



Optimization of suspect and non-target analytical methods using GC/TOF for prioritization of emerging contaminants in the Arctic environment

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ABSTRACT

Numerous chemicals have been manufactured through industrial activities and used as consumer products since the late 18th century. Non-target analysis is a new analytical tool to detect many chemicals in environmental samples and to prioritize emerging contaminants. In this study, suspect and non-target analytical methods were optimized using gas chromatography coupled with time-of-flight (GC/TOF) to propose contaminants of emerging concern for the Arctic environment. A suspect analytical method was developed with qualification and qualifier ions, isotopic ratios, and retention times of 215 contaminants including persistent organic pollutants (POPs) to establish an in-house library. Non-target analytical method was also optimized with a deconvoluted ion chromatogram, which is a form that can possibly match the mass spectrum of the NIST library. Multiple environmental samples, such as seawater, air, soil, sediment, sludge, and iceberg, collected from the Arctic region were analyzed with suspect and non-target analysis of GC/TOF after the clean-up procedure with a solid phase extraction (SPE) cartridge. The commonly detected contaminants in the Arctic environmental samples were siloxanes, organophosphate flame retardants, phthalates, synthetic musk compounds, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. Among them, siloxanes and organophosphate flame retardants were proposed to be contaminants of emerging concerns for the Arctic environment. This is the first report to prioritize emerging contaminants in the Arctic environment with suspect and non-target analysis of GC/TOF.

1. Introduction

Numerous chemicals have been manufactured through industrial activities and used as consumer products since the late 18th century. Presently, the Chemical Abstracts Service (CAS) has registered over 145 million chemicals in their database system (CAS, 2019). Although many studies have reported on the relationships between chemical exposure and ecotoxicological effects, only a few chemicals have been regulated by international and domestic authorities. It is essential to establish

legislative actions and regular monitoring programs for chemicals with risks posed to the environment as well as humans. Prioritization is the first step for the monitoring and/or regulation of existing chemicals in the environment. The purpose of prioritization is to designate certain chemicals as either high-priority or low-priority for further risk evaluation. However, a targeted analytical method is insufficient for the prioritization of environmental contaminants, because it misses non-targeted compounds in environmental samples during the experimental procedure and instrument analysis. In addition, the measured

Abbreviations: CAS, Chemical Abstract Service; GC, gas chromatography; LC, liquid chromatography; MS, mass spectrometry; HRMS, high resolution mass spectrometry; TOF, time-of-flight; AMAP, Arctic Monitoring and Assessment Program; POPs, persistent organic pollutants; Hg, mercury; DCM, dichloromethane; GPC, gel permeation chromatography; GF/F, glass fiber filter; WWTP, wastewater treatment plant; SPE, solid phase extraction; EI, electron ionization; m/z, mass-to-charge; PFTBA, perfluorotributylamine; IRM, internal reference mass; NIST, National Institute of Standards and Technology; PCDD/Fs, polychlorinated dibenzo-p-dioxins and furans; DL-PCBs, dioxin-like polychlorinated biphenyls; OCPs, organochlorine pesticides; PBDEs, polybrominated diphenyl ethers; PCNs, polychlorinated naphthalenes; CLBs, chlorobenzenes; PAHs, polycyclic aromatic hydrocarbons; DP, dechlorane plus; NBFRs, novel brominated flame retardants; OPFRs, organophosphate flame retardants; SMCs, synthetic musk compounds; BUVs, benzotriazole ultraviolet stabilizers; TIC, total ion chromatogram; log K_{ow} , logarithm octanol-water partitioning coefficients; DIC, deconvoluted ion chromatogram; D5, decamethylcyclopentasiloxane; D6, dodecamethylcyclohexasiloxane; L4, decamethyltetrasiloxane; L5, dodecamethylpentasiloxane; L6, tetradecamethylhexasiloxane; LRAT, long-range atmospheric transport; RTI, retention time index

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concentrations of target contaminants are not sufficient enough to account for their whole toxicity in environmental samples (Hong et al., 2016; Simon et al., 2013; Yue et al., 2015).

