass error (ppm)	Observed RT (min)	Total Fragments Found	# of detected sample (ourof6)
Heptadecafluorooctane sulfonic acid (Perfluorooctane sulfonic acid)	498.9313	2.2	5.93	7	6/6
Perfluorodecanoic acid (Perfluorocapric acid)	512.9609	1.7	6.18	3	1/6
Perfluoroheptanoic acid	362.9697	0.2	5.47	3	6/6
Perfluorohexanoic acid (Undecaflorohexanoic acid)	312.9735	2.3	5.16	3	6/6
Perfluorononanoic acid	462.9635	0.5	5.95	7	5/6
Perfluorooctanesulfonic acid	398.9373	1.7	5.48	3	6/6
Perfluorooctanoic acid	412.9671	1.7	5.72	5	6/6
Perfluoropentanoic acid	262.9764	1.6	4.65	3	6/6
Perfluorohexane sulfonic acid	398.9371	0.5	5.50	6	4/6

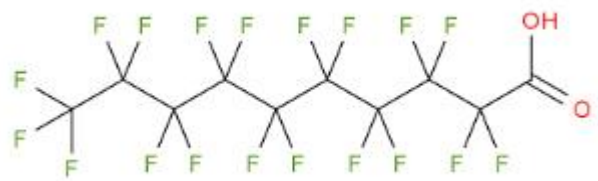
Figure 5. Confirmed PFC chromatogram in negative mode of GAC(2nd-5) extracted by methanol.

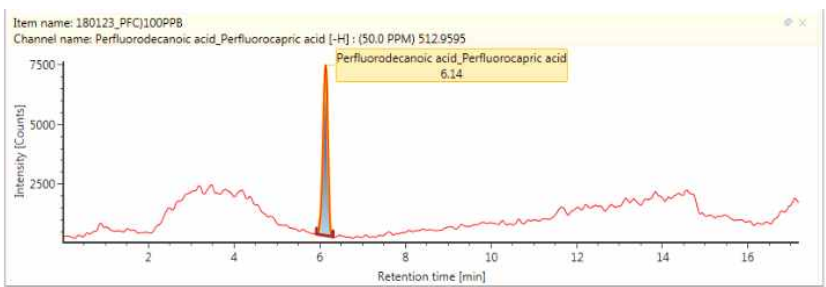
1) Heptadecafluorooctane sulfonic acid



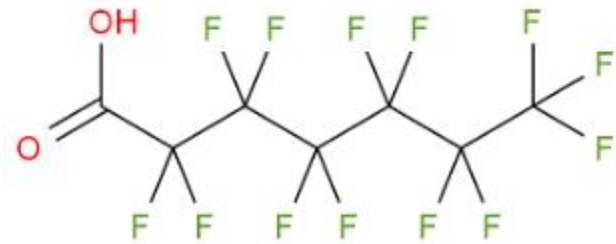


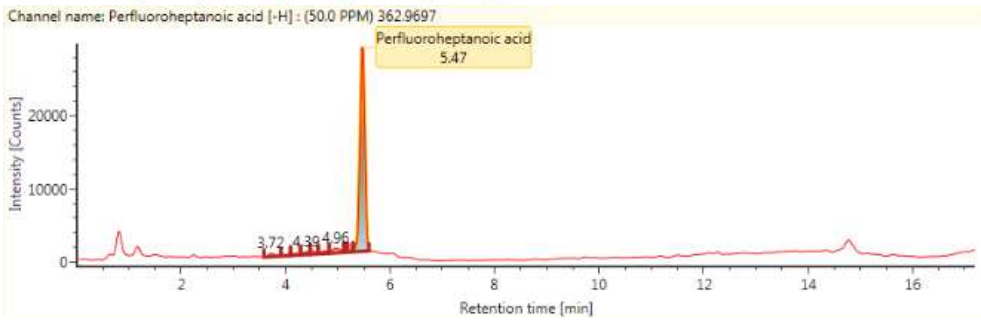
2) Perfluorodecanoic acid



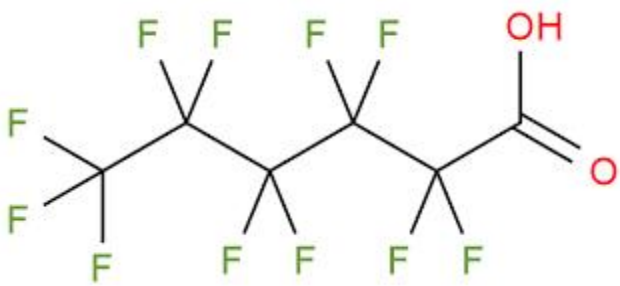


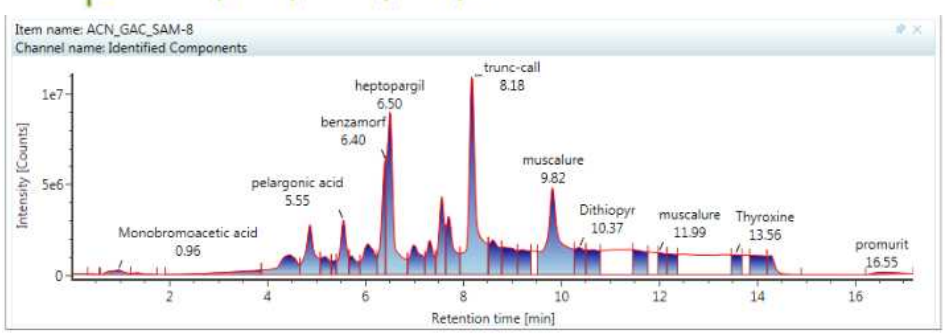
3) Perfluoroheptanoic acid



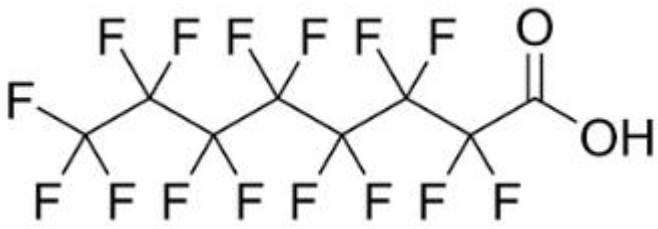


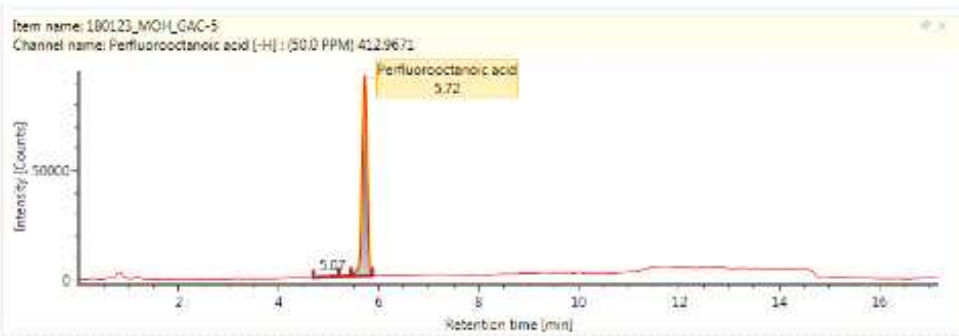
4) Perfluorohexanoic acid (Undecafluorohexanoic acid)



