Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Martin Haraldsvik

Non-target Screening of Emerging Organic Pollutants in Siberian Sediments

Master's thesis in Sustainable Chemical and Biochemical Engineering
Supervisor: Bo Yuan
Co-supervisor: Murat V. Ardelan, Nicolas Sanchez
June 2023

NTNU
Norwegian University of Science and Technology

Martin Haraldsvik

Non-target Screening of Emerging Organic Pollutants in Siberian Sediments

Master's thesis in Sustainable Chemical and Biochemical Engineering
Supervisor: Bo Yuan
Co-supervisor: Murat V. Ardelan, Nicolas Sanchez
June 2023

Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

NTNU
Norwegian University of
Science and Technology

Abstract

Despite its remoteness, the Arctic is increasingly threatened by pollution, notably chemical runoff. In response, this study examines both targeted and non-targeted analytical methods, employing these techniques to evaluate sediment samples from Siberia's coastline. Two extraction methods were assessed, one intended for the analysis of polar substances and the other for non-polar substances, and their potential use in non-target screening applications was evaluated. Both methods were tested with spiked and un-spiked sediment samples from the Barents Sea, followed by their application to analyze sediment samples from the Kara Sea.

The method for non-polar substances was analyzed with direct injection into a quadrupole time-of-flight mass spectrometer (Q-TOF) and tested with a spiking mixture encompassing a wide range of chlorinated paraffins (CPs). The method displayed reasonable recoveries (57-70%) across all compounds tested and thus shows promise as an extraction method for use in non-target screenings of non-polar compounds in sediments.

The method for polar substances was analyzed using two different mass spectrometers coupled to an ultra-performance liquid chromatograph (UPLC). The mass spectrometers used were a Q-TOF mass spectrometer and a triple quadrupole (QqQ) mass spectrometer. The method was tested with a spiking mixture containing 40 per- and polyfluoroalkyl substances (PFAS) encompassing a wide range of physiochemical properties. The method exhibited excellent recoveries (85-130%) for smaller (C<9) perfluoro sulfonic acids (PFSAs) and fluorotelomer sulfonates (FTSs), while also being able to detect 29 of the 40 compounds in the spiking mixture in concentrations of 1 ng/g when analyzed using non-target screening methods. Therefore, the extraction method demonstrates potential for both targeted analysis of smaller PFSAs and FTSs, and non-target analysis of polar compounds in sediments.

Following this, the polar extraction method was used to perform both a targeted and a non-targeted analysis of samples taken from six diverse locations in the Kara Sea, ranging from the coastline to more remote offshore sites. The targeted screening yielded identifications of eleven PFAS compounds and semi-quantitative results for three of these. The compounds identified in the samples were PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFECHS, 4:2 FTS, 6:2 FTS, 8:2 FTS, and ADONA. Notably, PFOS was found in concentrations of 0.1 to 0.45 ng/g of wet sediment, 4:2 FTS was found in concentrations of up to 0.4 ng/g of wet sediment, and 6:2 FTS was found in concentrations of up to 0.3 ng/g of wet sediment.

The non-targeted screening of the Kara Sea sediments yielded data on 60 features, 29 of which were given possible identifications. The trends of the 12 features with the highest responses were examined, and it was discovered that three of the compounds showed no spatial trends, three showed significantly higher responses in the samples from the Yenisei and Ob River plume, and six showed the highest response in a sample from shallow waters in the middle of the Kara Sea.

Sammendrag

Til tross for sin avsidesliggende beliggenhet, er Arktis i økende grad truet av forurensning, særlig fra kjemisk avrenning. I lys av dette undersøker denne studien både målrettede og ikke-målrettede analytiske metoder, og anvender disse teknikkene for å evaluere sedimentprøver fra Sibirs kystlinje. To ekstraksjonsmetoder ble vurdert, en beregnet for analyse av polare stoffer og den andre for ikke-polare stoffer, og deres potensiale for bruk i ikke-målrettede analyser ble evaluert. Begge metodene ble testet med fra Barentshavet med og uten tilsatte test-stoffer, etterfulgt av deres anvendelse for å analysere sedimentprøver fra Karahavet.

Metoden for ikke-polare stoffer ble analysert med direkte injeksjon i et kvadrupol time-of-flight massespektrometer (Q-TOF) og testet med en stoffblanding som omfattet et bredt spekter av klorerte parafiner (CP). Metoden viste rimelige utvinningsrater (57-70 %) av alle testede forbindelser og virker derfor lovende som en ekstraksjonsmetode for bruk i ikke-målrettede analyser av ikke-polare forbindelser i sedimenter.

Metoden for polare stoffer ble analysert ved bruk av to forskjellige massespektrometre koblet til en ultra-ytelses væskekromatograf (UPLC). De anvendte massespektrometrene var et Q-TOF massespektrometer og et trippelt kvadrupol (QqQ) massespektrometer. Metoden ble testet med en stoffblanding inneholdende 40 per- og polyfluoralkylsubstanser (PFAS) som omfattet et bredt spekter av fysiokjemiske egenskaper. Metoden viste utmerket utvinning (85-130%) for mindre (C<9) perfluorsulfonsyrer (PFSA) og fluortelomersulfonater (FTS), samtidig som den var i stand til å påvise 29 av de 40 forbindelsene i stoffblandingen i konsentrasjoner på 1 ng/g når analysert ved bruk av ikke-målrettede analyse metoder. Derfor viser utvinningsmetoden potensiale for både målrettet analyse av mindre PFSAer og FTSer, og ikke-målrettet analyse av polare forbindelser i sedimenter.

Videre ble den polare utvinningsmetoden brukt til å utføre både en målrettet og en ikke-målrettet analyse av prøver tatt fra seks forskjellige lokasjoner i Karahavet, alt fra kystlinjen til mer avsidesliggende offshore-steder. Den målrettede analysen resulterte i identifikasjon av elleve PFAS-forbindelser, og semikvantitative resultater for tre av disse. Forbindelsene identifisert i prøvene var PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFECHS, 4:2 FTS, 6:2 FTS, 8:2 FTS og ADONA.

PFOS ble funnet i konsentrasjoner på 0,1 til 0,45 ng/g vått sediment, 4:2 FTS ble funnet i konsentrasjoner på opptil 0,4 ng/g vått sediment, og 6:2 FTS ble funnet i konsentrasjoner på opptil 0,3 ng/g vått sediment.

Den ikke-målrettede analysen av sedimentene fra Karahavet ga data om 60 mulige forbindelser, hvorav 29 ble gitt mulige identifikasjoner. Trendene til de 12 forbindelsene med høyest respons ble undersøkt, og det ble oppdaget at tre av forbindelsene ikke viste romlige trender, tre viste signifikant høyere respons i prøvene fra Jenisej- og Ob-elven, og seks viste høyest respons i en prøve fra grunt vann midt i Karahavet.

Preface

This thesis is part of a master's degree in the Sustainable Chemical and Biochemical engineering (MSCHEMBI) from the autumn semester 2021 to the spring semester 2023. The project was performed independently from any external interests.

The extraction methods tested in this thesis were developed to aid in non-target screening of persistent organic pollutants in sediments, with the goal of using these methods in future projects employing non-target screening methods. The discovery of general extraction methods for use in non-target screening of sediments is of great interest in the field of analytical chemistry, and could greatly benefit future research into persistent organic pollutants.

Trondheim, 12. June 2023

Martin Haraldsvik

Acknowledgements

My deepest gratitude for making this project possible to realize goes to the following people:

My main supervisor Bo Yuan, for project planning, valuable feedback, and interesting discussions throughout the project and pre-project. My co supervisors Murat Van Ardelan and Nicolas Sanchez, for guidance and support during the project. Susana Villa Gonzales, for invaluable assistance with chromatographic analysis and data processing. Stephen Gustav Kohler, who played a significant role in the sourcing of the samples. Ingeborg Antonsen Lysberg, for helpful aid in research, and motivational card-game breaks. Junjie Zhang, for general aid with laboratory equipment.

Lastly, I would like to thank my family, especially my parents and grandmothers, for both enabling and encouraging my interest in science throughout my life with countless experiment sets, museum trips, and science related books and magazines.