Accurate measurement of contaminants in environmental samples is a difficult task, because the environmental sample matrix, such as air, water, soil, and sediment, is complex. Despite this, targeted analytical methods have been successfully developed for several decades, and provide good sensitivity as well as reliable identification and quantification of contaminants that exist at trace levels. To date, many scientific approaches have been developed and upgraded for monitoring organic contaminants in the environment using gas chromatography (GC) and liquid chromatography (LC) based on mass spectrometry (MS) (Hernández et al., 2015; Park et al., 2018). Recent advances in analytical instrumentation have resulted in the evolution of high-resolution MS (HRMS) coupled with GC or LC to accurately measure the mass of target contaminants (Zhang et al., 2014). Non-target analysis is a new analytical tool to detect all of the existing chemicals in environmental samples (Hernández et al., 2015). Time-of-flight (TOF)/MS was recently introduced for non-target analysis, which enables the measurement of the entire mass spectrum of chemicals with a greater sensitivity than standard quadrupole MS (Moschet et al., 2018; Zhang et al., 2014). In addition, TOF/MS has been applied for prioritization of contaminants with analytical data processing from environmental samples for a specific site (Guyader et al., 2019).

The Arctic is far away from contamination sources such as industrial and agricultural activities. The Arctic Monitoring and Assessment Program (AMAP) has designated persistent organic pollutants (POPs) and mercury (Hg) as priority pollutants that disturb the Arctic ecosystems (AMAP, 2016). POPs and Hg contamination in the Arctic environment mostly originates from long-range transport through the atmosphere and ocean from low latitudes (Wania, 2003; Gouin et al., 2004). Considering the large amount of production and consumption of a variety of chemicals, emerging contaminants could be an important threat to the Arctic ecosystem. The presence of certain chemicals in the Arctic, where there is no local source, implies evidence of ubiquitous chemicals on a global scale. In the present study, suspect and non-target analytical methods were optimized with GC/TOF to identify the wide ranges of chemicals that existed in multiple environmental samples from the Arctic region. This is the first study to report a scientific-based procedure to prioritize emerging contaminants in the Arctic environment based on suspect and non-target analysis of GC/TOF.

2. Materials and methods

2.1. Standards and reagents

All of the standards were obtained from Accustandard (New Haven, CT, USA), Dr. Ehrenstorfer GmbH (Augsburg, Germany), Sigma-Aldrich (St. Louis, MO, USA), Tokyo Chemical Industries America (Portland, OR, USA), Wako Pure Chemicals (Tokyo, Japan), and Wellington Laboratories (Guelph, ON, Canada). Ultra-residue analysis grade hexane and dichloromethane (DCM) were obtained from J.T. Baker (Phillipsburg, NJ, USA). Bio-beads S-X3 for gel permeation chromatography (GPC) were purchased from Bio-Rad Laboratories (Hercules, CA, USA). Sep-Pak Vac C₁₈ (500 mg/6 cc), silica gel (1 g/6 cc), florisil (500 mg/6 cc), and Oasis HLB (150 mg/6 cc) cartridges were purchased from Waters (Milford, MA, USA). Nonane (reagent plus grade, 99%) and granular copper (ACS reagent, 10–40 mesh, ≥ 99.9%) were obtained from Sigma-Aldrich.

2.2. Sample collection

Environmental samples, such as seawater, sediment, soil, sludge, and iceberg, were collected from Ny-Ålesund, Svalbard, during July 2016. Forty liters of surface seawater samples ($n = 4$) were collected in pre-cleaned PP bottles using a stainless steel basket. Water samples

were filtered using a glass fiber filter (GF/F, Whatman, 47 mm diameter, > 0.7 μm). The filtrate (dissolved phase) was used in a further pretreatment step. Surface sediment samples ($n = 4$) were collected using a Van-veen grab sampler from a research vessel, and soil samples ($n = 7$) were collected using a stainless steel spoon after washing. Sludge samples were taken directly from a wastewater treatment plant (WWTP) located at research stations in Kings Bay. Iceberg samples were also collected near the shoreline of Kings Bay. After washing the iceberg samples with distilled water, they were melted at room temperature and then treated as seawater samples. Particulate matter samples ($n = 3$) from ambient air were collected from the Zeppelin station in Ny-Ålesund, Svalbard, using a high volume air sampler (HV-RW, Sibata, Saitama, Japan) between April and September 2015. The detailed information on the sampling locations is summarized in Table S1 and Fig. S1. The collected samples were individually wrapped in pre-cleaned aluminum foil and then kept in a refrigerator. All of the samples were transported to the laboratory and kept in a freezer at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.3. Experimental procedures

Water samples including filtered seawater and melted iceberg were extracted using a solid phase extraction (SPE) cartridge, which was pre-washed with 50% DCM in hexane and conditioned with Milli-Q water (Moon et al., 2008; Hernández et al., 2015). The sediment ($\sim 10\text{ g}$), soil ($\sim 10\text{ g}$), filter paper of ambient air, and sludge ($\sim 1\text{ g}$) were extracted in a Soxhlet apparatus with 200 mL of 25% DCM in hexane for 16 h. Activated copper was added into the extracts to remove sulfur and then the extracts were concentrated to approximately 1 mL using a rotary evaporator. To select the clean-up method, the efficiency was tested and compared with different kinds of SPE sorbents, such as HLB (150 mg), C₁₈ (500 mg), silica gel (1 g), and florisil (500 mg), in the cartridges. After the clean-up procedure of extracts with the SPE cartridge, the eluents were concentrated to approximately 1 mL and then dried at room temperature. The residues were dissolved in 100 μL of nonane for instrumental analysis.

