Prioritization of emerging contaminants in the Arctic environment using target and non-target screening analysis

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Introduction

The Arctic, which is far away from industrial and urbanized areas, is a safe place from environmental pollution. However, some contaminants can reach the Arctic environment due to long-range transport through atmosphere and ocean from lower latitude regions[1]. Currently, tens of thousands of chemicals are on the market, and new substances are increasingly being produced. Many of registered chemicals could have similar properties to legacy contaminants, including long-range transportability to the Arctic region. However, most of these chemicals are not subject to domestic or global regulations due to limited information on environmental occurrence. The Stockholm Convention has added several chemicals as new persistent organic pollutants (POPs), but these contaminants were nominated through target analytical techniques by many researchers. Considering rapid growth of chemical industry, emerging contaminants are of scientific concerns in Arctic ecosystem. Thus, it is essential to develop the suitable tool for prioritization of emerging contaminants with concurrent analytical technology. Improved analytical techniques, and research and screening programs continue to reveal the presence of chemicals that had not been previously detected or were not expected to exist in the Arctic environment. Although newly detected in the Arctic, chemicals of emerging concern are often used presently or have been in the environment for several decades. The implication for the detected chemicals in the Arctic environment could be important because it provides strong evidences concerning widespread contamination globally as emerging contaminants. As new chemicals and their decomposition products continue to be discovered, the concept of the elements that make up environmental contaminants may also change and updated regulatory action may be required. The objective of this study is to prioritize emerging contaminants based on target and non-target screening analysis (NTSA) for multiple environmental matrices, such as seawater, sediment, soil, sludge, air, and glacier, collected from the Arctic regions.

Materials and methods

Sample collection and chemical analysis

Environmental samples were collected from Ny-Ålesund, Svalbard, the Arctic during July, 2016. Ny-Ålesund is located in northwest Spitsbergen, which is the largest island in the Svalbard archipelago in the Arctic Ocean. It is surrounded by a variety of high Arctic ecosystems, making it an ideal base for conducting Arctic research. A total of 17 samples, which are comprised of seawater, sediment, soil, sludge, air, and glacier, were collected at different sites. Forty liters of surface seawater samples were collected in pre-cleaned PP bottles using a stainless steel basket, and then were filtered using glass fiber filters. The filtrate (dissolved phase) was used in the further pretreatment steps. Surface sediment was collected using a Van-veen grab sampler from a research vessel and soil sample was collected using stainless steel spoon. The collected samples were individually wrapped in pre-cleaned aluminum foil and then immediately frozen with dry-ice. They were then transported to the laboratory and kept in a freezer at -20°C until analysis. All samples were extracted in a Soxhlet apparatus with 200 mL of 25% DCM in

hexane for 16 h. The extracts were concentrated to approximately 1 mL using rotary evaporator under the room temperature. After filtration and extraction, the samples passed by Oasis HLB (150 mg, Waters) cartridge[2], previously conditioned with methanol and Milli-Q water. After drying under vacuum, analytes were eluted with dichloromethane and hexane. The eluants were concentrated and dissolved in nonane for instrumental analysis.

Instrumental analysis

The detection of target and non-target compounds was performed using Agilent GC 7890B coupled with Q-TOF 7200 with a Agilent 7693 autosampler. The method was developed to analyze 208 target compounds in a single run. The Q-TOF was operated in electron ionization (EI) mode with an ionization voltage set at 70 eV. Q-TOF mass spectrometer (MS) was operated at 100 mS/spectrum in the mass range *m/z* 50-600 and the resolution was about 13,000 at *m/z* 131 and 17,000 at *m/z* 502 with 4 Ghz high resolution mode. The transfer line and ionization source temperature were set at 280°C and 230°C, respectively. A DB-5MS UI (30 m x 0.25 mm i.d.; 0.25 μm film thickness) was used for the separation of the target compounds. 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 was helium at a constant flow rate of 1mL/min. A solvent delay of 4 min was used to prevent damage in the capillary column and ion source filament. MassHunter Quantitative Analysis B.05 and Unknown Analysis B.05 were applied for the treatment of data. The National Institute of Standards and Technology (NIST) Library (ver. 2009) was used for matching the non-targeted compounds.

Workflow of target and non-target screening analysis

The two individual steps of target and non-target screening analysis using GC/Q-TOF are illustrated in Figure 1. The total ion chromatogram (TIC) was used to identify multi-residue target compounds with matching the retention time, and qualification ion using the in-house library. After target analysis, the non-target analysis was also performed to identify unknown chemicals in multi-media matrices. Mass spectrum of each compound from the deconvoluted ion chromatogram (DIC) was used to identify the non-target compounds using the NIST library.

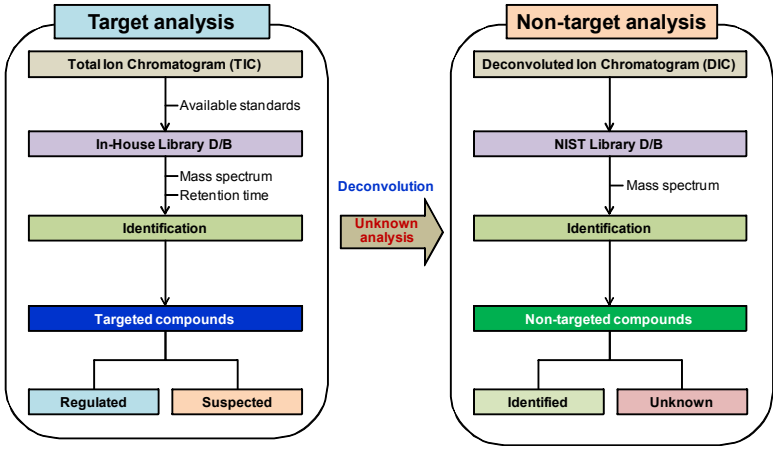

Figure 1. Workflow for target and non-target screening analysis.