List of Tables

Table 1:Water solubility and pKA range for PFCAs, PFSAs, and FTSs. 23
Table 2: Original IDs of samples and their new number. 24
Table 3: Concentrations of standards, SCCPs, MCCPs, and LCCPs in the standard and spiking solutions. 26
Table 4: Formulas, names, and structures of Internal standards and PFCA compounds in the PFAS spiking mix and internal standard solution. 28
Table 5: Formulas, names, and structures of PFSA and FTS compounds in the PFAS spiking mix. 29
Table 6: Formulas, names, and structures of miscellaneous compounds in the PFAS spiking mix. 30
Table 7: Gradient elution program using a mobile phase mixture of HPLC-grade water with 2 mM ammonium acetate (A) and methanol (B). 31
Table 8: 6-minute method Gradient elution program using a mobile phase mixture of HPLC-grade water with 2 mM ammonium acetate (A) and methanol (B) 32
Table 9: 10-minute method Gradient elution program using a mobile phase mixture of HPLC-grade water with 2 mM ammonium acetate (A) and methanol (B) 32
Table 10: Overview of results from nontarget screening of SCCPs, MCCPs, and LCCPs in Barents sea sediments. 33
Table 11: Matrix effect, and absolute and relative recoveries of compounds in spiked samples from the targeted analysis. 34
Table 12: Compounds detectable in the spiked samples with the 6-minute and 10-minute methods. 36
Table 13: Compounds detected in the samples from the Kara and Barents sea. 38
Table 14: Compounds detected in the six samples from the Kara sea. 39

Table of Figures

Figure 1: The Non-target screening workflow, with important considerations per step. 16
Figure 2: Schematic illustration of a HPLC instrumentation 17
Figure 3: Illustration of an ESI operating in positive mode. 18
Figure 4: Schematic illustration of a triple quadrupole 19
Figure 5: Q-TOF-MS Schematic, from Allen and McWhinney [45]. 20
Figure 6: Sampling locations of the samples from the Kara sea. 25
Figure 7: Mass spectrums of PFOS, 6:2 FTS, and PFOA in spiked samples from the 6-minute method. . 35
Figure 8: Chromatograms of PFOS, 6:2 FTS, and PFOA in spiked samples from the 6-minute method.. 35
Figure 9: Combined spectrums of PFOS, 6:2 FTS, and PFOA in spiked samples from the 6-minute method.. 35
Figure 10: Combined spectrum of PFOA 13C8 in 0.9 ppb standard solution, 1 ppb matrix match solution and 1 ppb spiked sample 37
Figure 11: The relative concentrations of PFOS, 4:2 FTS, and 6:2 FTS per sample location 39
Figure 12: The responses from three of the features identified in the Kara sea sediments. 40
Figure 13: The responses of the six features with the highest response in sample 3. 40

Abbreviations

POPs	Persistent Organic Pollutants
IPBES	Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services
UNEP	United Nations Environment Programme
COP	Conference of Parties
POPRC	Persistent Organic Pollutants Review Committee
LRT	Long-range transport
PFAS	Per- and polyfluoroalkyl substances
LC	Liquid Chromatograph
MS	Mass Spectrometer
PAH	Polyaromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PFOA	Perfluorooctanoic acid
DDT	Dichlorodiphenyltrichloroethane
HCB	Hexachlorobenzene
AMAP	Arctic Monitoring and Assessment Program
HRMS	High-resolution Mass spectrometer
PBT	Persistent, Bioaccumulating, Toxic
MS-MS	Tandem mass spectrometer
RT	Retention time
m/z	Mass to charge ratio
PLE	Pressurized liquid extraction
ASE	Accelerated solvent extraction
LLE	Liquid-liquid extraction
RP	Reverse Phase
MeOH	Methanol
MP	Mobile phase
DCM	Dichloromethane
EtOAc	Ethyl acetate
GPC	Gel-permeation chromatograph
HPLC	High-performance liquid chromatography
UPLC	Ultra high-performance liquid chromatography
SP	Stationary phase
NPC	Normal-phase chromatography
RPC	Reverse-phase chromatography
GSC	Gas-solid chromatography
GLC	Gas-liquid chromatography
EI	Electron impact
ESI	Electrospray ionization
CI	Chemical ionization
Q-TOF	Quadrupole-time-of-flight
Q-Orbitrap	Quadrupole-Orbitrap
TOF	Time-of-flight
DC	Direct current
RF	Radio frequency
CID	Collision induced dissociation
MRM	Multiple Reaction Monitoring
LOD	Limit of detection

Table of Contents

Abstract 1
Sammendrag 2
Preface 3
Acknowledgements 3
List of Tables 4
Table of Figures 5
Abbreviations 6
1 Introduction and Background 9
1.1 Marine Pollution 9
1.2 The Arctic 9
1.3 POPs 10
1.3.1 The Stockholm Convention 10
1.3.2 Identifying new POPs 11
1.3.3 PFAS 11
1.3.4 Chlorinated Paraffins 11
1.3.5 Transport 12
1.3.6 Effects on Arctic Wildlife 13
1.3.7 Permafrost and Global warming 14
1.3.8 Emerging Organic Pollutants 14
1.4 Non-target Screening Background 15
1.4.1 The Non-target screening Workflow 16
2 Instrument and Method Theory 17
2.1 High Performance Liquid Chromatography 17
2.2 Electron Spray Ionization 17
2.3 Mass Spectrometry 18
2.3.1 Triple Quadrupole Mass Spectrometry 18
2.3.2 Quadrupole Time-Of-Flight Mass Spectrometry 19
2.4 QA and QC 21
2.4.1 LOD and LOQ 21
2.4.2 Standards 21
2.4.3 Recovery and matrix effect 22
2.5 Properties of PFAS 22
3 Method 24
3.1 Sampling and Sample Treatment 24
3.2 Extraction 26
3.2.1 CP extraction 26

3.2.2 PFAS extraction 27
3.3 Analysis 31
3.3.1 Analysis of Non-polar Compounds CPs (QTOF) 31
3.3.2 Analysis of Polar Compounds PFAS (UPLC-QqQ) 31
4 Results 33
4.1 Method Development 33
4.1.1 Target Analysis of Non-polar Compounds Using CPs as Test Chemicals 33
4.1.2 Target Analysis of Polar Compounds using PFAS as Test Chemicals 33
4.1.3 Non-target Analysis Based on Polar Substance Extracts 34
4.2 PFAS detection and non-target analysis in the Arctic sediment samples 38
5 Discussion 41
5.1 Limitations and Considerations 41
5.2 Sampling and Treatment Discussion 41
5.3 Challenges Encountered During the Extraction Process 42
5.4 Non-polar Extraction Advantages, Disadvantages, and Improvement Potential 43
5.5 Polar Extraction Method Discussion 43
5.6 Comparing Extraction Techniques: Sample Size Constraints and Results 44
5.6.1 Discussion on Non-polar Target Screening Results 44
5.6.2 Evaluating Polar Extraction: Insights from Targeted and Non-Target Screening of PFAS Samples 44
5.6.3 Insights and Implications from Arctic Sediment PFAS Analyses: Trends, Sources, and Potential Influences 45
5.6.4 Detecting and Tracing Non-target Features in Kara Sea Samples 46
6 Conclusion 47
References 48
Appendix 51
A: Targeted screenings compound details 51
B: Targeted screening chromatograms 55
C: Non-target results 69

1 Introduction and Background

1.1 Marine Pollution

The 2019 UN Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES) assessment highlights marine pollution as a major challenge, and states that less than 20% of the worlds wastewater is adequately treated prior to discharge into the environment [1]. The assessment further states that between 300 and 400 million tons of toxic sludge, heavy metals, solvents, and other industrial waste are discarded into the world's waterways every year [1]. In the UN's Sustainable Development Goal target 14.1, states pledge to: ''By 2025, prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution." [2]

Marine pollution can be divided in two primary types: trash and chemical pollution [3].

Chemical pollution, also known as nutrient pollution, comes primarily in the form of runoff from human activities like agriculture, mining, and industry. This runoff transports the chemical pollution into local waterways or the sea. Fertilizers used in agriculture causes increased concentrations of nitrogen and phosphorus, which can cause algal blooms. These algal blooms can starve the local ecosystem of nutrients or produce toxins, leading to negative effects on health and the environment, as well as hurting local ecosystems and industries dependent on the ocean [3].

Marine trash encompasses all manufactured products that end up in the ocean, which are mostly made of plastic. The majority of marine trash originates from terrestrial sources [3]. These sources include poor waste management, littering, and strong winds. Shopping bags, beverage bottles, cigarette butts, bottle caps, food wrappers, and fishing gear are all common types of marine debris made of plastic [3]. Marine trash made of plastics are particularly problematic, as plastics typically take hundreds of years to decompose.
fish and marine mammals and birds can become entangled in larger pieces of plastic, while smaller pieces of plastic can be mistaken for food, potentially clogging up the digestive tracts of wildlife, and the smallest can be consumed by small organisms and transported up the food chain. When small organisms feed on microplastics, they absorb chemicals from the plastics into their tissues. Microplastics have been detected in a many marine species at all levels of the food-web, and bioaccumulate [3].

While plastic is decomposing it tend to break down into microplastics [4], during this process various chemicals leak out of the plastic into the surrounding water [5] or into the tissue of organisms that have consumed the plastic [3].