2.4. GC/TOF analysis and software for data processing

Gas chromatography (7890B; Agilent Technologies, Santa Clara, CA, USA) coupled with time-of-flight (7200; Agilent Technologies) (GC/TOF) was used for suspect and non-target analysis for multiple environmental samples. A nitrogen generator (NM321A; Peak Scientific, Billerica, MA, USA) was used to support the collision cell work. A DB-5MS (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) capillary column was used to separate the organic contaminants that existed in the samples. The oven temperature was programmed from 80 °C for 1 min and increased to 200 °C at 10 °C/min, and then finally ramped at 5 °C/min to 300 °C and held for 5 min. The carrier gas used was helium at a constant flow rate of 1 mL/min. The TOF/MS was operated under the positive electron ionization (EI) mode at 70 eV. The ranges of TOF/MS used in our study ranged from 35 to 1000 as mass-to-charge (m/z) at 100 mS/spectrum. The MS resolution was obtained as approximately 13,000 at m/z 131 and 17,000 at m/z 502 under a high resolution mode of 4 Ghz. MS-analysis grade per-fluorotributylamine (PFTBA) was used for mass calibration, which was conducted for every sample in order to obtain accurate mass in the samples. Helium was introduced into the ion source as an internal reference mass (IRM) correction during the TOF analysis. The temperatures of the transfer line and ionization source were maintained at 280 °C and 230 °C, respectively. A solvent delay of 4 min was used to prevent damage to the capillary column and filament of the ion source. MassHunter Quantitative Analysis B.07.04 and Unknown Analysis B.07.01 (Agilent Technologies) were used for analytical data processing. The National Institute of Standards and Technology (NIST) library (ver. 2014) was also used for identifying the unknown compounds

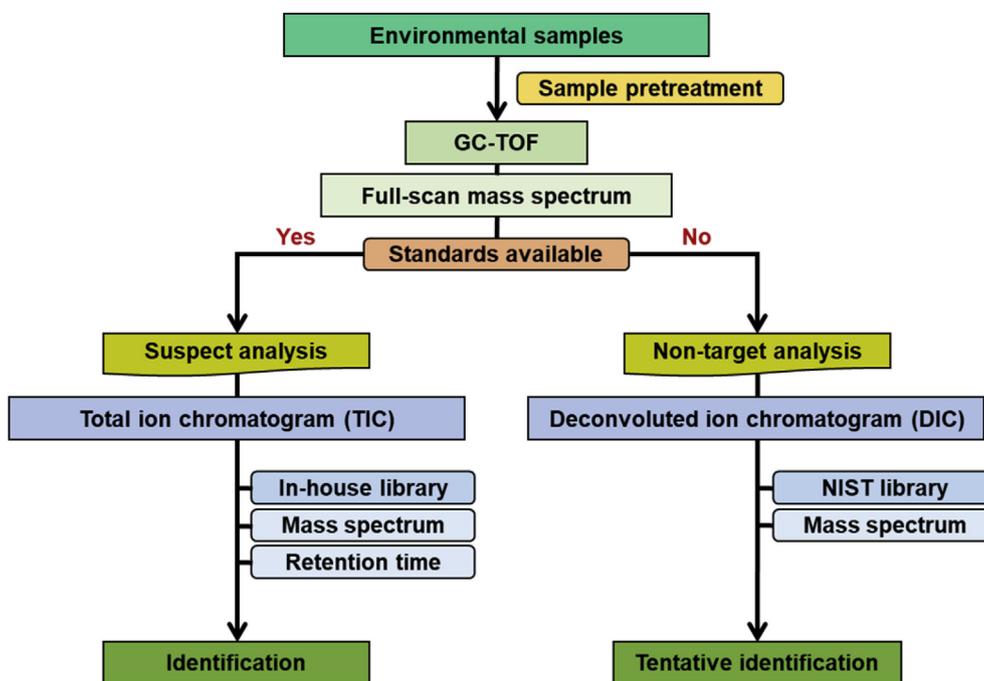


Fig. 1. Workflow of suspect and non-target screening analysis with a gas chromatography coupled to time-of-flight (GC/TOF) in multiple environmental samples.

detected in the samples.