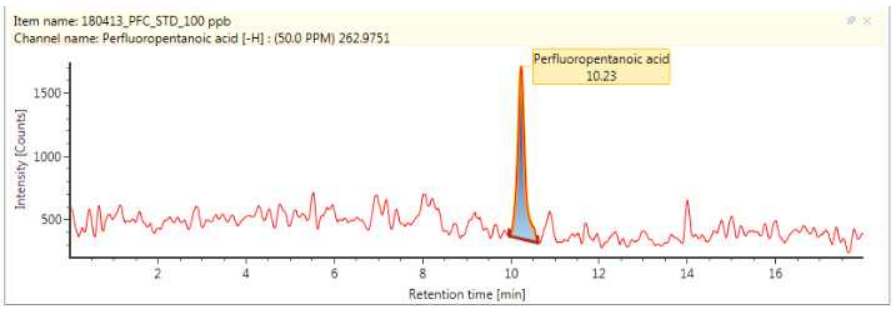


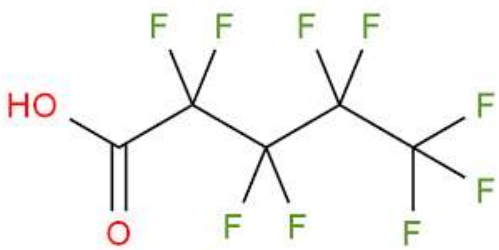
5) Perfluorooctanoic acid



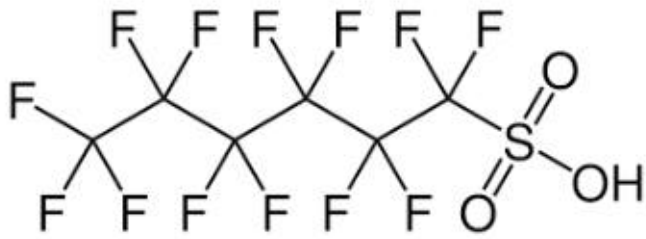


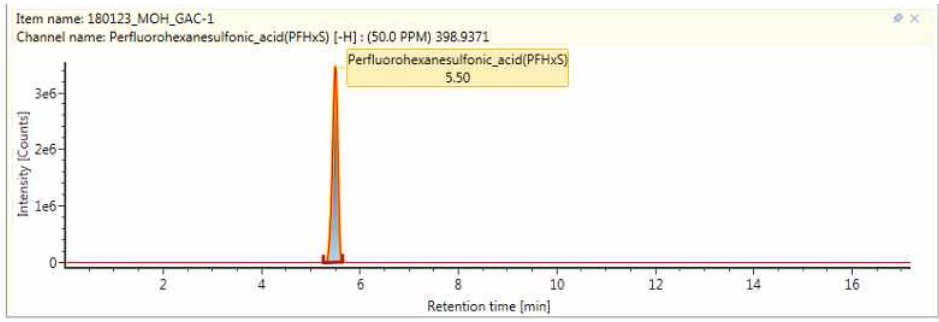
6) Perfluoropentanoic acid





7) Perfluorohexanesulfonic acid





3.2. Suspect screening

As data acquisition was performed at full-scan mode for accurate mass measurement with Q-TOF-MS, a post-target screening approach was undertaken, where searching and identification of other interesting compounds could be done at any time without performing additional analyses or without using reference standards(Wang et al., 2012).

In this study, the post-target analysis was performed by home-made library matching. The investigation of those post-target compounds has been described in some reports in the literature(Sjerps et al., 2016; Wode et al., 2015; Cotton et al., 2016). Some of their characteristics are listed in Table 1. The screening procedure comprised the following steps. In the TOF-MS mode, using theoretical molecular mass of the selected compounds, chromatograms of extracted precursor ions were gained from total ion chromatograms. The mass error between experimental and theoretical molecule mass was less than 5 ppm, which implied that the selected compounds may occur in the samples. Further confirmation should be performed by accurate mass measurement of characteristic fragment ions of suspected compounds with reference standard.

During the application of the above-described screening procedure to GAC extracted sample analysis, tentative contaminants were identified. Data acquisition filter is applied for response value in the most 30 components for each samples,

then build up component list which is identified same compound at least two out of six sample which is extracted by acetonitrile. Table 4 is the frequency order of response value.

Then we distinguished the major identified component that has mass filter erroer(<2 ppm), response value(>10000). To this group, manual labelling is processed by checking the peak that has a good peak shape. This data processing method is done to 14 GAC samples extracted by Acetonirile and 6 GAC samples extracted by methaol. The 6 GAC filters are picked by chromatogram and the number of identifed component in first extraction samples by acetonitrile. Then another 29 GAC filter is extracted by dichloromethane. And 19 tap water sampled is analyzed.

In GAC filter samples extracted by acetonintrile, identified components were such as Heptopargil (Plant growth regulator), Hexalure (Insect attractant, Straight chain lepidopteran pheromone), Muscalure (Insect attractant, Dipteran attractant), Ostramone (Insect attractant, Straight chain lepidopteran pheromone), Pelargonic acid (Herbicide), Trunc-call (Insect attractant, Coleopteran attractant), Curcumenol (Rodenticide), Acequinocyl (Acaricide), Dinoseb (Dinitrophenol herbicide), Sodium naphthenate (Plant growth regulator, Auxin), Tioxymid (Benzamide fungicide), Triamcinolone (Synthetic corticosteroid), Abscisic acid (Plant growth regulator, Growth inhibitor), Ethiozin (Triazinone herbicide), Propyl isome (Synergist), 2-Hydroxyibuprofen (Entheogen, Hallucinogen, Phenethylamine, Psychedelic), Ametridione (Triazinone herbicide), Chloromebuform (Formamidine acaricide), Cyperquat (Quaternary ammonium

herbicide), Methoprene (Insecticide, Juvenile hormone mimic), Silafluofen (Pyrethroid ether insecticide), Bioallethrin (Pyrethroid ester insecticide), Butopyronoxyl (Insect repellent), Ethephon (Plant growth regulator, Defoliant, Ethylene releaser), Glufosinate (Herbicide), Ipsenol (Insect attractant, Coleopteran attractant), Japothrins (Pyrethroid ester insecticide), Matrine (Botanical insecticide), Methyl eugenol (Insect attractant), Selamectin (Avermectin acaricide, Avermectin insecticide), Terallethrin (Pyrethroid ester insecticide) in negtive mode.

In GAC filter samples extracted by methanol, identified components were such as Crotamiton (Acaricide, Insecticide), Ferimzone (Fungicide, Pyrimidine fungicide), Profluthrin (Pyrethroid ester insecticide), Ametoctradin (Triazolopyrimidine fungicide), Heptopargil (Plant growth regulator), Metalaxyl-M (Acylamino acid fungicide, Anilide fungicide), Primetaphos (Anaesthetic), Rebemide (Insect repellent), Zengxiaoan (Insect repellent, Synergist) in positive mode and Pelargonic acid (Herbicide), α-multistriatin (Insect attractant, Coleopteran attractant), Dimethyl carbate (Insect repellent), Terallethrin (Pyrethroid ester insecticide), Japothrins (Pyrethroid ester insecticide), Oxpoconazole fumarate (Conazole Imidazole fungicide), Piperonyl cyclonene (Synergist), Thifluzamide (Anilide fungicide, Thiazole fungicide), Uniconazole (Conazole fungicide (triazoles), Plant growth regulator, Growth retardant), Eugenol (Insect attractant), Ibuprofen (Analgesic, Anti-inflammatory, NSAID), Lincomycin (Veterinary drug),

Naproxen (Analgesic, Anti-inflammatory, Antipyretic, NSAID), Natamycin (Antibiotic fungicide), Nisoldipine (Antihypertensive,

Calcium channel blocker) in negative mode.