1.2 The Arctic

The Arctic is a remote area, located far from most major pollution sources, yet it still carries traces of human-made pollution like plastics, gasses, soot, and pesticides [6]. Some pollution in the arctic can be traced to local sources, like local combustion of wood or fossil fuels, local industry, or local waste water, much of the pollution in the arctic is transported large distances from other sources of pollution [7] through the ocean, rivers, or air. These contaminants in the pollution can have far reaching negative effects on human health and the environment [6]. Two common categories of pollutants found in the arctic are heavy metals and persistent organic pollutants (POPs), both of which can potentially bioaccumulate in the food chain [8].

Compared to other marine regions the arctic ocean remains relatively clean, yet the amount of pollution in the Arctic is increasing. Major contributors include industrial development and military activity, particularly nuclear activities, for example the nuclear fuel reprocessing plants at Sellafield and Cap de la Hague, along with the influx from global sources, like industry and transportation [7].

As of 2017 there's an estimated 8.3×10^6 metric tons of plastic in the Arctic Ocean, in addition to chemical pollution, and this number is expected to reach 34×10^6 metric tons by 2050 [9].

Several of the Arctic Council's Working Groups are closely monitoring and addressing the impacts of pollutants and contaminants on the Arctic ecosystems. Their findings have raised awareness on the serious implications of pollution in the Arctic and contributed to both national actions and international conventions [6].

1.3 POPs

POPs are particularly problematic for arctic wildlife due to their fat-soluble, as most arctic wildlife rely on fat stores as insulation. Fat-soluble pollutants accumulate in the animal's fatty tissues, and are released into the body when the fat is broken down due to either fasting or starvation [10].

1.3.1 The Stockholm Convention

The Stockholm Convention on Persistent Organic Pollutants is an international environmental treaty. The convention entered into effect on the 17. of May 2004, with the aim to reduce or eliminate the use of POPs in order to "Protect human health and the environment from persistent organic pollutants."[11]. The convention is the result of a global call to action against POPs in 1995 by the United Nations Environment Programme (UNEP). The UNEP [12] defines POPs as chemicals that:

- remain intact for exceptionally long periods of time (many years).
- become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air.
- accumulate in living organisms including humans, and are found at higher concentrations at higher levels in the food chain.
- are toxic to both humans and wildlife.

As of September 2022 the convention is signed by the European Union and 185 countries. Notable countries that have not ratified the convention include the USA, Israel, and Malaysia.

POPs are currently widely distributed over large regions as a result pollution from human activity over the last decades, this also includes areas without local sources of POPs [8, 10], additionally some POPs are found all around the globe [12]. The widespread contamination of both the environment and foodstuffs from POPs over long periods of time has resulted in both acute and chronic toxic effects in humans and many other species due to sustained exposure for periods of time that can span generations [12].

POPs also concentrate in living organisms through bioaccumulation. The highest exposures to POPs can be found in fish, predatory birds, mammals, and humans, due to being high up in the food chain [12] [13]. When an animal travels, any POPs absorbed by the animals travel with it. As a result of these two processes, POPs can be found in both people and animals living in the Arctic, thousands of kilometers from any major POPs source [12] [10].

POPs can cause several negative effects in both animals and humans. These include cancer, hypersensitivity and allergies, disruption of the immune system, and reproductive disorders. Some POPs are considered endocrine disruptors, which damage the immune and reproductive systems of any humans or animals exposed to them by altering the hormonal system. This effect can be transferred from parent to offspring, and can cause both developmental and carcinogenic effects [12].

1.3.2 Identifying new POPs

When the Stockholm Convention was adopted, a provision was made for a procedure to identify additional POPs, and the criteria considered when doing so. The Persistent Organic Pollutants Review Committee (POPRC) was established at the first meeting of the Conference of the Parties (COP1), to consider additional chemicals nominated for listing under the Convention.

31 experts nominated by parties from the five UN regional groups compose the POPRC, and review nominated chemicals in three stages [12].

1. The POPRC determines whether the chemical fulfills POP screening criteria detailed in Annex D of the Convention, relating to its persistence, bioaccumulation, the potential for environmental long-range transport (LRT), and toxicity.
2. Any substance that is deemed to fulfill these requirements, will have a risk profile drafted according to Annex E, to evaluate whether the substance is likel, to lead to significant adverse human health and/or environmental effects as a result of its LRT and therefore warrant global action.
3. If the POPRC finds that global action is warranted, a risk management evaluation is developed, according to Annex F, reflecting socioeconomic considerations associated with possible control measures. Based on this, the POPRC decides to recommend that the COP list the substance under one or more of the annexes to the Convention.

1.3.3 PFAS

Per- and polyfluoroalkyl substances (PFAS) is a group of chemicals that has been of particular concern as POPs and emerging organic pollutants in recent years. PFAS are a versatile group of highly fluorinated aliphatic substances containing at least one fully-fluorinated carbon atom ($–CF_2–$) and usually a terminal functional group such as an alcohol, amide or organic acid [14], and are used in many applications, especially industrial, due to their high thermal and chemical stability and oil and water repellent properties [15]. These properties unfortunately also cause problematic environmental impacts. The high C–F bonding strength (485 kJ/mol) makes PFAS thermodynamically stable and highly resistant to many forms of degradation, including hydrolysis, metabolism and photolysis [14]. The toxicity of PFAS was observed several decades ago, but the widespread environmental occurrence of PFAS and their associated public health effects was not acknowledged by the scientific community until the early 2000s [16-18]. PFAS can currently be detected in trace concentrations in biological and environmental matrices worldwide [14, 19-21]. The persistency of PFAS makes it accumulate even at trace levels in different environmental matrices, which makes them challenging to analyze. Currently, most analysis of PFAS is carried out in professional laboratories utilizing liquid chromatographs coupled with mass spectrometers (LC-MS) [14]. Another challenge regarding the analysis of PFAS is that most of the thousands of PFAS on the global market are unknown and often called “PFAS precursors”, with only ~28 PFAS are currently being analyzed quantitatively [14].

1.3.4 Chlorinated Paraffins

In 2017 short-chain chlorinated paraffins (SCCPs) were included in the POPs list [12]. These compounds fall under a category of industrial chemicals called chlorinated paraffins (CPs), which are extensively manufactured and utilized. CPs are commonly used in industry as plasticizers, flame retardants, additives for paints, coatings, sealants, and as high-pressure additives in metal-processing liquids [22].

As of 2017 approximately 1.3 million tons of CPs are produced globally each year, with SCCPs accounting for about 30% of the total production [22]. The primary contributors to the global CP production are medium-chain chlorinated paraffins (MCCPs) and long-chain chlorinated paraffins (LCCPs).

The production of SCCPs, MCCPs, and LCCPs results in complex mixtures of polychlorinated straight alkanes with carbon chain length ranges of 10 – 13, 14 – 17, and > 17 respectively. Each CP homologue consists of CP molecules with identical carbon and chlorine numbers [22].

All three classes of CPs have demonstrated persistence, bioaccumulation, and potential for long-distance transport, and have been detected in a variety of environmental settings worldwide [22]. A significant concern regarding CPs impact on mammalian health is developmental toxicity. Additionally, endocrine-disrupting effects have been identified across all three classes of CPs [22].

1.3.5 Transport

Pollution transported by wind and ocean currents are regarded as the primary sources of contaminants in the Arctic. This pollution has its source in the densely populated, industrialized parts of the world [10]. As the majority of the pollution in the arctic has its origin in other parts of the world, the arctic can be used as an indicator region for both emerging and legacy contaminants. Detection of a contaminant in the Arctic indicates that it is poorly degradable, transported long distances, and bioaccumulates [10].

There exist some local sources of pollution in certain areas of the Arctic. Contaminants like POPs (Poly aromatic hydrocarbons (PAH), Polychlorinated Biphenyls (PCB), PFAS) and siloxanes enter the environment from sewage and garbage from settlements in the Arctic, while mining operations, such as those on Svalbard and in the Pechengsky district and Siberia introduce pollution in the form of PAHs, PCBs and heavy metals [10].

Contaminants reaching the Arctic by air or water and pollution from local sources are not the only sources of contaminants in the arctic however, and legacy contaminants that are no longer produced or used can remain in, and be a problem for, both the environment and animals for many years [10]. These legacy, persistent, contaminants are therefore considered a secondary source of pollution in the arctic [10].

1.3.5.1 Currents

Ocean currents is one mode of transport for contaminants ocean currents. The transport of pollutants from their source by ocean currents may take several decades as ocean currents move slowly, and when the pollutants reach the Arctic, they may then stay in the Arctic Ocean for several centuries [10]. A delay in the detection of contaminants transported this way is with respects to production and environmental measures, as transport from industrial areas if the world to the Arctic via ocean currents is so slow. Pollutants found in the ocean are often either discarded directly into the sea or transported to the sea by rain. Most pollutants transported by ocean currents are water-soluble, while less soluble pollutants may become bound to particles and sink to the seafloor, where they are stored in the sediments. Areas where pollutants are deposited and stored are called sinks [10]. Studies suggest that the primary means of transport for Perfluorooctanoic acid (PFOA) is transport by ocean currents [10], and that 35% of long-range transported PCBs reaching Svalbard are transported by sea [10].