3. Results and discussion

3.1. Establishment of an in-house library for suspect analysis

A total of 215 compounds were selected as target contaminants of the in-house library for suspect analysis using a GC/TOF. These contaminants were mostly comprised of POPs and pseudo-POPs reported for their occurrence in low latitude and/or Arctic environments (AMAP, 2016, 2017a; 2017b; Rigét et al., 2010). Some of the POPs included polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), dioxin-like polychlorinated biphenyls (DL-PCBs), non-dioxin-like PCBs, organochlorine pesticides (OCPs; e.g., DDTs, HCHs, and chlordanes), polybrominated diphenyl ethers (PBDEs), polychlorinated naphthalenes (PCNs), chlorobenzenes (CLBs), and polycyclic aromatic hydrocarbons (PAHs). Several pseudo-POPs, such as dechlorane plus (DP), novel brominated flame retardants (NBFRs), organophosphate flame retardants (OPFRs), phthalates, siloxanes, synthetic musk compounds (SMCs), and benzotriazole ultraviolet stabilizers (BUVSS) were included in the present study. The standard solutions of all of the contaminants used in our study were diluted at 100 ng/mL and then injected into a GC/TOF to obtain the total ion chromatogram (TIC) of individual contaminants. Detailed information on retention time, mass spectra, qualification ion, and qualifier ion from individual contaminants was used for the identification of the samples using the in-house library for suspect analysis (Table S2). Based on the physico-chemical properties of all of the contaminants established in the in-house library, the optimized analytical method in our study covered organic chemicals with the properties of molecular weight from 128 to 1500 and logarithm octanol-water partitioning coefficients ($\log K_{ow}$) from 0.81 to 12.0. This result indicated that most of the organic contaminants that existed in the environment could be detectable with the present analytical system by GC/TOF.

3.2. Selection of a clean-up procedure for GC/TOF analysis

Environmental samples such as water, soil, sediment, and sludge are complex matrices of a “cocktail of chemicals” that result in many

inferences for GC-based analysis. Although GC/TOF analysis provides qualitative and quantitative analysis of a wide range of organic contaminants, clean-up is an essential procedure for removing the matrix effect in environmental samples. However, the clean-up procedure was carefully considered to minimize the loss of many organic contaminants present in real samples for suspect and non-target analysis. In our study, four kinds of cartridges containing different sorbents, such as HLB, C₁₈, silica gel, and florisil, were compared for clean-up procedures. All of the SPE cartridges were pre-washed with 12 mL of 50% DCM in hexane and then conditioned with 12 mL of hexane. After loading the native standard solutions into the cartridges, the solutions were eluted with 12 mL of 50% DCM in hexane. The standards comprised 215 contaminants of 100–500 ng, depending on the sensitivity for GC/TOF analysis. The eluents were concentrated and dissolved in 100 μ L of nonane for instrumental analysis. Overall, the HLB SPE cartridge showed the best recovery (mean: 78%) for all of the spiked standards and was chosen for the clean-up procedure in our study. The mean recovery of spiked standards into the blank samples for silica gel, C₁₈, and florisil was 72%, 65%, and 64%, respectively (Table S3). A previous study also used the HLB SPE cartridge for the clean-up procedure for the determination of organic contaminants by suspect and non-target analysis with GC/TOF (Hernández et al., 2015). To check the efficiency of the HLB SPE cartridge, the TICs before and after the clean-up procedure applied in real samples are presented in Fig. S2.

3.3. An optimized method of suspect and non-target analysis

The workflow of suspect and non-target analysis for the determination of organic contaminants in environmental samples with a GC/TOF is presented in Fig. 1, which is similar to those reported in previous studies (Portolés et al., 2014; Moschet et al., 2018). After the sample pretreatments including extraction and the clean-up procedure with a SPE cartridge, GC/TOF analysis was conducted to obtain a full-scan mass spectrum of the samples. This step was the same procedure with qualitative and quantitative analysis using a GC/MS or a GC/MS/MS. For suspect analysis, the mass spectrum obtained in the samples was first matched with qualification and qualifier ions, isotopic ratios, and retention times of standards archived in the in-house library using MassHunter software (ver. B.07.04). Examples of the TIC, mass