In GAC filter samples extracted by dichloromethane, identified components were such as Dipropetryne (Pesticide), Estradiol (Sex hormone), ipsdienol (Insect attractant, Coleopteran attractant), prosulfalin (Herbicide), orysastrobin (Fungicide), Temazepam (Benzodiazepine, Hypnotic, Sedative), dibutyl phthalate (Insect repellent), tris(1-chloro-2-propyl)phosphate (flame retardants, pesticides, plasticizers), Valaciclovir (antiviral drug), metalaxyl-M (Fungicide), 2-Ethylhexyl-diphenyl-phosphate (plasticizer), prosulfalin (Herbicide), tridemorph (Fungicide, Morpholine fungicide), DEHP (plasticizer), S-metolachlor (Herbicide, Chloroacetanilide herbicide), zengxiaoan (Insect repellent, Synergist) in positive mode and sophamide (Acaricide, Insecticide), epocholeone (Plant growth regulator), mecoprop-P-isobutyl (Herbicide, Phenoxypropionic herbicide), Prohydrojasmon (Plant growth regulator, Growth inhibitor), Cinerin I (Botanical insecticide), Penthiopyrad (Pesticide, Fungicide), bachmedesh (Plant growth regulator), Pyraclonil (Herbicide, Nitrile herbicide), Fenapanil (midazole fungicide), MCPB (Phenoxybutyric herbicide), Valifenalate (Acylamino acid fungicide), Butroxydim (Cyclohexene oxime herbicide), Juvenile hormone I (Insecticide, Juvenile hormone), Chlorempenthrin (Pyrethroid ester insecticide), Acequinocyl (Acaricide), paichongding (Insecticide), Sesamex (Synergist), Triamcinolone (Synthetic corticosteroid), Isamidofos (Nematicide, Organothiophosphate nematicide), Diethatyl-ethyl (Chloroacetanilide herbicide), MCPA-ethyl (Phenoxyacetic herbicide), Tolvaptan (Diuretic, Vasopressin receptor antagonist),

Bendroflumethiazide (Antihypertensive, Diuretic, Thiazide), Di(2-ethylhexyl)adipate_DEHA (plasticizer), Malonoben (Insecticide), Chlorphonium (Plant growth regulator, Growth inhibitor), Kasugamycin (Antibiotic fungicide, Bactericide), Piprotal (Synergist) in negative mode.

In tap water samples, identified components were such as Fluacrypyrim (Methoxyacrylate strobilurin acaricide), TCA-ethadyl (Halogenated aliphatic herbicide), Propaphos (Organophosphate insecticide), Orysastrobin (Methoxyiminoacetamide strobilurin fungicide), Terallethrin (Pyrethroid ester insecticide), Terbuchlor (Chloroacetanilide herbicide), Cyclethrin (Pyrethroid ester insecticide), Chlorphonium chloride (Plant growth regulator, Growth inhibitor), Triazamate (Insecticide), Allosamidin (Insecticide), Bicyclopyrone (Herbicide) in positive mode and Piperalin (Fungicide), Terbuchlor (Chloroacetanilide herbicide), Flumorph (Morpholine fungicide), Fenoprofen (Analgesic, Anti-inflammatory, NSAID), Heptadecafluorooctanesulfonic acid (Cyclodiene insecticide), Aspon (Pesticide, Insecticide), Pencycuron (Fungicide), Methiopyrisulfuron (Pyrimidinylsulfonylurea herbicide), Rhodojaponin-III (Botanical insecticide), Zinc naphthenate (Fungicide, Mammal repellent), Chlorphonium chloride (Plant growth regulator, Growth inhibitor), Flurprimidol (Plant growth regulator, Growth retardant), Gibberellic acid (Plant growth regulator, Gibberellin), Trifop (Aryloxyphenoxypropionic herbicide) in negative mode.

Figure 6. Data processing flowchart for suspect screening.

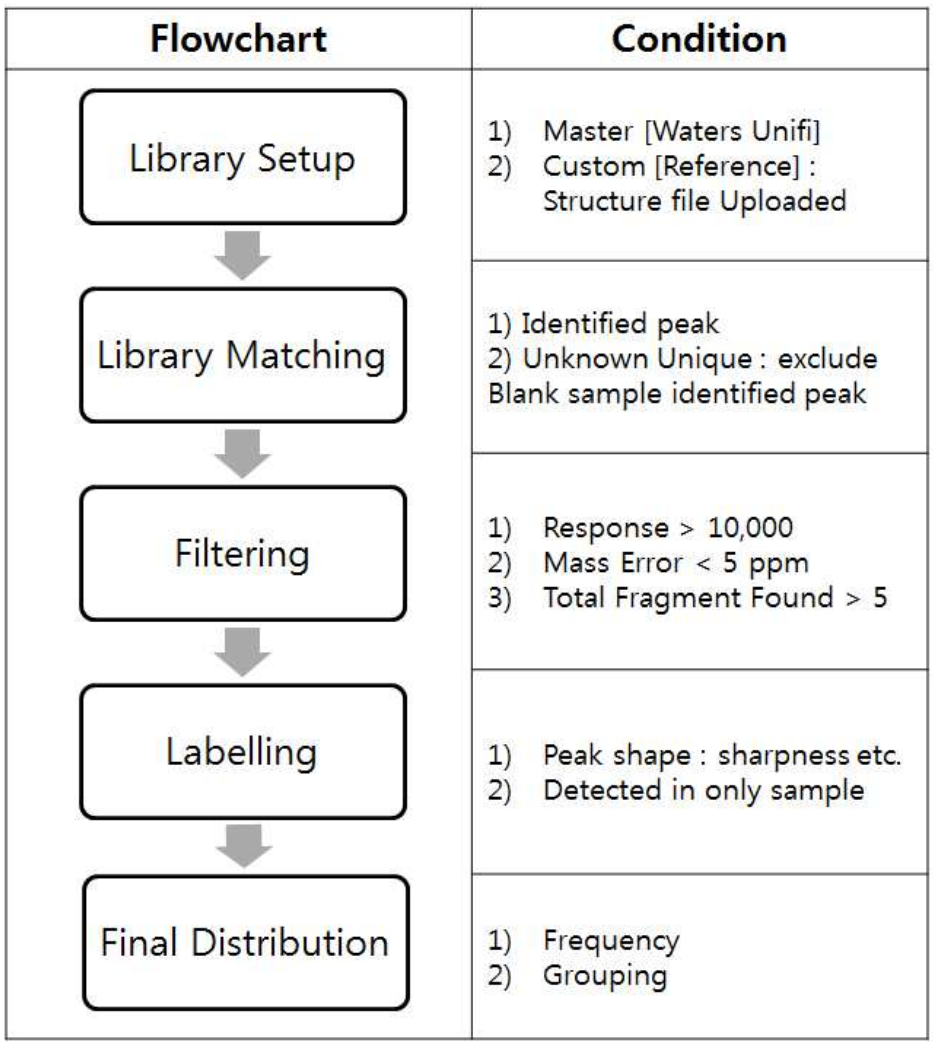


Table 4-1. Identified compound list in negative mode of GAC(N=15) extracted with acetonitrile.

Group	Compound	Identified (%)
Plant growth regulator	Heptopargil	100
Insect attractant	Hexalure	100
Insect attractant	Muscalure	100
Insect attractant	Ostramone	100
Herbicide	Pelargonic acid	100
Insect attractant	Trunc-call	100
Rodenticide	Curcumenol	75
Acaricide	Acequinocyl	58
Dinitrophenol herbicide	Dinoseb	50
Plant growth regulator, Auxin	Sodium naphthenate	50
Benzamide fungicide	Tioxymid	50
Synthetic corticosteroid	Triamcinolone	42
Plant growth regulator	Abscisic acid	33
Triazinone herbicide	Ethiozin	33
Synergist	Propyl isome	33

Table 4-2. Identified compound list in negative mode of GAC(N=15) extracted with acetonitrile.

Group	Compound	Identified (%)
Entheogen	2-Hydroxyibuprofen	25
Triazinone herbicide	Ametridione	25
Formamidine acaricide	Chloromebuform	25
Quaternary ammonium herbicide	Cyperquat	25
Insecticide	Methoprene	25
Pyrethroid ether insecticide	Silafluofen	25
\Pyrethroid ester insecticide	Bioallethrin	17
Insect repellent	Butopyronoxyl	17
Plant growth regulator	Ethephon	17
Herbicide	Glufosinate	17
Insect attractant	Ipsenol	17
Pyrethroid ester insecticide	Japothrins	17
Botanical insecticide	Matrine	17
Insect attractant	Methyl eugenol	17
Avermectin acaricide	Selamectin	17
Pyrethroid ester insecticide	Terallethrin	17

Table 5. Identified compound list in positive mode of GAC(N=6) extracted with methanol.