1.3.5.2 Air

Transport via the atmosphere is both the fastest and most common mode of transport for pollutants, especially for volatile and semi-volatile compounds, and pollutants can be transported from their source in industrial parts of the world to the Arctic in as little as just a few days from their release into the air [10]. Transport by air can be split into two categories: volatile and semi-volatile, and particle bound. Volatile and semi-volatile pollutants behave differently from pollutants bound to particles in the air, typically being transported as gasses, falling to the ground as precipitation when temperatures drop. This leads to volatile and semi-volatile compounds falling to the ground in winter in most of the world, before then being brought back into the air during the spring. The lower temperature near the poles however makes the transport of these compounds back into the air more difficult, and thus these

pollutants tend to accumulate in colder climates, particularly the Arctic. It is estimated that aerial transport accounts for 45% of PCBs reaching Svalbard [10].

Aerial transport of pollution varies from season to season, due to the different properties exhibited by the atmosphere during different seasons. Transport is greatest in winter and spring, and lowest during summer. The Arctic winters are characterized by a stable high pressure over the North Pole. This keeps the air masses relatively stationary for a long period of time, which gives airborne pollutants more time to precipitate out of the air and into terrestrial and marine ecosystems [10]. The increased temperature during the Arctic summer generates more dynamic weather, which leads to less precipitation of pollutants from the air [10].

1.3.6 Effects on Arctic Wildlife

There has been observed negative effects of pollutants in Arctic animals high in the food chain. Reduced reproduction and increased offspring mortality, and impaired hormone and immune systems are among the observed effects are. These effects have been observed in polar bears, harp seals, glaucous gulls, and arctic char [10].

1.3.6.1 Birds

The upper parts of the Arctic food web are occupied by several seabirds. Some of these seabirds are fish eaters, while others are carrion eaters. Both carrion and fish are however food sources high in pollutants, especially fat-soluble pollutants, which puts these seabirds at risk [10]. One of these seabirds is the Brünnich's guillemot. The eggs of these were analyzed in 1993, 2002, 2003 and 2007, and showed decreasing concentrations of PCBs dichlorodiphenyltrichloroethane (DDT), and toxaphene, while the concentrations of hexachlorobenzene (HCB) remained unchanged [10]. Another species of seabird is the Glaucous gulls. Glaucous gulls from Bjørnøya were analyzed between 1972 and 2006, and showed high levels of PCBs, DDT, HCB, chlordane, and other legacy pollutants. There were also detected high levels of brominated flame retardants, fluorinated compounds, and other emerging pollutants [10]. It has been shown that the pollutant load in these seabirds affect the enzyme and immune defense systems, hormones, reproduction, and survival [10].

1.3.6.2 Mammals

At the top of the Arctic marine food web are Polar bears. As a result of this, polar bears are exposed to high levels of bioaccumulating pollutants and persistent organic pollutants. Persistent organic pollutants have demonstrated negative effects on the hormone, vitamin, enzyme, and immune systems of polar bears [10], and research indicates that higher pollutant loads in polar bears may be correlated with higher offspring mortality [10]. Recently there has been discovered many previously unknown halogenated compounds in polar bear serum [13].

Another predator high in the Arctic food web is the arctic fox. Arctic foxes mainly eat birds and carrion, and are linked to both terrestrial and marine food webs. The combination of arctic foxes relatively high exposure to pollutants and large variations in the amount of stored fat throughout the year makes them especially vulnerable to pollutants stored in lipids, as these are released into the body when the fat is burned for energy. The amount of stored fat in arctic foxes varies from over 20 % in November-December to 6 % in the summer [10]. A study of young arctic foxes from West Spitsbergen has shown a reduction in persistent organic pollutants between 1997 and 2010 (Andersen et al. unpublished) [10].

1.3.7 Permafrost and Global warming

Permafrost is defined as ground (soil or rock and any ice and organic material inclusions) that remains at or below 0°C for two consecutive years or longer [23]. The role of permafrost in the carbon cycle, infrastructure, and natural hazards is being increasingly acknowledged [24].

Rising global temperatures may affect both how pollutants are transported and deposited, and the amount of research into this is increasing [10]. One possible effect of permafrost thawing is remobilization of pollutants trapped in the frost back into the air. This has already been observed with the most volatile compounds. Research has shown that this is happening to several POPs and mercury, particularly in the interface between sea, air and ice [10].

1.3.8 Emerging Organic Pollutants

The 2016 assessment of chemicals of emerging arctic concern by the Arctic Monitoring and Assessment Program (AMAP) included 150 chemicals and groups of compounds reported in the Arctic [25]. However, this is just a tiny fraction of the ~150 000 chemicals registered for use in Europe and North America in the past 30 years [26].

A recent study by Muir et al. (2019) [26] reviewed computer based screening for POPs, as well as targeted, suspected, and non-target screening approaches for identifying previously unidentified chemicals of concern. Lists of suspected chemicals generated by computer-based screenings is typically used in targeted and suspected screenings typically use, while non-target screenings search for complete unknowns by mass, isotope patterns, retention time, and fragmentation patterns. Non-target screening is a relatively new approach enabled by advancements in high-resolution mass spectrometry (HRMS) coupled to liquid chromatography (LC) or 1- or 2-dimensional gas chromatography (GC, GC-GC). Non-target screening is increasingly used to search for chemicals in environmental and biological samples, and shows great promise in screening for POPs end emerging organic pollutants [13, 27-33].

The study by Muir et al. (2019) [26] found that even after recent updates many compounds found in chemical inventories in both Europe and North America exhibit POP-like characteristics. 253 of 3421 said compounds were in the REACH (2018) inventory, 1138 were on the US EPA TSCA list [34], and 279 were on the USEPA Chemical Data Reporting list. Additionally, a study by study by Strempel et al. (2012) [35] found that 5.2% of chemicals registered between 1982 and 2007 in the ELINCS had persistent, bioaccumulating, or toxic (PBT) characteristics.

1.4 Non-target Screening Background

The development of high-resolution mass spectrometry (HRMS) coupled to gas and liquid chromatographic systems has led to a new trend in analytical chemistry, especially in environmental analysis [31]. Non target screening methods are used to complement data from targeted analytical methods. Non-target screenings typically use tandem MS (MS-MS) to obtain fragmentation that can aid in the identification of compounds in addition to retention times, isotope patterns, and mass to charge ratios [31, 36], which can be used to identify the compounds present in the sample through the use of advanced data processing tools and comparison with mass spectral libraries. A follow-up targeted analysis can be used to more confidently confirm the presence and concentration of particular compounds of interest detected during the non-target screening [36].

Following is a summary of three main approaches towards substance identification from Schymanski et al. (2015) [31]

1. A targeted screening is used for quantitative and semi-quantitative analysis of a single or a small group of specific compounds. A reference standard is used to aid in confirmation and quantification and should have similar properties to the target analyte(s).
2. A suspected screening is used to confirm the presence of a compound or group of compounds that is, based on prior information, suspected to be present in the sample. Although a reference standard often not available in a suspected screening, the structure is known, and thus the RT, mass to charge ratio (m/z), fragmentation, and isotopic ratios can be used for confirmation.
3. A non-target screening has no target compound(s), and thus there is no prior information available. The screening provides information on m/z, fragmentation, isotopic ratios, and RT of the compounds in the sample, which is then used to form a list of suspected compounds and structures present in the sample, which can then be confirmed by suspected or targeted screenings.

While non-target screenings produce large amounts of data on the compounds present in a sample, the existing information available is still a limiting factor for identification. This may limit the number of compounds that be positively identified in a sample, and how useful the information gathered from the screening is in predicting characteristics of interest regarding the sample, like toxicity without time-consuming follow-up studies. Recent advances in software that can predict structures of compounds given the information gathered from the non-target screening shows promise as a way to counteract this limitation. A recent paper by Peets et al. (2022) [37] presents a new method to rapidly assess the toxicity of compounds and mixtures using non-target screening with MS-MS followed by a machine learning algorithm to predict toxicity based on the fragments produced. This method focuses on functional groups, that are more easily identified from fragments, and is tested and validated with existing toxicological data. This and similar methods have the potential to significantly reduce the time and cost of analyzing the toxicity of pollution in water, and might be develop further for other uses in ecotoxicology. A crucial consideration when analyzing samples with respect to pollution, is the effect on flora and fauna. As different toxic compounds might enhance or inhibit the toxicity of each other in complex solutions, making it challenging to accurately predict the toxicity.