spectrum, and extracted ion chromatogram in sediment samples are presented in Fig. S3. The qualitative ion and qualifier ion ratios at < 30% tolerance and retention time ± 0.5 s were set as acceptable levels for identification of contaminants from the in-house library. After the confirmation of all of the contaminants from suspect analysis based on the in-house library, non-target analysis was performed to identify unknown compounds detected in the samples with the NIST library. Due to the many overlapping chromatograms of TIC in the samples, all of the TICs were extracted by the Unknown Analysis software (ver. B.07.04) as a deconvoluted ion chromatogram (DIC), which is a form used to possibly match the mass spectrum provided by the NIST library. Each DIC was used for the identification of unknown compounds detected in the samples based on the matching score (> 80) of mass spectra archived in the NIST library. A matched mass spectrum of a compound detected in sediment samples based on the DIC and NIST library is shown in Fig. S4. In our study, the deconvolution conditions were set as follows: 50, 100, 200, 300, and 400 for retention time size factor; minimum number of ion peaks > 5; and maximum number of ion peaks < 10 in the Unknown Analysis software. Contaminants detected in procedure blanks were systemically subtracted in the sample batch.

3.4. Application of suspect and non-target analysis for the Arctic environmental samples

Arctic environmental samples such as seawater, air, soil, sediment, iceberg, and sludge were evaluated via suspect and non-target analysis with GC/TOF. Based on the number of contaminants commonly detected in multiple environmental samples within the same matrix, the highest number of contaminants detected was found for sludge ($n = 43$), followed by seawater ($n = 34$), sediment ($n = 25$), air ($n = 23$), soil ($n = 19$), and iceberg ($n = 4$) (Fig. 2). This result suggests that discharges of effluents and sludge could be potential sources of organic contamination in the Arctic environment. In our previous studies, we have reported that WWTP activity is a major source of organic contaminants for the receiving environments (Moon et al., 2008; Lee et al., 2014a, 2014b, 2015). The contaminants detected in different environmental matrices with suspect analysis are presented in Fig. 3. The overall contaminant patterns showed that a number of emerging contaminants were more contributable than those of regulated contaminants, such as POPs, to the total contaminant numbers detected in the Arctic samples. In our study, the major contaminants were similar for all of the environmental samples as siloxanes and OPFRs, which collectively accounted for 44–75% of the total number of contaminants for each matrix. In particular, cyclic siloxanes, such as

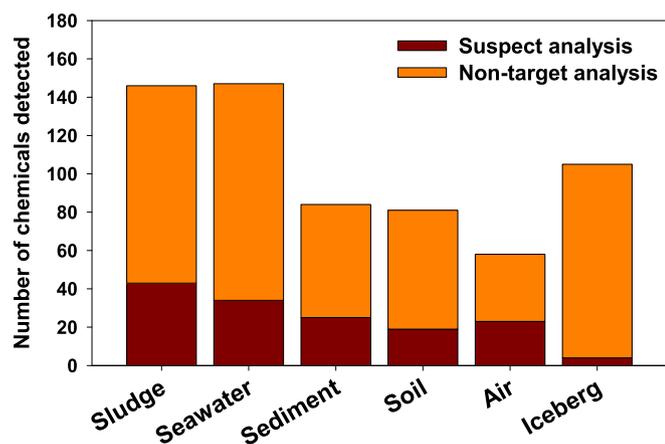


Fig. 2. Numbers of identified contaminants by suspect and non-target analysis of GC/TOF in multiple environmental samples, such as sludge, seawater, sediment, soil, air, and iceberg, collected in the Arctic environment. The detected contaminants by suspect analysis were excluded for non-target analysis.

decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6), were predominantly detected in all of the environmental matrices, except for the air samples. Similar results were reported for the occurrence of siloxanes in multiple environmental samples in the Arctic (Knudsen et al., 2007; Warner et al., 2010; Krogseth et al., 2017). In particular, cyclic siloxanes and lower-molecular-weight linear siloxanes, such as decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), and tetradecamethylhexasiloxane (L6), were predominantly detected in air samples, suggesting the long-range atmospheric transport (LRAT) of these contaminants to the Arctic environment. However, considering the presence of siloxanes in sludge, it should be considered that local contamination originated from research station activities in the surveyed regions (Warner et al., 2010; Krogseth et al., 2017). Our findings suggest widespread contamination by siloxanes in the Arctic environment as concerns for emerging contaminants.