Group	Component	Detected
Antibiotic(veterinary)	Danofloxacin	3/6
Antifungal drugs (antipruritic)	Crotamiton	2/6
Fungicide	Ferimzone	6/6
	Propiconazole	6/6
Insect repellent	Diethyltoluamide	6/6
Insecticid	Profluthrin	5/6
Pesticide	Ametoctradin	1/6
	Heptopargil	5/6
	Metalaxyl-M	6/6
	Primetaphos	5/6
	Rebemide	5/6
	Zengxiaoan	6/6
Metabolite of Pesticide	Spiromesifen-Metabolite-M01	2/6
EDC	Bisphenol-A	4/6
Hormone	17α-Ethinylestradiol	2/6
	19-Norethindrone	2/6
	19-Nortestosterone	3/6
	Dehydroepiandrosterone	2/6
	Estriol	2/6
	Trenbolone	4/6
PPCP	Ketamin (q)	2/6
	Pyridostigmine	6/6
	Fadrozole	1/6
	Tilidine	5/6
Plasticizer	Dibutyl adipate	3/6

Table 6. Identified compound list in negative mode of GAC(N=6) extracted with methanol.

Group	Component	Detected
Disinfection Byproduct	Monobromoacetic acid	6/6
Herbicide	Pelargonic acid	4/6
	17β-estradiol (E2)	1/6
	α-multistriatin	5/6
Insect repellent	Dimethyl carbate	6/6
Insecticid	Terallethrin	1/6
Pesticide	Japothrins	6/6
	Oxpoconazole fumarate	1/6
	Piperonyl cyclonene	1/6
	Thifluzamide	3/6
Plant growth retardant	Uniconazole	2/6
PPC	Eugenol	2/6
	Ibuprofen	4/6
	Lincomycin	3/6
	Naproxen	6/6
	Natamycin	2/6
	Nisoldipine	5/6

Table 7. Identified compound list in positive mode of GAC (N=27) extracted with dichloromethane.

Group	Component	Freq(%)
Pesticide	Dipropetryne	100
Sex hormone	Estradiol	100
Insect attractant, Coleopteran attractant	Ipsdienol	100
Herbicide	Prosulfalin	96
Fungicide	Orysastrobin	85
Benzodiazepine, Hypnotic, Sedative	Temazepam	74
Insect repellent	Dibutyl phthalate	67
flame retardants, pesticides, plasticizers	tris(1-chloro-2-propyl) phosphate	56
antiviral drug	Valaciclovir	44
Fungicide	Metalaxyl-M	41
plasticizer	2-Ethylhexyl-diphenyl-phosphate	33
Herbicide	Prosulfalin	33
Morpholine fungicide	Tridemorph	33
plasticizer	DEHP	26
Chloroacetanilide herbicide	S-metolachlor	19
Insect repellent, Synergist	Zengxiaoan	4

Table 8. Identified compound list in negative mode of GAC (N=27) extracted with dichloromethane.

Group	Component	Freq(%)
Acaricide, Insecticide	sophamide	100
Plant growth regulator	epocholeone	96
Phenoxypropionic herbicide	mecoprop-P-isobutyl	96
Plant growth regulator, Growth inhibitor	prohydrojasmon	85
Botanical insecticide	cinerin I	78
Pesticide, Fungicide	penthiopyrad	78
Plant growth regulator	bachmedesh	74
Herbicide, Nitrile herbicide	pyraclonil	70
Fungicide, Imidazole fungicide	fenapanil	67
Phenoxybutyric herbicide	MCPB	67
Acylamino acid fungicide	valifenalate	67
Cyclohexene oxime herbicide	butroxydim	63
Insecticide, Juvenile hormone	juvenile hormone I	63
Pyrethroid ester insecticide	chlorempenthrin	59
Acaricide	acequinocyl	52
Insecticide	paichongding	41
Synergist	sesamex	37
Synthetic corticosteroid	Triamcinolone	26
Organothiophosphate nematicide	isamidofos	22
Chloroacetanilide herbicide	diethatyl-ethyl	15
Phenoxyacetic herbicide	MCPA-ethyl	15
Diuretic, Vasopressin receptor antagonist	Tolvaptan	15
Antihypertensive, Diuretic, Thiazide	Bendroflumethiazide	11
plasticizer	Di(2-ethylhexyl)adipate	11
Insecticide	malonoben	11
Plant growth regulator, Growth inhibitor	chlorphonium	4
Antibiotic fungicide, Bactericide	kasugamycin	4
Synergist	piprotal	4

Table 9. Identified compound list in positive mode of Tap water sample (N=19) by solid phase extraction.

Group	Component	Freq(%)
Methoxyacrylate strobilurin acaricide	fluacrypyrim	74
Halogenated aliphatic herbicide	TCA-ethadyl	42
Organophosphate insecticide	propaphos	37
Methoxyiminoacetamide strobilurin fungicide	orysastrobin	32
Pyrethroid ester insecticide	terallethrin	21
Chloroacetanilide herbicide	terbuchlor	16
Pyrethroid ester insecticide	cyclethrin	16
Plant growth regulator, Growth inhibitor	chlorphonium chloride	11
Insecticide	triazamate	11
Insecticide	allosamidin	11
Herbicide	bicyclopyrone	11

Table 10. Identified compound list in negative mode of Tap water sample (N=19) extracted with methanol.

Group	Component	Freq(%)
Fungicide	piperalin	58
Chloroacetanilide herbicide	terbuchlor	53
Morpholine fungicide	flumorph	16
Analgesic, Anti-inflammatory, NSAID	Fenoprofen	5
Cyclodiene insecticide	Heptadecafluorooctane sulfonic acid	5
Pesticide, Insecticide	Aspon	5
Fungicide	Pencycuron	5
Pyrimidinylsulfonylurea herbicide	methiopyrisulfuron	5
Botanical insecticide	rhodojaponin-III	5
Fungicide, Mammal repellent	zinc naphthenate	5
Plant growth regulator, Growth inhibitor	chlorphonium chloride	5
Plant growth regulator, Growth retardant	flurprimidol	5
Plant growth regulator, Gibberellin	gibberellic acid	5
Aryloxyphenoxypropionic herbicide	trifop	5

IV. Discussion

Suspect screening has the ability to prioritize less well-known compounds, not yet included in target monitoring and provides a relatively fast approach to screen non-target data complementary to target screening(Sjerps et al., 2016). In this study, we tentatively identified various component group such as PPCPs(cabamazephine, iopromide and so on), pesticide (alachlor, simazine-2-hydroxy and so on), endocrine disrupting compound (bisphenol-a, 17a-estradiol, DEHP and so on).

Non-targented analysis (NTA) of unmatched features should be done since suspect list of library is not complete. It would be done for some peaks of high response for some samples detected in future study. This increase candidate list that would have most likely resulted in a higher percentage of features being assigned formulas.

Furthermore, additional ionization sources, such APCI or APPI, could be used to ionize compounds that were not detected under ESI conditions. Future studies should also consider including a gas chromatography (GC) component to explore a larger chemical space.

Another limitation, as with most suspect and non-target screening, is the inability to estimate concentration. Future studies should explore ways of estimating instrument responses for compounds without the use of standards. Future studies

should also focus on quantitative target screening including exposure level for risk assessment(Newton et al., 2018).