1.4.1 The Non-target screening Workflow

The result of the pre-project was the formulation of a generalized six-step non-target screening workflow, with the identification of important considerations for all six steps. The six steps are as follows: Sampling, Extraction, Preparation, Screening, Data processing, and Confirmation. The workflow and important considerations for each step is summarized in figure 1.

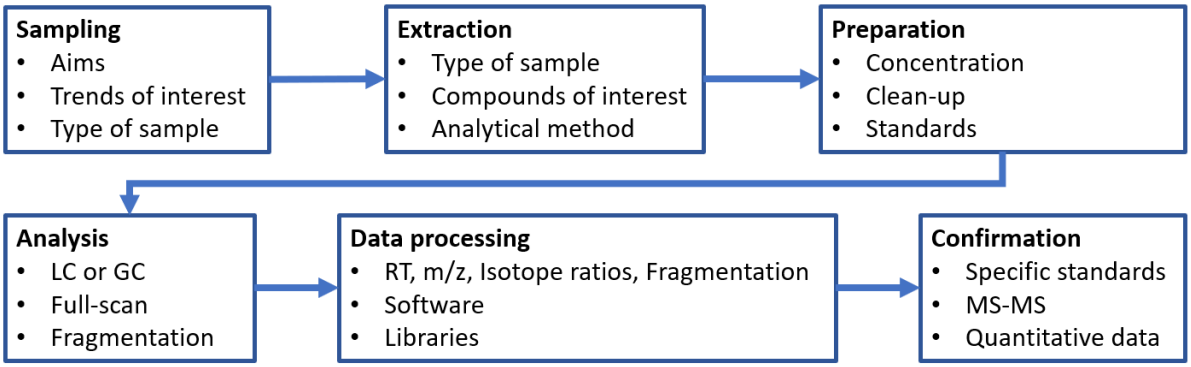


Figure 1: The Non-target screening workflow, with important considerations per step.

2 Instrument and Method Theory

2.1 High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) is a qualitative and quantitative technique which separates analytes in a liquid mobile phase under high pressures. The pressures are normally up to 400 bar, but even higher pressures can be achieved [38]. Different mobile phases (MP) and stationary phases (SP) can be used depending on the characteristics of the target analytes, separated into two main categories; normal-phase chromatography (NPC), and reverse-phase chromatography (RPC). The MP typically consist of two different solvents, with the ratio of these often being varied throughout the procedure in what's called a gradient elution program. This gives an opportunity to exploit the polarity of the analytes, where the changing of the solute over time affects the retention of the analytes [39]. In NPC, the SP is polar, while the MP is a mixture of less polar organic solvents, while in RPC the SP is nonpolar, or less polar, and the MP is a polar mixture of water and/or more polar organic solvents. RPC is the most popular liquid chromatography method, as it gives greater versatility of applications. The instrumentation of HPLC is generally built like the illustration in figure 2, and contains a solvent delivery system, injector, column, and detector.

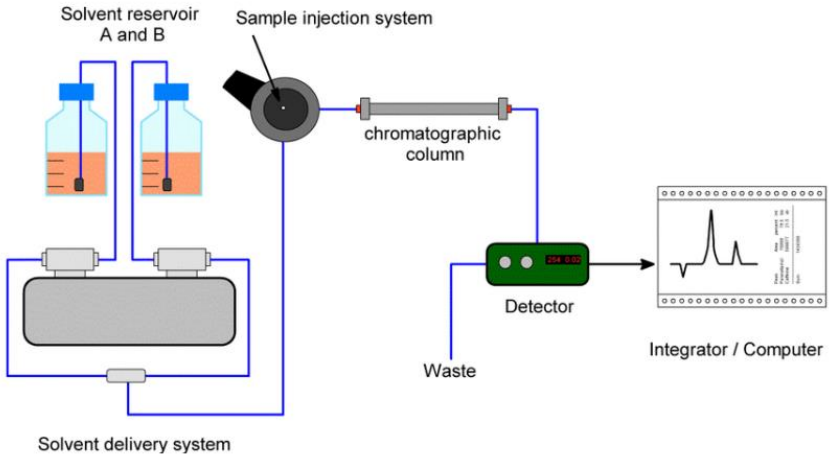


Figure 2: Schematic illustration of a HPLC instrumentation, from Scherf-Clavel (2016) [40]

Several different detectors can be employed with HPLC, among others the UV detector, fluorescence detectors, light scattering detectors and mass spectrometers. [38].

2.2 Electron Spray Ionization

Electron spray ionization is an atmospheric ionization method, and thus not compatible with GC, used for compounds with polar groups. In ESI different types of compounds are ionized differently, acids deprotonate, bases protonate, while neutral compounds either protonate or deprotonate depending on the conditions. The ionization of compounds is achieved through pH adjustment and occurs in the mobile phase [40]. The process of ESI is illustrated in figure 3.

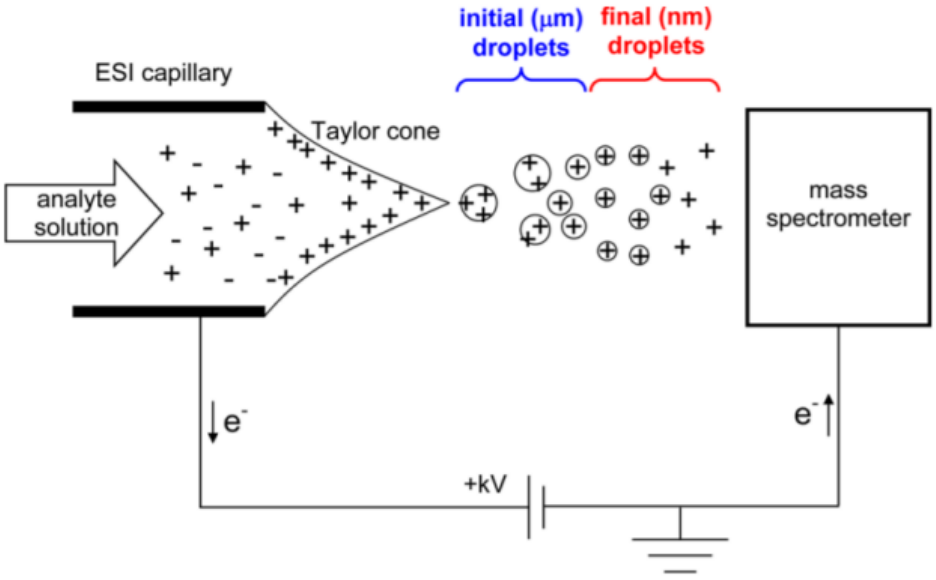


Figure 3: Illustration of an ESI operating in positive mode, from Konermann et al. (2013) [41].

The mobile phase is sent through a metal capillary with a potential of 3-6 kV, a positive potential generates positive ions, and a negative potential generates negative ions. This creates a spray of fine droplets directed at a sampling opening located between 1 and 3 cm from the capillary tip [40]. The ions are transferred to the gas phase by shrinking the charged droplets from the capillary through evaporation of the solvent from the droplets. A coaxial gas flow and heat are used to aid the evaporation of the solvent. As the droplets shrink the coulomb repulsion within the droplets eventually overcomes the surface tension, and the droplets split. This repeats several times, until the ions end up in the gas phase. There are two models explaining the last step. According to the evaporation model the ions are desorbed into the gas phase when the droplets reach a size of 10 nm. Alternatively, according to the charge residue model, the droplets continue to split until each droplet contains at most one ion and the solvent evaporates until the ions are left in the gas phase [40].

2.3 Mass Spectrometry

2.3.1 Triple Quadrupole Mass Spectrometry

A quadrupole is a type of mass analyzer that is made of four identical, parallel, rod-shaped poles called a quadrupole. A quadrupole uses variable direct current (DC) and radio frequency (RF) to create an oscillating electrical field [38]. This field can operate as a mass filter for the selection of a specific m/z, or in RF only mode where all ions are transmitted through the quadrupole. When operated as a mass filter the ions with selected m/z will resonate stably, and the m/z selected can be varied by varying the electrical field of the quadrupole [38]. A triple quadrupole (QqQ) unit consists of three linear connected quadrupole units. In a QqQ Only the first (Q1) and the third unit (Q3) are used for scanning as regular mass analyzers, while the second quadrupole (Q2) acts as a collision cell where ions are bombarded by neutral gas molecules, such as nitrogen or argon, to induce fragmentation by a process known as collision induced dissociation (CID). The Q2 can also act in RF-only mode without subsequent fragmentation of ions [41]. The energy of the collisions can be controlled to control the fragmentation. Figure 4 illustrates the schematics of a triple quadrupole [41].