OPFRs and phthalates were the next predominant contaminants in different types of samples from Arctic environment. However, these contaminants were not detected in iceberg samples. Previous studies have reported the occurrence of OPFRs and phthalates in air, seawater, sediment, and snow of the Arctic environments (Sühling et al., 2016; Li et al., 2017; Ma et al., 2017). Similar to siloxanes, the contamination pathways (either LRAT or local sources) of these contaminants in the Arctic environment should be clarified. Several emerging contaminants, such as SMCs, BUVSs, and NBRFs, were also detected in most of the samples, implying ubiquitous contaminants in the Arctic environment. POPs, such as PCBs (CBs 8, 18, 110 and 180), OCPs (β -hexachlorocyclohexane and heptachlors), CLBz (1,3,5-chlorobenzene and HCB), and PBDEs (mostly BDE 47), and PAHs (naphthalene, fluorene, acenaphthylene, phenanthrene, anthracene, benzo[ghi]perylene, chrysene, and benzo[a]anthracene) were detected in the samples, which is consistent with those reported in previous studies (Rigét et al., 2010; Hung et al., 2016; Sofowote et al., 2010). In particular, the lower-molecular-weight POPs and PAHs were mainly detected in all of the environmental samples because these contaminants are easily transported over long distances by the atmospheric current (Hung et al., 2016). Despite this, the number of POPs detected in the Arctic samples was smaller than those of emerging contaminants, because POPs existed at low levels due to decreasing trends in POPs in the Arctic environment (Rigét et al., 2010; Hung et al., 2016).

Non-target analysis was also conducted for the Arctic environmental samples. Although more than several thousand mass spectra were generated from the DIC in the samples, approximately 100 compounds per sample were well-matched (> 80) with the NIST library (Fig. 4). The number of compounds commonly identified in multiple environmental samples within the same matrix was manually recorded. Similar to suspect analysis, the number of compounds identified were similar for the seawater ($n = 113$), sludge ($n = 103$), soil ($n = 102$), and iceberg ($n = 101$) samples. The number of identified compounds in the air ($n = 35$) and sediment ($n = 59$) samples were lower than those found in the other samples. Unexpected identification over 100 compounds in the iceberg samples could be associated with unique chemical reactions that occurred in ice during the freezing and melting processes. Previous studies have reported the formation of organic compounds as degradation byproducts in the ice due to the freeze concentration effect (Ju et al., 2017; Choi et al., 2018). The lists of identified chemicals in multiple environmental samples from the Arctic region by non-target analysis are summarized in Table 1.

3.5. Suggestion of emerging contaminants in the Arctic environment

Emerging contaminants in the Arctic environment were chosen based on the simultaneous occurrence of contaminants in multiple environmental samples identified by the suspect and non-target analysis (Fig. S5). Several contaminants existed in a specific matrix (e.g., seawater and air) depending on their physico-chemical properties.