The use of an granular activated filter to capture contaminants from drinking water likely biased the experimental design towards compounds with sufficiently large Kow values to interact with the filter. It is possible that some compounds which may be of relevance to human health, probably very polar compounds, passed through the filter without capture and, thus, were not retained in the samples. The instrumental analysis could have been expanded in several ways to increase the percent of total features identified. Desorption condition needed to be studied for future study since distribution tentatively identified contaminat list has a different pattern following several kinds of extraction organic solvents even though under the same instrumental analysis condition.

Results from this suspect screening analysis were likely affected by methodological procedures related to the extraction, cleanup, LC-QTOF analysis, and data filtering steps. Indeed, some chemicals commonly found in drinking water were not identified here. For example, Diclofenac is commonly found in drinking water samples, was among the list of chemicals used for suspect screening, and yet were not identified in the study samples. It is possible that Diclofenac was not present in the study samples. However, it is also possible that Diclofenac was simply not detectable given the method parameters. Future studies will explore aspects of the method that may be optimized for different classes of chemicals, and across a broad concentration range(Rager et al., 2016).

In this study, various components were identified in Tap water samples and GAC water purifier filters by suspect screening. Most of contaminants candidates list is composed of pesticide and pharmaceuticals since the reference analysis condition is for the pesticide screening methods(Hernández et al., 2015). According to analysis mode (positive and negative) and extraction solvents (methanol, acetonitrile) and sample type (tap water, GAC filter), components list which is ordered by frequency level has different composition. They are classified in several groups of master library served by software UNIFI Waters Scientific Information System (Waters Corp., Milford, USA).

In tap water samples, identified components were pesticeds such as acaricide (fluacrypyrim), herbicide (TCA-ethadyl, Terbuchlor, Bicyclopyrone, Methiopyrisulfuron, Trifop), insecticide (Propaphos, Terallethrin, Cyclethrin, Triazamate, Allosamidin, Aspon, Rhodojaponin-III, Heptadecafluorooctanesulfonic acid), fungicide (Orysastrobin, Piperalin, Flumorph, Pencycuron, Zinc Naphthenate), plant growth regulator (Chlorphonium, Chlorphonium Chloride, Flurprimidol, Gibberellic acid), analgesic (Fenoprofen). The most frequently detected component is Fluacrypyrim(74 %). It is distinguied with Methoxyacrylate strobilurin acaricide and detected as pesticide-residue in food stuffs(Amadeo et al., 2008). Monitoring value detected in surface or drinking water samples are hardly reported in reference recently.

In GAC filter samples extracted by dichloromethane, The most frequently detected components were Dipropetryne (Pesticide), Estradiol (Sex hormone), Ipsdienol (Insect attractant, Coleopteran

attractant), Sophamide (Acaricide, Insecticide). Futhermore, tris(1-chloro-2-isopropyl) phosphate(56%) and 2-Ethylhexyl-diphenyl-phosphate(38%) were identified in GAC samples. Park et al.(2018) reported organophosphae flame retardants (OPFRs) in Korea. 9 OPFRs were monitored in 44 tap water samples. The predominant compounds in tap water were tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-isopropyl) phosphate (TCIPP), and tris(2-butoxyethyl) phosphate (TBOEP) and 2-Ethylhexyl-diphenyl-phosphate was not monitored in this reference. By the way, tris(1-chloro-2-isopropyl) phosphatewere detectedin all tap water samples. Lee et al. (2016) also reported organophosphae flame retardants (OPFRs) in Korea. 10 OPFRs were monitored in tap water (n = 75), purified water (n = 42), and bottled water (n = 10). The predominant OPFR compounds in drinking water were tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroethyl) phosphate (TCPP), and tris(2-butoxyethyl) phosphate (TBEP) and tris(1-chloro-2-isopropyl) phosphate (TCIPP) was not monitored in this reference. 2-Ethylhexyl-diphenyl-phosphate were detected in drinking water samples (5.5 %). The frequency gap between Tap sample and GAC sample is caused by detection limit or instrumental condition. In this study, we use LC-QTOF-MS but reference study used GC-MS. According to the characteristics of components, optimum instrumental approach has to be met detection frequency and concentration level. That is why universial screening by suspect screening has to be done not for monitoring tool but for contaminants candidate identification.

Nowadays, we are at an early step in studying the identification

of suspect screening, as instrumentation and software are still in progress and are getting more complete and easier to use. Specific, step-wise, automated workflows that take into consideration the advantages of HR-MS instruments are still missing for suspect and non-target analysis. Exclusion parameters and sufficient filtering are necessary for the prioritization of peaks and elimination of false-positive and false-negative results. Non-target screening should be an extra step for elucidating the rest of the unknown peaks, evaluating not only the most intense, but ideally the most relevant, also according to toxicity. Therefore, new computational tools for toxicity prediction or coupling with high-throughput toxicity tests would be preferable(Bletsou et al., 2015).

V. Conclusion

Suspect screening methods using LC-QTOF MS were performed to investigate a variety of micropollutants present in drinking water by desorption technology of Granular activated carbon water purifier filters. The analysis method developed in this study has been shown to be a powerful tool for universal screening and identification of presence of micropollutants in drinking water.

Target screening is done to analysis perfluoroalkyl compounds (PFCs) for desorption extracts of spent granular activated carbon filter installed in water purifier. The GAC extracted sample with methanol was screened for the 8 target PFCs using known retention times, accurate masses and fragment ions. All target compounds were detected and confirmed with reference standard. 6 out of 8 PFCs components were detected in all GAC samples, which is Heptadecafluorooctane sulfonic acid(Perfluorooctane sulfonic acid), Perfluorodecanoic acid(Perfluorocapric acid), Perfluoroheptanoic acid, Perfluorohexanoic acid, Perfluorononanoic acid, Perfluorooctanesulfonic acid, Perfluorooctanoic acid, Perfluoropentanoic acid, Perfluorohexane sulfonic acid.

Suspect screening is applied to analysis tap water samples and desorption extracts of spent granular activated carbon filter installed in water purifier. Its utility in this study is illustrated in our identification of several compounds that would not otherwise

be monitored in drinking water. The need for a more comprehensive suspect screening approach is highlighted by the large number of features present in the samples, and the limited number of which that were confirmed or tentatively identified. We have demonstrated candidate contaminants list that prioritized frequency ranking by response data for which standards were not available on hand.

This study indicates that granular activated carbon used in water filtration systems likely remove micropollutants having a wide range of physicochemical properties. As a result, this study could detect some micropolutants which is hardly detected in tap water present in trace level by direct analysis. Also, this study could overcomes drinking water sampling limitation and enables time-lapse monitoring for contaminants having concentration fluctuation.

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국문초록

먹는 물 처리에 사용된 입상 활성탄 필터의 신규 오염물질 표적 스크리닝

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먹는 물이 다양한 유기 화합물로 광범위하게 오염되고 있다. 최근 고분해능 질량분석기를 이용하여 환경 시료 중에 존재하는 신규 오염물질과 변종 물질을 조사하는 시도가 증가하고 있다. 신종 오염물질에 대한 종합적인 스크리닝 분석법은 다양한 미량 오염물질의 존재와 농도에 대한 제한점을 극복할 수 있게 해준다. 고분해능 질량분석기를 이용한 목적, 표적, 비표적 성분에 대한 스크리닝은 미량 수준으로 존재하는 예측할 수 없는 미지 물질을 확인하기 위해 계속해서 개발 및 최적화되고 있다.

본 연구에서 국내 정수기에 설치된 입상 활성탄 필터에 대하여 표적 스크리닝 방법을 적용하였다. 전국에서 수거된 만기 사용 필터와 함께 사용하지 않은 새 필터도 바탕시료로 분석하였다.