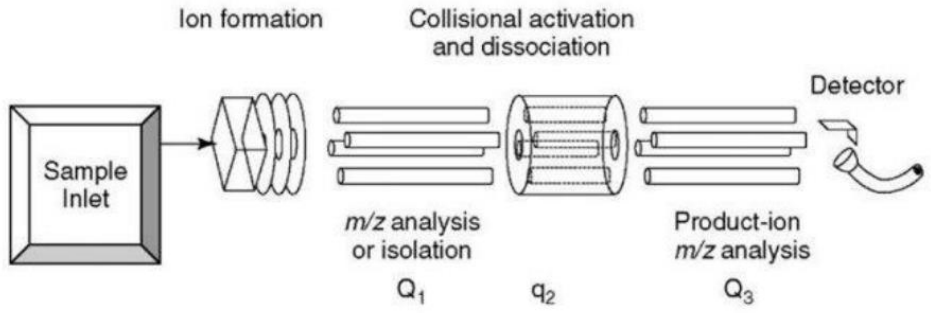


Figure 4: Schematic illustration of a triple quadrupole, from Ullmann's Encyclopedia of Industrial Chemistry [43]

Multiple reaction monitoring (MRM) is the most common quantification method used in conjunction with QqQ. In MRM, Q1 separates an ion known as the precursor or parent ion, that corresponds to the compound of interest [41]. The ion is then fragmented in the collision cell, Q2, which produces multiple daughter ions. The daughter ions are then analyzed in Q3. The transition from parent ion to daughter ion is highly specific for each compound, which makes MRM a highly specific method of quantification. The most abundant daughter ion is typically chosen for quantification, and the second most abundant daughter ion is chosen for qualification. The high specificity and mass selectivity of MRM enables separation of compounds with identical chemical properties but different masses, such as isotope marked compounds [41]. The triple quadrupole is a low resolution MS, better suited for targeted screening.

2.3.2 Quadrupole Time-Of-Flight Mass Spectrometry

Q-TOF-MS is a 'hybrid' instrument combining quadrupole technologies with a time-of-flight mass analyzer. Q-TOF-MS instrumentation closely resembles that of a triple-quadrupole mass spectrometer, with the third quadrupole being replaced by a time-of-flight tube. Both Q1 and Q2 operate in the same way as in a triple quadrupole [42]. After leaving Q2, the ions are reaccelerated into the ion modulator region of the time-of-flight analyzer, where they are accelerated orthogonally to their original direction by being pulsed by an electric field. This gives all the ions the same kinetic energy as they enter the flight tube, which is a field free drift region where mass separation occurs. Ions with a smaller mass will drift with a higher velocity, and thus use shorter time to reach the detector [42]. A reflection device is utilized in modern time-of-flight analyzers to correct for kinetic energy dispersion and spatial spread of ions that have the same *m/z* but varying velocities. The result of this reflection correction is that ions with the same *m/z* will reach the detector at the same time. Additionally, the reflection device increases the flight path length which improves mass resolution [42]. A schematic of a Q-TOF-MS is illustrated in figure 5.

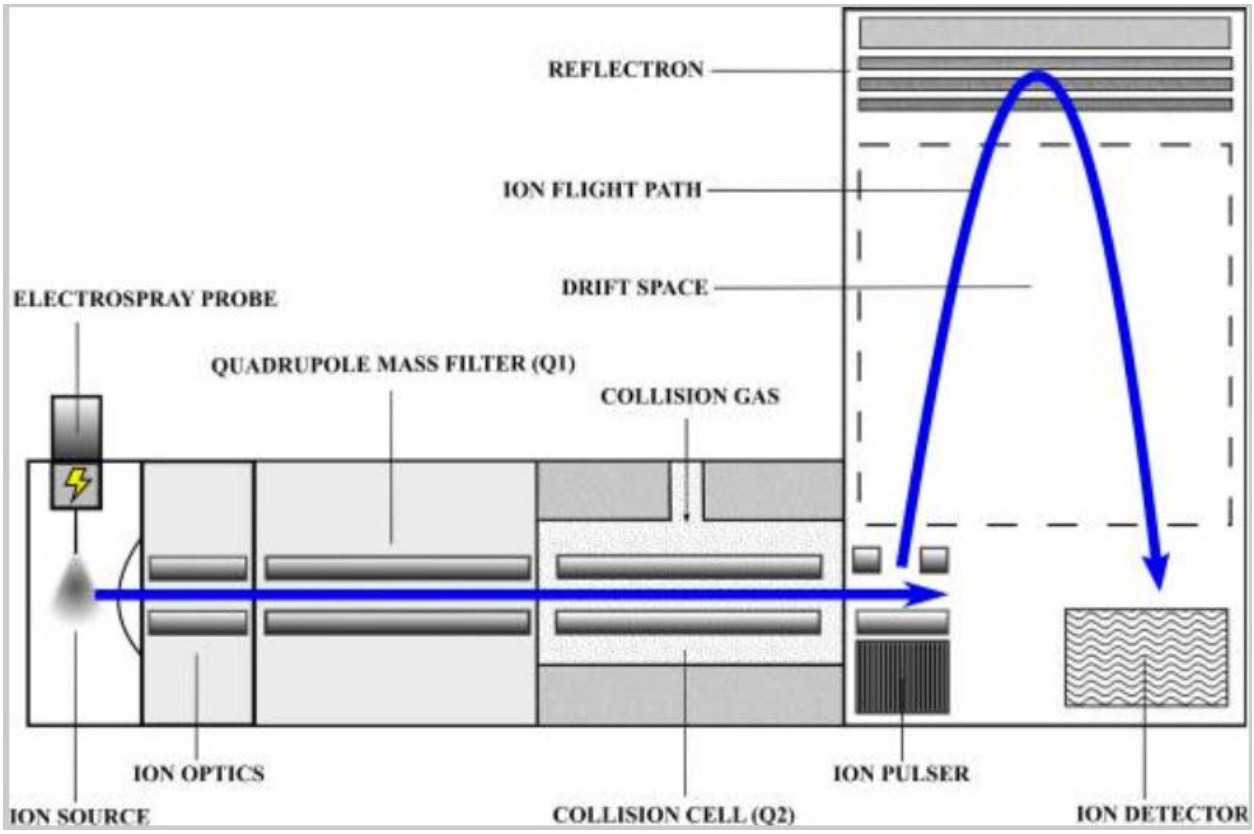


Figure 5: Q-TOF-MS Schematic, from Allen and McWhinney [45].

Since Q-TOF-MS is a hybrid instrument, utilizing both quadrupole and time-of-flight technology, two different scan types can be used for data acquisition. By using the Q2 in RF mode, the Q-TOF-MS gives an accurate scan of the masses of the unfragmented precursor ions. In this mode Q1 can be used in RF mode to provide a full scan, or as a mass filter to select specific masses or ranges of masses to be analyzed. This is known as single MS mode [43]. The second mode, known as MS-MS mode, functions the same way as a triple quadrupole tandem MS, but with Q3 being replaced with the TOF tube [43].

2.4 QA and QC

2.4.1 LOD and LOQ

Limit of detection (LOD) and limit of quantification (LOQ), or lower limit of quantification (LLOQ) and upper limit of quantification (ULOQ), are the defined as the measure, of concentration or quantity, that can be detected (LOD) or quantified (LOQ) with reasonable certainty for a given analytical procedure.
LOD and LOQ can be determined using several different methods, and the LLOQ often being derived from the LOD, with an LLOQ equal to 3.3 times the LOD being a typical choice [44].

One of the more common ways of determining LOD and LOQ is by signal to noise ratio (SN). With this method the height, or absolute strength of the signal, being compared to the average strength of the surrounding noise. When using this method, it is typical to use a SN of 3:1, but in cases where higher certainty is need, a SN of 10:1 might be used. When using a LOD of SN 3:1 it is typical to use SN 10:1 as the LOQ [44] [45].

Another method is the use of limit of blank (LOB), in this method the average signal from blank samples is calculated, and the LOD is defined as the mean signal of the blanks plus n times the standard deviation, with n being a numerical value corresponding to the desired confidence level[46] [47], n=2 or n=3.3 are typically used.

Using a calibration curve to determine LOD and LOQ is a popular and precise method, but requires the analysis to include the calibration curve solutions, a series of standard solutions with different concentrations covering the expected signal range. When using a calibration curve, the LOD is set as 3.3 times the standard deviation of the blank, the regression line, and the y-intercepts of the regression line, and the slope of the calibration curve[45].

When using a calibration curve the LLOQ is either calculated from the LOD, or set as the point where the calibration curve goes from being curved to linear. The ULOQ is the highest concentration in the calibration curve [45].