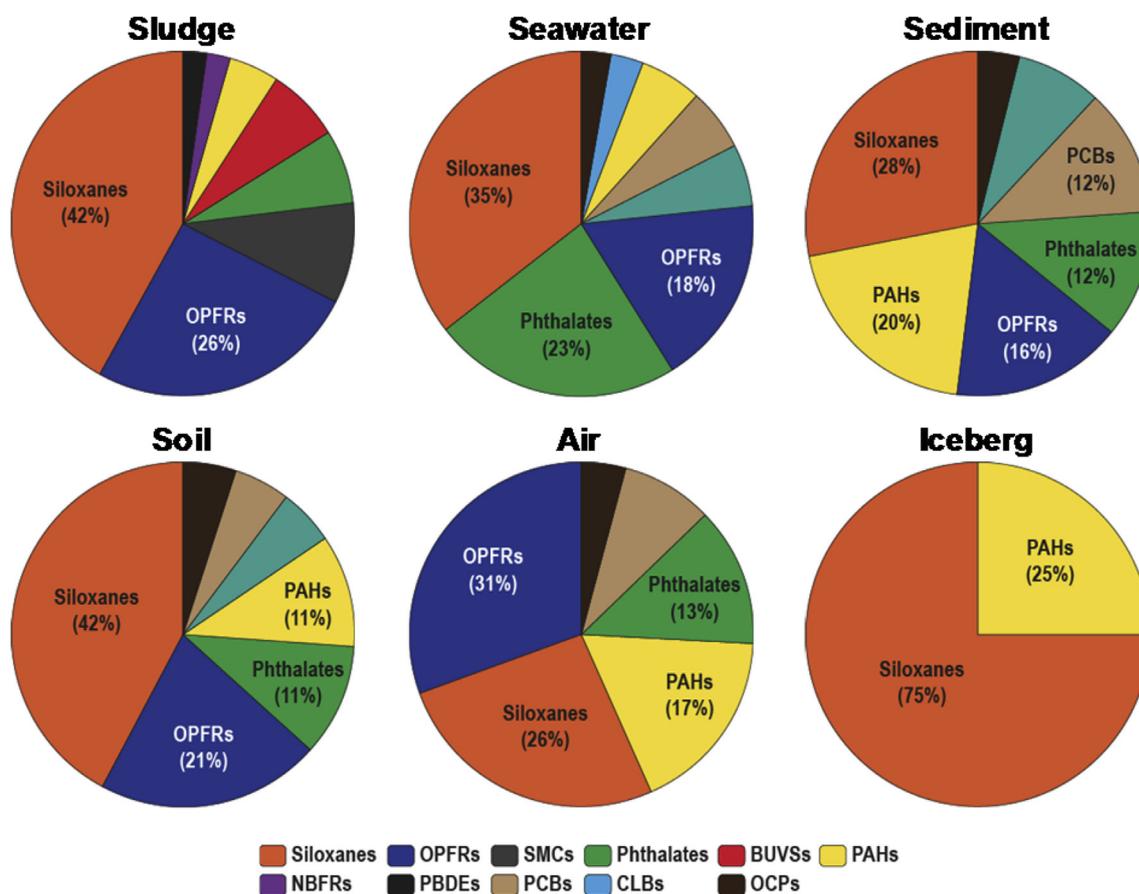


Fig. 3. Percentage of detected contaminants by suspect analysis of GC/TOF in multiple environmental samples, such as sludge, seawater, sediment, soil, air, and iceberg, collected in the Arctic environment. Contaminant groups over 10% of total contaminant numbers are shown with the label on the pie-graph.

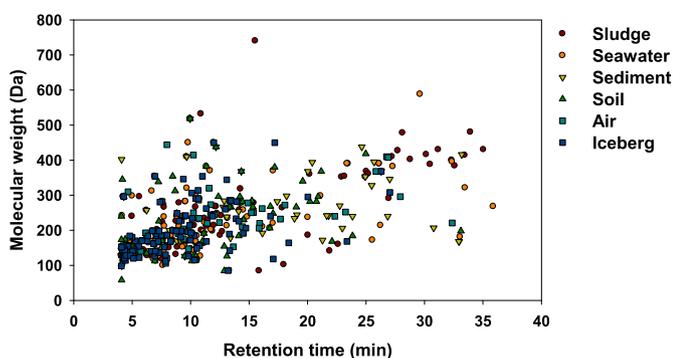


Fig. 4. Identified compounds in multiple environmental samples, such as sludge, seawater, sediment, soil, air, and iceberg, collected in the Arctic regions by non-target analysis of GC/TOF. The graph was illustrated as mass of compounds versus retention time detected. Parenthesis indicates the numbers detected in each environmental matrix.

However, the simultaneous occurrence of contaminants in multiple matrices implied strong persistence, such as POPs and/or the presence of an on-going contamination source. In our study, the suspect analysis showed 23 contaminants including PAHs, PCBs, siloxanes, phthalates, OPFRs, and SMCs as commonly detected contaminants in the Arctic environmental samples. Although over 100 chemicals from each environmental matrix were identified by non-target analysis, only two contaminants, D7 (a cyclic siloxane) and stearic acid (which is used in personal care products), were commonly detected contaminants in the Arctic environment. Among the chemical groups proposed as commonly identified contaminants, PCBs and PAHs are well-known

contaminants, and have been regularly monitored from the AMAP and some countries near the Arctic region. Moreover, siloxanes and OPFRs were detected in almost all of the environmental matrices, implying their potential for being emerging contaminants in the Arctic environment. Only a few studies have reported the occurrence of siloxanes, OPFRs, and phthalates in the Arctic environment (Sühling et al., 2016; Krogseth et al., 2017; Li et al., 2017; Ma et al., 2017; Lebedev et al., 2018). Unlike the legacy POPs, such as PCBs, the contamination sources, pathways, and ecological risks of these contaminants were not assessed.

Recent studies on non-target analysis with GC/TOF have been conducted for multiple environmental samples from specific locations. To our knowledge, this is the first report on suspect and non-target analysis for Arctic environmental samples. However, it should be noted that several limitations should be considered for the results observed in our study. Thus, further studies should include more advanced data, such as quantification of contaminants, use of internal and surrogate standards for quality control, and the retention time index (RTI) with alkane mixtures (Zhang et al., 2014; Moschet et al., 2018). Moreover, to assess the bioaccumulation and biomagnification potentials of certain contaminants in Arctic ecosystems, biotic samples should be used for further studies. Nevertheless, the results of the present study emphasized the presence of several emerging contaminants in the Arctic environment.