Results and discussion:

Target and non-target screening analysis

In the seawater samples, the number of detected target compounds was five, and suspected compounds ranged from 27 to 29 with a mean of 28. Among target compounds, three compound groups were detected: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs). Other target compound groups such as polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), dioxin-like PCBs, and polyborminated diphenyl ethers (PBDEs) were not detected in all the samples. Of the suspected compounds, siloxanes were the mostly abundant, and phthalates, organophosphate flame retardants (OPFRs), synthetic musk compounds (SMCs), and chlorobenzens (CLBz). The other suspected compounds such as polychlorinated naphthalaenes (PCNs), dechlorane plus (DP), novel brominated flame retardants (NBFRs: DBDEP and BTBPE), and benzotriazole ultraviolet stabilizers (BUVSs) were not detected. In sediment and soil samples, the numbers of detected target compounds ranged from 2 to 15 (mean: 7), and suspected compounds ranged from 7 to 23 (mean: 14). Among the target compounds, three compound groups were detected: PAHs, PCBs, and OCPs. Other target compounds group such as PCDD/Fs, DL-PCBs and PBDEs were not detected. Of the suspected compounds, the predominant compunds were siloxanes, followed by OPFRs, phthalates, and SMCs. Other suspected compounds such as PCNs, CLBs, DP, NBFRs, and BUVSs were not detected. The number of detected target compounds was three and one for sludge and glacier samples, respectively. Moreover, 40 and 3 suspected compounds were found in the sludge and glacier samples, respectively. Of the target compounds, 2 compound groups were detected: PAHs and PBDEs in sludge, and PAHs in glacier. Among suspected compounds, siloxanes were the most abundant (18 in sludge; 3 in glacier). Furthermore, others were detected in sludge only: OPFRs, SMCs, phthalates and BUVSs, and NBFRs. Other suspected compounds such as PCNs, CLBs, and DP were not detected. After the target screening analysis, non-targeted compounds were classified into identified and unknown compounds. The number of identified and unknown compounds in seawater, sediment, soil, sludge, and glacier samples were found to be 267 and 442, 197 and 459, 206 and 439, 306 and 415, and 247 and 156, respectively.

Prioritization of emerging contaminants for the Arctic environments

To prioritize contaminants of emerging concerns in the Arctic environment, compounds were chosen by the simultaneous occurrence for multiple environmental matrices. The commonly detected compounds in the multiple environmental matrices were found to be 2, 21, and 2 compounds on the regulated, suspected, and identified lists, respectively (Figure 2). Among the regulated compounds, PAHs and PCBs were found in the multiple matrices. In the suspected compound list, siloxanes were found to be dominant, followed by OPFRs, phthalates, and SMCs as emerging contaminants for Arctic regions. Many chemicals were identified by NTSA, but only 2 chemicals were identified as commonly detected chemicals for the Arctic environment samples. In summary, targeted and non-targeted compounds in various environmental samples collected in the Arctic environment were identified using target and non-target analysis with GC/TOF system. PAHs, PCBs, siloxanes, phthalates, OPFRs, SMCs, and several hydrocarbons were proposed as priority pollutants in the Arctic environments and some chemical groups could be regarded as emernging contaminants (e.g., siloxanes and OPFRs). This study provides a scientific-based decision-making procedure for prioritizing emerging pollutants in the Arctic environment based on target and non-target screening analysis.

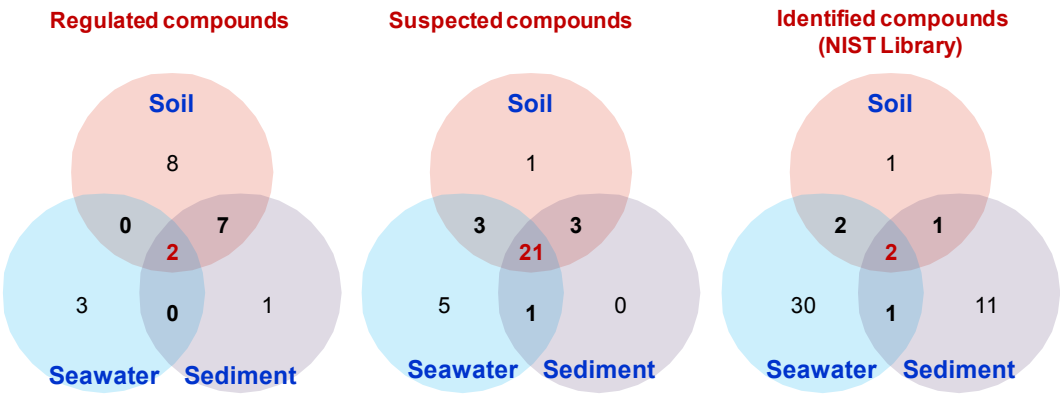

Figure 2. Venn diagrams for determining the priority contaminants for the Arctic environment

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References:

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