2.4.2 Standards

External and internal standard method are the two most common types of standards used in analytical chemistry [38]. The external standard method is based on known standards of varying concentration run separately from the samples to create a response curve. The sample concentration can be determined by comparing the response from the sample with the response from the standard. The standard should be prepared in the same matrix as the sample [38]. In the internal standard method, the standards are added to the sample at some stage of sample preparation before analysis. The internal standard must be different from the analyte and should have no interaction with the analyte or the matrix. The matrix should also not contain the any of the standard beforehand. It is important that the standard has similar properties to the analyte, to ensure they are extracted and detected at rates comparable to the analyte. The ratio of analyte signal to internal standard signal is plotted against the concentration of analyte in the standard solution, and the analyte concentration can be determined by the resulting curve [38]. The benefit of using internal standard over external is that internal standard method can correct for losses during the preparation of the sample after the standard was added, since the ratio of internal standard and analyte concentration will be constant even with loss of volume. In the external standard method the accuracy and precision of the sample injection volume is critical [38].

2.4.3 Recovery and matrix effect

Loss of some analyte during treatment, pretreatment and work-up of samples in analysis of complex matrices is common. This loss can be calculated and accounted for by calculating recovery, giving a measure of the efficiency of the extraction. This is done by spiking the samples with a known amount of internal standard prior to work-up and treatment, and comparing the estimated concentration in the analyzed sample with the actual concentration in the sample after addition of the standard. A general formula for calculation of recovery % is shown in equation 2.1 [48].

$$Recovery\ (\%) = \frac{Measured\ concentration}{Original\ concentration} * 100\% \quad (2.1)$$

A measurement related to recovery is matrix effect, which is calculated to determine how and to what degree the matrix affects the signal of an analyte. A special variant of spiked samples, matrix match samples, which are spiked with a known concentration after extraction as opposed to prior to extraction.
A formula for calculating matrix effect is shown inequation 2.2 [49].

$$Matrix\ effect\ (\%) = \left(\frac{A_{\overline{MM}} - A_{\overline{B}}}{A_{STD}} - 1\right) * 100\% \quad (2.2)$$

Where $A_{\overline{MM}}$ is the average area of the peaks in the matrix match samples, $A_{\overline{B}}$ is the average area of the peaks in the procedure blanks, and A_{STD} is the area of the peak in the standard solution with the same concentration as the matrix match samples.

2.5 Properties of PFAS

The physical and chemical properties of a compound have a significant impact on extraction and analysis methods. Properties like water solubility, log K_{OW}, log $K_{OC,}$ and pK_A affects how a compound is extracted. The available data on these properties for PFAS compounds is limited, and data on water solubility, log K_{OW}, and pK_a and other related properties is, to the authors knowledge, not available for many PFAS compounds like Perfluorooctanoic Sulfonamides and Fluorotelomer sulfonic acids. Two papers, Goss (2008) [50] and Rayne et al. (2009) [51] provide predicted pK_As for PFCAs and derivatives, and PFSAs respectively. Goss (2008) reports pK_As in the range of -0.2 to 0.8 for PFCAs with C4-12, while Rayne et al. (2009) reports pK_As in the range of -8.6 to -2.6 for PFSAs with C4-8. Two other sources of data on the properties of PFAS compounds include SGS and the Interstate Technology Regulatory Council (ITRC) provide comprehensive datasets on many properties for many different PFAS compounds. The data from ITRC [52] is compiled from many different sources, and the range of reported values for a property of a compound often spans several orders of magnitude, making the data difficult to use. The data collected by the ITRC on log K_{OC} for PFAS compounds are in the range of 0.5 to 6 in sediment, with most compounds having a log K_{OC} between 2.0 and 4.0 [52]. SGS provides reliable and up to date data, however the data is severely limited for most groups of PFAS excluding PFCAs and PFSAs. An overview of the available data on the properties of PFAS from SGS, Goss (2008) [50] and Rayne et al. (2009) [51] is shown in table 1. The pK_A is presented as the range of values per group of chemicals.

Table 1:Water solubility and pKA range for PFCAs, PFSAs, and FTSs.

Compound	Solubility in water (g/L)	pKa range
PFBA	Miscible	-0.2 to 0.8
PFPeA	112.6	
PFHxA	21.7	
PFHpA	4.2	
PFOA	3.4-9.5	
PFNA	9.5	
PFDA	9.5	
PFUnA	0.004	
PFDoDA	0.0007	
PFTriDA	0.0002	
PFTDA	0.00003	
PFBS	46.2-56.6	-8.6 to -2.6
PFHxS	2.3	
PFOS	1.5	
PFDS	0.0002	
4:2 FTS	27.9	1.3
6:2 FTS	1.3	
8:2 FTS	0.06	
10:2 FTS	0.002	

3 Method

The primary goal of this thesis was to test two extraction methods for sediment samples, one for the analysis of polar substances and the other for non-polar substances. Both methods were tested with spiked and un-spiked samples of pooled sediments from the Barents sea. The non-polar extraction method was tested with a CP spiking mixture, and the polar extraction method was tested with a PFAS spiking mixture. Both spiking mixtures encompassed compounds with a wide range of physicochemical properties to their respective groups. The intent was to evaluate the usefulness of both extraction methods in both targeted and non-targeted screening applications.

The secondary goal of this thesis was to use the evaluated extraction methods, along with both targeted and non-targeted screening techniques, to analyze sediment samples from the Kara sea to provide both qualitative and quantitative data on POPs and their distribution in the Kara sea.

3.1 Sampling and Sample Treatment

The samples were donated by Murat van Ardelan from a larger set of samples used in a Master's thesis by Anzjøn (2022)[53]. The sampling locations of the samples used is presented in figure 6, the samples were given a number from 1 to 6 in this thesis for simplicity's sake. The original sample IDs and new number is presented in table 2. The sampling was done by a Russian team in 2021 using a multi-corer. The samples used are from the final block section and were divided into plastic tubes with a lid in the ship's laboratory within 4-8 hours of sampling. The samples were initially collected with metals as the intended target analytes, and such were collected with plastic equipment. Sampling was done according to ISO 5667-19 (ISO 2004). The samples were stored in a freezer during transportation and were sent to Trondheim, Norway, from Russia. In Trondheim, the samples were put in the freezer (-22 °C) until treatment. All equipment used in the sample preparation was washed with 1,2 M ultra-pure HNO_3 and MilliQ water. Sample preparation was performed in a laminar flow chamber under low clean airflow to avoid contamination. The samples were frozen in 50 mL tubes after sampling. To reduce the freeze-drying time, the samples were subsampled into smaller tubes (25 mL). These tubes were cleaned with 1 M HNO_3 for approximately 12 hours and then rinsed three times with MilliQ water. The frozen sediment samples were thawed in a refrigerator and approximately 15 mL of sediment was transferred with a plastic spatula. The subsamples were then put back into the freezer for at least 24 hours, ensuring the entire sample was frozen before freeze-drying.

Table 2: Original IDs of samples and their new number.