4. Conclusions

Suspect and non-target analytical methods with GC/TOF were optimized to propose priority pollutants in the Arctic environment. For suspect analysis, over 200 compounds were registered as target

Table 1
Chemicals detected in the seawater, sediment, and soil samples collected from the Arctic environment based on non-target analysis.

Retention time (min)	Compound Name	CAS No.	Formula	Molecular Weight	Uses
4.25	Benzene, (1-methylethyl)-	98-82-8	C9H12	120	^a
4.28	Cyclotetrasiloxane, octamethyl-	556-67-2	C8H24O4Si4	296	Siloxanes
4.81	Decane, 2,4-dimethyl-	2801-84-5	C12H26	170	–
5.76	1-Octanol, 2-butyl-	3913-02-08	C12H26O	186	Fatty alcohol
7.04	4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)but-3-en-2-one	1203-08-3	C13H18O	190	–
8.47	1-tridecanol	112-70-9	C13H28O	200	Fatty alcohol
9.07	2-exo-methyl-2-endo-(1-oxacyclohex-2-yloxy)bicyclo[2.2.1]heptane	–	C13H22O2	210	–
9.67	Octyl tetraicosyl ether	–	C32H66O	466	–
9.96	Cycloheptasiloxane, tetradecamethyl-	107-50-6	C14H42O7Si7	518	Siloxanes
10.38	2-(1,3-Dioxolan-2-yl)-1-(2-furyl)ethene	–	C9H10O3	166	–
10.74	4-Methyl-benzoic acid 4-[(3-hydroxy-benzoyl)-hydrazonomethyl]-phenyl ester	–	C22H18N2O4	374	–
11.13	5-Oxo-3,3,6-trimethylbicyclo[4.2.0]octane-7-(exo)-carbonitrile	–	C12H17NO	191	–
11.20	1,2-Benzenedicarboxylic acid, diethyl ester	84-66-2	C12H14O4	222	Phthalates
11.72	Tridecane	629-50-5	C13H28	184	Alkane hydrocarbon
12.17	Docosyl octyl ether	–	C30H62O	438	–
12.41	1,4-Benzenediol, 2-(1,1-dimethylethyl)-5-(2-propenyl)-	73685-60-6	C13H18O2	206	Essential oil of several plant
12.54	cis-1,4-Cyclohexanediamine, N1,N1,N4-triethyl	–	C12H26N2	198	–
13.09	1-Heptadecene	6765-39-5	C17H34	238	–
13.31	1-Nonadecene	18435-45-5	C19H38	266	Natural substances
13.38	3,4-Dihydro-5-methoxy-2,2,8,8-tetramethyl-2H,8H-pyrano [3,2-g]chromen-4-one	–	C17H20O4	288	–
13.46	n-Nonadecanol-1	1454-84-8	C19H40O	284	Fatty alcohol
14.33	Carbonic acid, eicosyl vinyl ester	–	C23H44O3	368	–
14.72	2-tert-Butyl-4-isopropyl-5-methylphenol	–	C14H22O	206	–
15.24	Inosine, 1-hydroxy-	5383-06-02	C10H12N4O6	284	Nucleoside
17.20	Acetic acid, 1,3,3-trimethyl-4-oxo-6-oxabicyclo[3.1.0]hex-2-yl ester	–	C10H14O4	198	–
17.45	Octadecanoic acid, methyl ester	112-61-8	C19H38O2	298	Fatty acid esterified with a methyl group
20.40	2,2',4,4'-TETRA-T-BUTYLDIPHENYL ETHER	–	C28H42O	394	–
24.95	4-(4-(Ethoxycarbonyl)-3-oxo-5-phenyl-2-3-dihydropyrazol-1-yl)benzoic acid	–	C19H16N2O5	352	–
25.06	(R,S)-5-Ethyl-6-methyl-3E-hepten-2-one	57283-79-1	C10H18O	154	Natural substances (tabaco)
25.85	9-Tricosene, (Z)-	27519-02-4	C23H46	322	Insect pheromone/pesticide

^a Not available.

contaminants in the in-house library with information on qualification and qualifier ions, isotopic ratios, and retention times. The non-target analytical method was optimized with a deconvoluted ion chromatogram, which is a possible form for matching the mass spectra to that in the NIST library. From suspect and non-target analysis, the commonly detected contaminants in the multiple samples from the Arctic environment were determined to be PCBs, PAHs, siloxanes, OPFRs, phthalates, and SMCs, similar to those reported in previous studies. In our study, siloxanes and OPFRs were proposed to be emerging contaminants for the Arctic environment. This is the first report on the application of suspect and non-target analysis with GC/TOF for assessment of Arctic environment contaminants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecoenv.2019.05.070>.

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