첫 단계로, 메탄올로 추출한 GAC 필터에 대해 목적물질인 9종의 과불화

합물에 대한 스크리닝 분석을 수행하였고, 원물질과 조각이온의 고분해능 질량정보를 방대하게 구축된 라이브러리와의 통계 분석을 통해 확인하고, 표준물질을 분석하여 머무름 시간을 통해 확증하였다. 9종의 과불화합물질 중 6개 물질이 모든 필터에서 검출되었고, 검출된 물질은 Heptadecafluorooctane sulfonic acid(Perfluorooctane sulfonic acid), Perfluorodecanoic acid(Perfluorocapric acid), Perfluoroheptanoic acid, Perfluorohexanoic acid, Perfluorononanoic acid, Perfluorooctanesulfonic acid, Perfluorooctanoic acid, Perfluoropentanoic acid, Perfluorohexane sulfonic acid 였다.

다음 단계로, 고분해능 질량분석기 full scan mode에서 측정된 Accurate mass로 표준물질을 이용한 추가적인 분석 없이 후행적으로 표적 스크리닝을 수행하였다. 입상 활성탄 탈착 시료를 이용하여, 잠정적인 오염물질이 확인되었다. 감도, 질량오차, 발견된 조각이온의 수 드의 데이터 필터 조건을 설정하고 하나씩 피크의 모양을 확인하면서 의미있는 피크를 가진 물질만 추출하여 최종 후보 물질 목록을 작성하였다.

1차로 14개 필터에 대하여, 추출 용매를 Acetonitrile로 하였을 때, 음이온 모드에서는, plant growth regulator (Heptopargil)를 포함한 15개 물질이 선정되었다. 1차 수집 필터에서 과불화합물이 검출된 6개 필터에 대하여 추출 용매를 Methaol로 하였을 때, 양이온 모드에서, veterinary antibiotic (Danofloxacin)를 포함한 25개 물질이 선정되었고, 음이온 모드에서는, disinfection byproduct (Monobromoacetic acid)를 포함한 17개 물질이 선정되었다. 마지막으로, 27개 필터를 추가적으로 수집하여, 추출 용매를 Dichloromethane 으로 하였을 때, 양이온 모드에서, pesticide (Dipropetryne), hormone (Estradiol)를 포함한 16개 물질이 선정되었고, 음이온 모드에서는, insecticide(Sophamide)를 포함한 28개 물질이 선정되었다.

다음으로 19개 수돗물을 수집하여, 고상추출법으로 분석하였을 때, 양이

온 모드에서, acaricide(fluacrypyrim)를 포함한 11개 물질이 선정되었고, 음이온 모드에서는, fungicide(piperalin)를 포함한 14개 물질이 선정되었다.

본 연구에서, 고분해능 질량분석기를 사용한 표적 스크리닝 기법은 먹는 물에 존재하는 미량 오염물질의 존재를 확인하는 범용적이고 강력한 도구임을 보였다. 이에 대한 가장 중요한 활용성은 입상 활성탄 탈착 시료에서 확인된 물질 중 대부분이 먹는 물에서 일반적으로 모니터링 되지 않는 새로운 물질이라는 점이다. 향후 시료에 존재하는 더 다양한 물질을 확인할 수 있는 보다 종합적인 스크리닝 분석조건 및 탈착 기법에 대한 심층적인 연구가 필요하다. 표준물질을 보유하지 않은 상태에서 제한적으로 질량 정확도, 감도와 검출된 피크이 모양과 검출 빈도에 따라서 잠정적인 우선순위 목록을 작성하였다.

이 결과들은 먹는 물 처리에 사용된 입상활성탄 필터가 미량오염물질을 효율적으로 제거하며, 추출된 시료를 활용하여 먹는 물에 미량으로 존재하는 오염물질을 분석할 수 있다는 것을 의미한다. 이 작업을 통해 최종 공급 단계에서의 농도 변화가 심한 제한점을 극복하는 미량 오염물질에 대한 장기 누적형 오염 물질 모니터링 기법이 될 것이다.

주요어 : 먹는 물, 미량오염물질, 입상 활성탄, 필터, 탈착, 표적 스크리닝, UPLC-QTOF

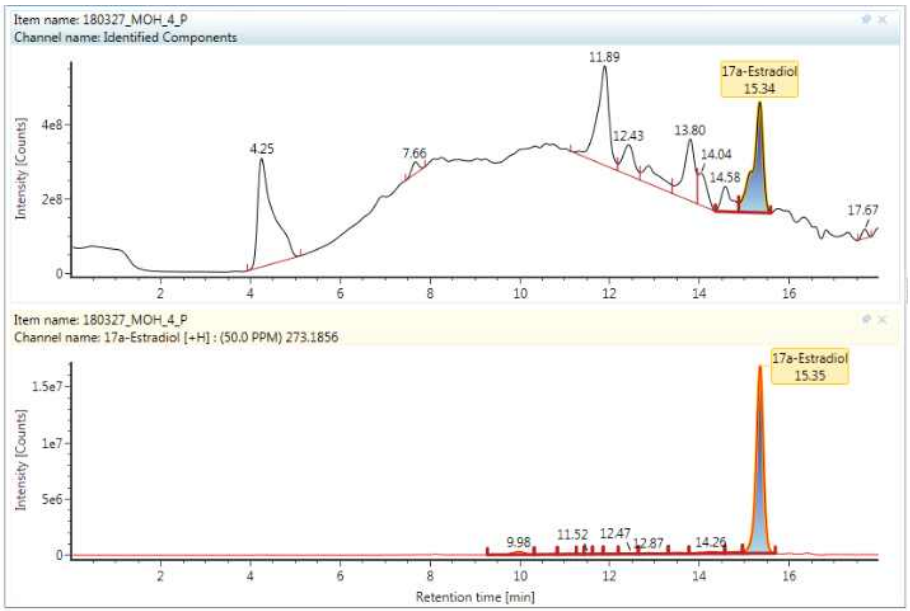
학번 : 2014-23401

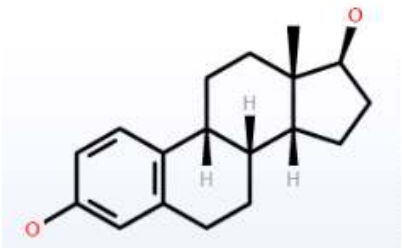
VI. Supplementary Information

Suspect screening of emerging contaminants in granular activated carbon filter used for drinking water treatment

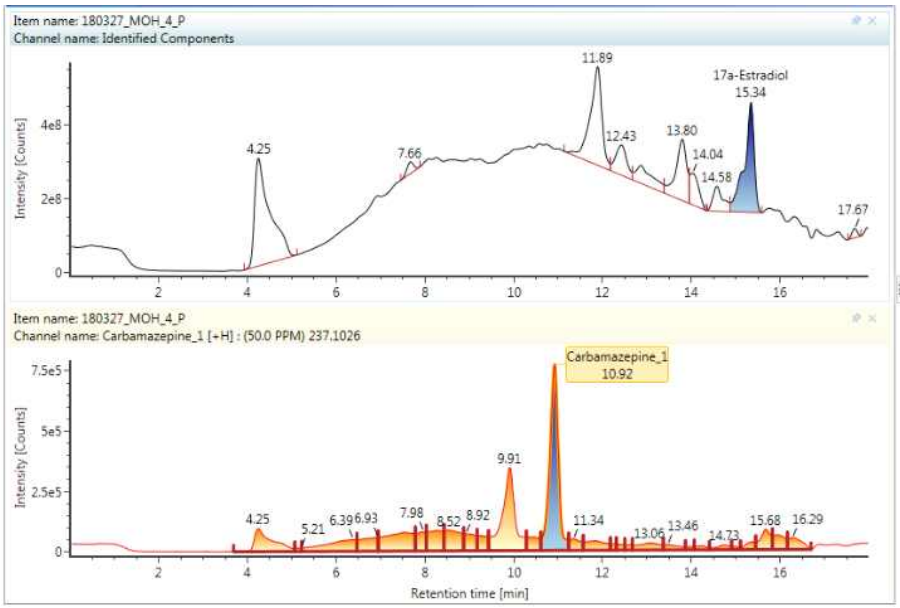
Table S1. Identified compound chromatogram

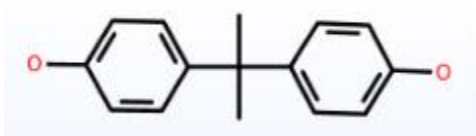
1) 17a-Estradiol



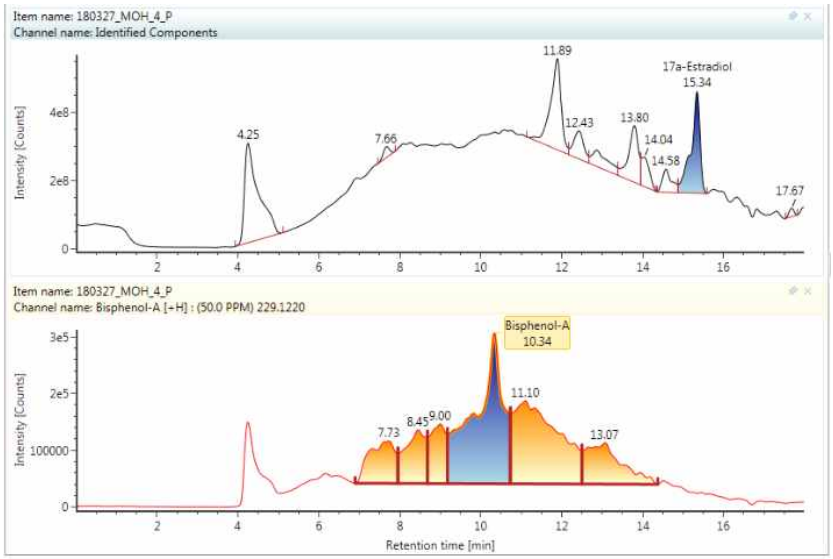


2) Bisphenol-a

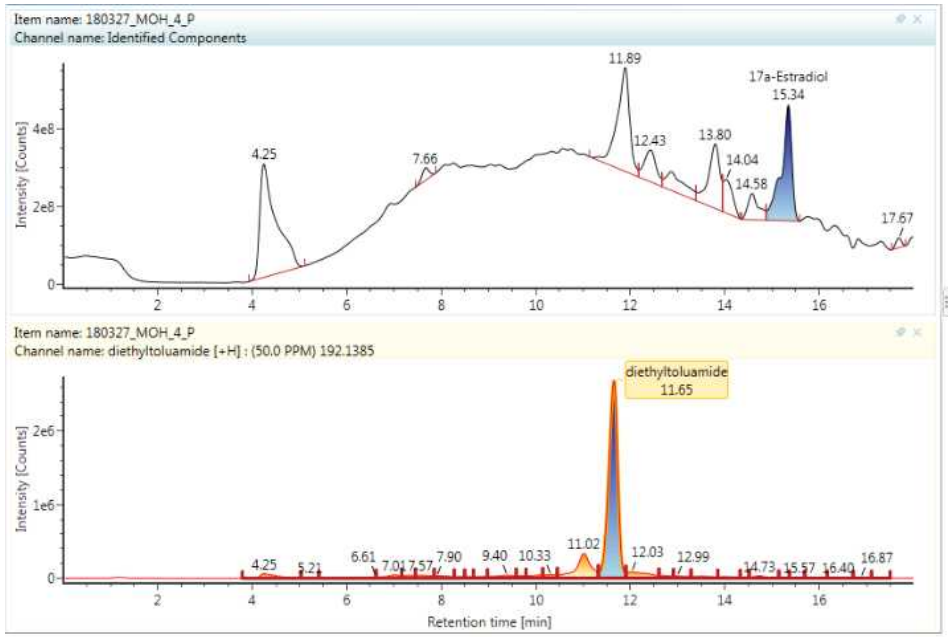


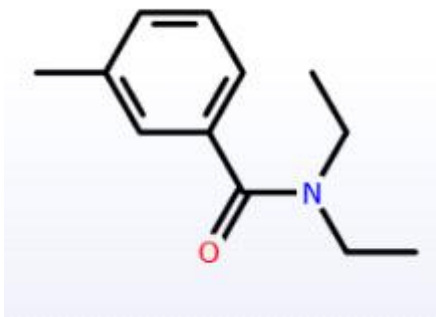


3) Carbamazepine

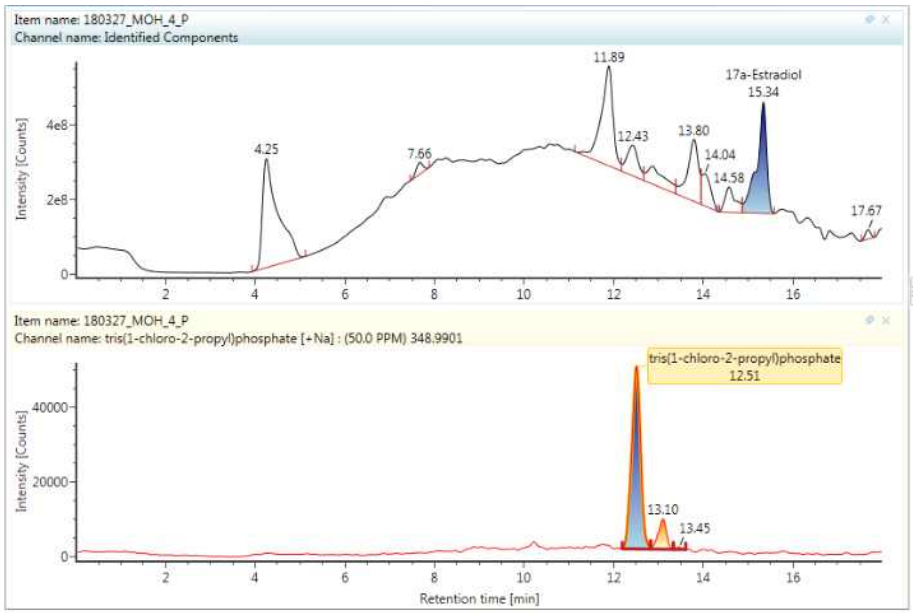


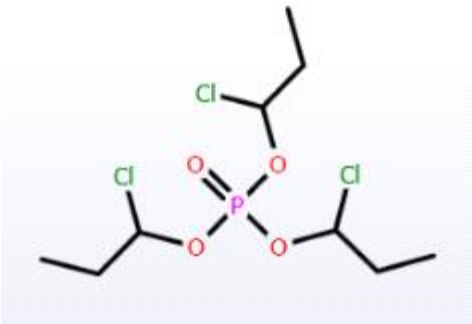
4) diethyltoluamide



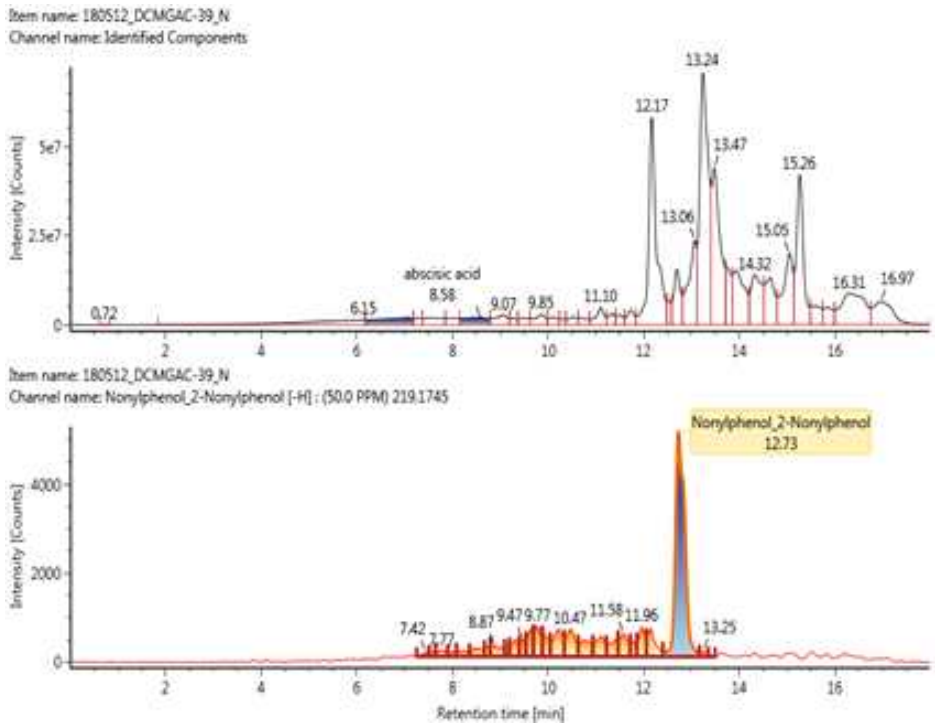


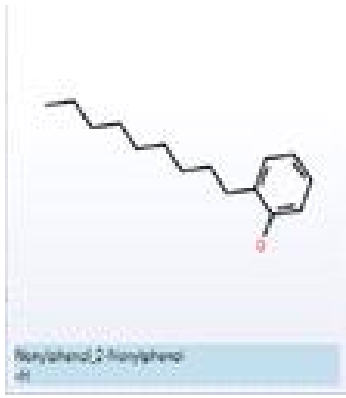
5) tris(1-chloro-2-propyl)phosphate



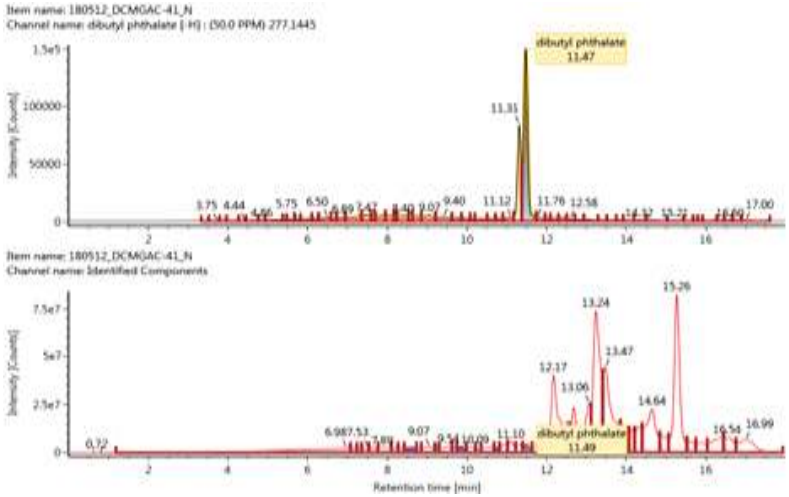


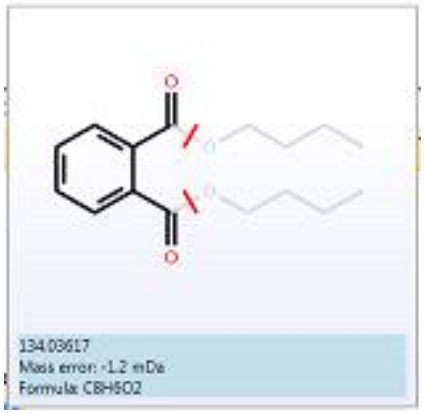
6) 2-Nonylphenol



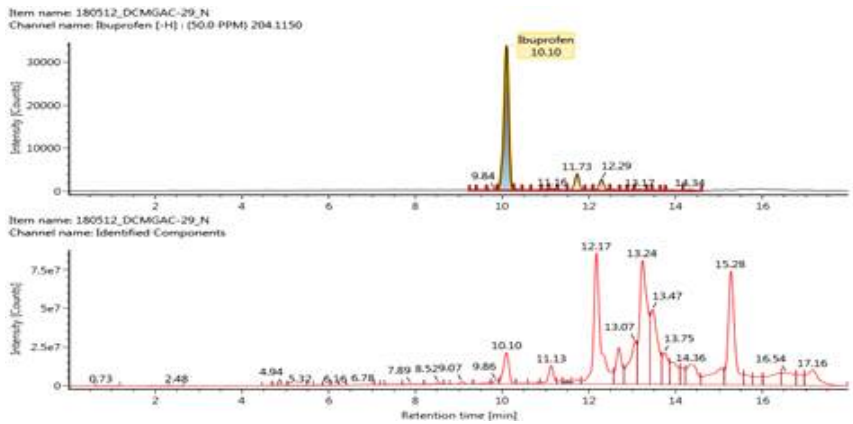


7) Dibutyl phthalate

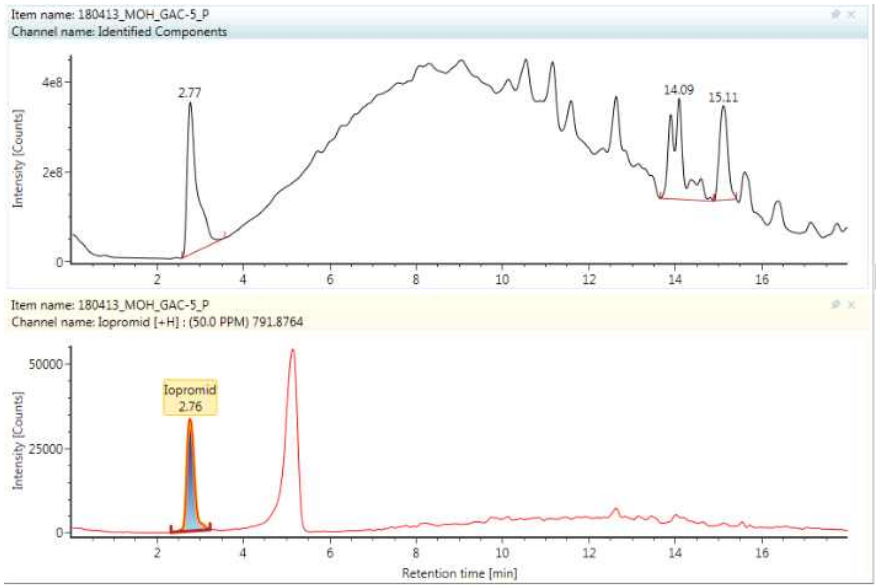


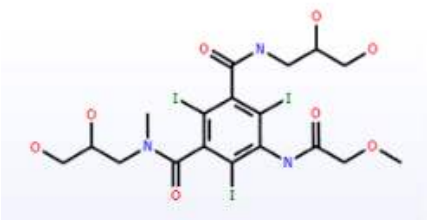


8) Ibuprofen


Item name: 180512_DCMGAC-29_N
Channel name: Ibuprofen (-H) : (50.0 PPM) 204.1150
Ibuprofen
10.10
Intensity [Counts]
30000
20000
10000
0
9.84
11.73
12.29
2
4
6
8
10
12
14
16
Item name: 180512_DCMGAC-29_N
Channel name: Identified Components
Intensity [Counts]
7.5e7
5e7
2.5e7
0
12.17
13.24
15.28
13.47
13.07
13.75
10.10
11.13
14.36
16.54
17.16
0.73
2.48
4.94
5.32
6.16
6.78
7.89
8.52
9.07
9.86
Retention time [min]

9) Iopromide


Item name: 180413_MOH_GAC-5_P
Channel name: Identified Components
Intensity [Counts]
4e8
2e8
0
2.77
14.09
15.11
2
4
6
8
10
12
14
16
Item name: 180413_MOH_GAC-5_P
Channel name: Iopromid [+H] : (50.0 PPM) 791.8764
Intensity [Counts]
50000
25000
0
Iopromid
2.76
Retention time [min]



10) DEHA(Di(2-ethylhexyl)adipate)