Original ID	Number
7253	1
7247	2
7218	3
7212	4
7194	5
7192	6

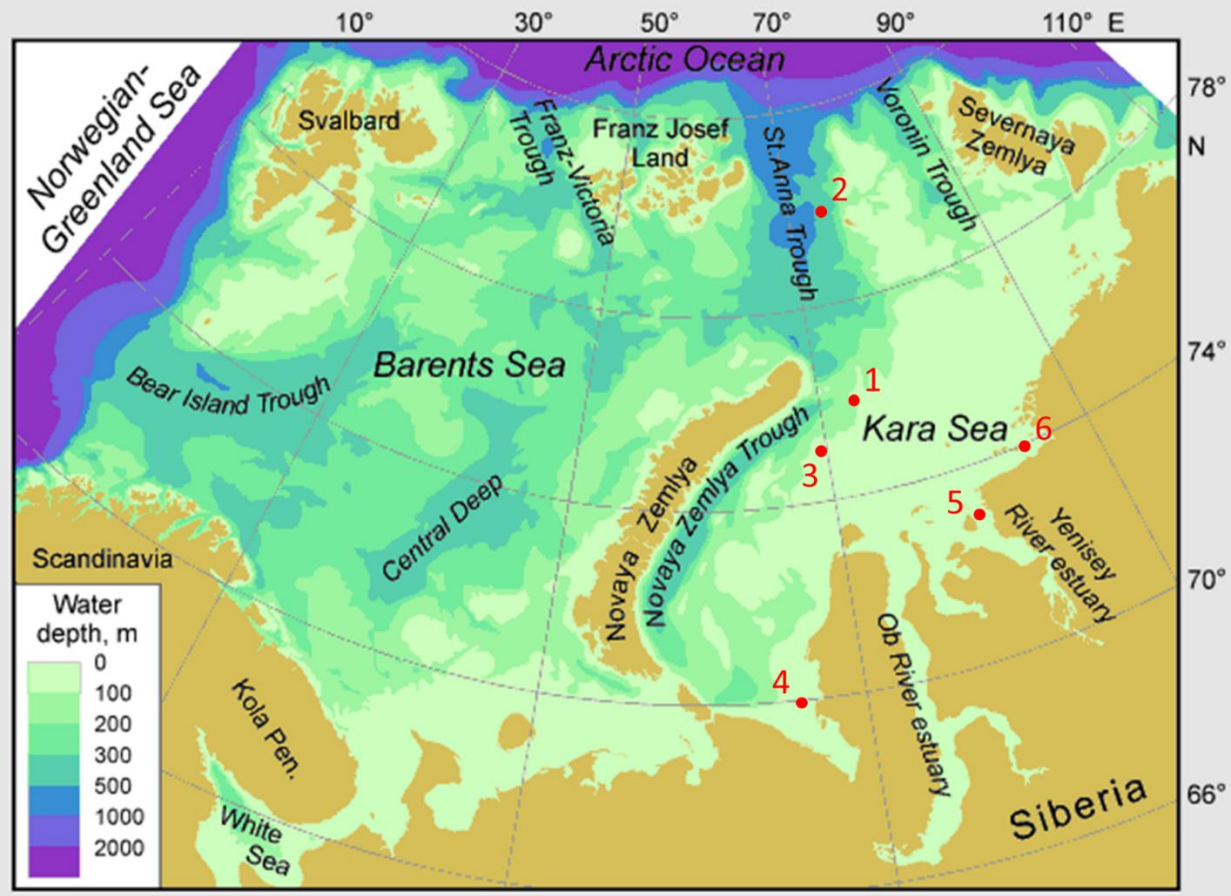


Figure 6: Sampling locations of the samples from the Kara sea. Graphic edited from polarbearscience.com.

3.2 Extraction

3.2.1 CP extraction

The CP extraction method is adapted from Nylund et al. (1992)[54].

All solvents used were HPLC grade (HiPerSolv CHROMANORM), and all reagents were of analytical purity (AnalR NORMAPUR). All containers and equipment were rinsed three times with HPLC grade acetone before use. The standard chemicals used are listed in Table A1.

A pooled sediment sample from the Barents Sea was used during method development. A total of nine samples were analyzed (3x sample, 3x spiked sample, and 3x blank). 50µL spiking solution was added to the spiked samples together with the internal standard (refer to table 3 and table A1 in appendix A for details), and the blanks used an appropriate amount of baked silica powder instead of sediment.
~3 grams of wet sediment were transferred to a weighed 50 ml centrifuge tube (tube A).

The tube was centrifuged (3500 rpm, 10 min), the supernatant was removed, the tube was weighed again, and the mass of the sediment was calculated. 10 mL of acetone and 50µL internal standard solution were added to the tube. The tube was then rotated (~30 rpm, 60 min). After rotation, the tube was centrifuged (3500 rpm, 10 min) again, and the supernatant was transferred to a new 50 ml centrifuge tube (tube B). 12.5 ml ultrapure water with a 0.2 M NaCl and 0.1 M phosphoric acid was added to the tube containing the supernatant (tube B). 10 mL of mix 3:1 of n-hexane and acetone was added to the tube containing the sediments (tube A). The tube (tube A) was then rotated (~30 rpm, 30 min) and centrifuged (3500 rpm ,10 min). The supernatant was transferred to tube B. Liquid-liquid extraction was then performed, the organic phase transferred to a 15 ml centrifuge tube (tube C), and the water phase re-extracted with 2.5 mL of a 9:1 mix of n-hexane and diethyl ether. The organic phase was again transferred to the 15 ml tube (tube C), and the combined organic phase was concentrated to ~2 ml in a water bath (35°C) with nitrogen flow. Copper powder was activated using 6M HCl (37% HCl diluted in ultrapure water), then rinsed 10 times with ultrapure water and 10 times with acetone.

After concentration, the sample was cleaned with activated copper powder, centrifuged at 3500 rpm for 10 minutes, then cleaned using Supelclean LC-Si SPE Tube (2 g silica gel, 12 mL). 14 ml of a 1:1 mix of n-hexane and DCM was used to flush the sample through the SPE cartridge. The sample was concentrated to ~0.1 ml in a water bath (35°C) with nitrogen flow, then diluted in 10 mL acetone. After dilution the sample was concentrated to 1mL in a water bath (35°C) with nitrogen flow before being transferred to a 2ml GC-vial.

Table 3: Concentrations of standards, SCCPs, MCCPs, and LCCPs in the standard and spiking solutions.

Category	concentration ng/uL
13C-1,5,5,6,6,10-Hexachlorodecane	**0,20**
13C-1,1,1,3,10,12,12,12-octachlorododecane	**0,20**
CP-mix (SCCPs)	1,94
CP-mix (MCCPs)	4,68
CP-mix (LCCPs)	9,29

3.2.2 PFAS extraction

The PFAS extraction method is adapted from Powley et al. (2005) [55].

All solvents used were HPLC grade (HiPerSolv CHROMANORM), and all reagents were of analytical purity (AnalR NORMAPUR). All containers and equipment were rinsed three times with HPLC grade methanol before use. The standard chemicals used are listed in Table A3.

A pooled sediment sample from the Barents Sea was used during method development. Sediment from six locations in the Kara Sea was also analyzed, with one replicate (n=1) per location. A total of eighteen samples were analyzed (3x pooled sample, 3x spiked pooled sample, 3x procedure blank, 6x individual samples, and 3x matrix match pooled samples). 10µL spiking solution (100 pg/uL 40x PFAS in methanol, refer to tables 4, 5, and 6, and tables A2 and A3 in appendix A for details) was added to the spiked samples together with the internal standard solution (1000 pg/uL ^{13}C PFOA, PFOS, and 6:2FTS in methanol, refer to table 4, 5, and 6, and tables A2 and A4 in appendix A for additional details), the blanks used an appropriate amount of baked silica powder instead of the sediments, and the matrix matched samples had the IS and spiking solution added at the end of the extraction, after being transferred to LC-vials. The six individual samples consisted of dried sediments instead of wet sediments, and an equivalent amount was added to the samples in question.

~1g of wet sediment or ~0.5g of dry sediment was transferred to a weighed 50 ml centrifuge tube. The tube was then weighed again, and the mass of the wet sediment was calculated. 10µL of internal standard was added together with 1ml of 200mM-NaOH in methanol and the sample was left to soak for 30 minutes.

100µL 2M HCl in MeOH was added, the tube was then capped and vortex-mixed before being placed in an ultrasonic bath for 10 minutes. The vortex-mixing and ultrasonic bath was repeated two more times, for a total of three times. The sample was then centrifuged (2000 rpm, 5 min) and the supernatant transferred to a 15 ml centrifuge tube. The sample was concentrated to ~1 ml by evaporation in a water bath (35°C) with nitrogen flow.

The concentrated sample was then transferred to a 1.5 ml Eppendorf centrifuge tube containing 25 mg Supelclean ENVI-Carb 120/400 and 50 µL glacial acetic acid. The sample was vortex-mixed, then centrifuged (10 000 rpm, 10 min) and the supernatant transferred to a 2 ml vial for storage.

Table 4: Formulas, names, and structures of Internal standards and PFCA compounds in the PFAS spiking mix and internal standard solution.

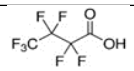
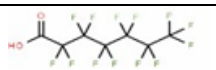
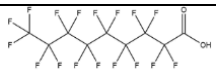
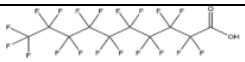
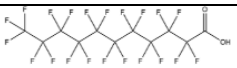
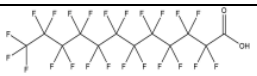
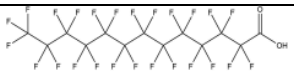
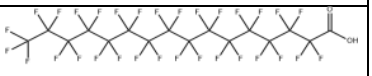
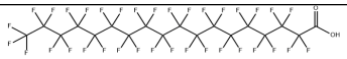
Compound	Formula	Name	Structure
PFOS 13C	**13C8F17O3S**	**Perfluorooctanesulfonate 13C8 sodium salt**	
6:2 FTS 13C	**C6(13C2)D4H1F13O3S**	**1D,2D-Perfluorooctane sulfonate (6:2) 13C2**	
PFOA 13C	**13C8HF15O2**	**Perfluorooctanoic acid 13C8**	
PFBA	C4HF7O2	Perfluorobutanoic acid	
PFPeA	C5HF9O2	Perfluoropentanoic acid	
PFHxA	C6HF11O2	Perfluorohexanoic acid	
PFHpA	C7HF13O2	Perfluoroheptanoic acid	
PFOA	C8HF15O2	Perfluorooctanoic acid	
PFNA	C9HF17O2	Perfluorononanoic acid	
PFDA	C10HF19O2	Perfluorodecanoic acid	
PFUnA	C11HF21O2	Perfluoroundecanoic acid	
PFDoDA	C12HF23O2	Perfluorododecanoic acid	
PFTriDA	C13HF25O2	Perfluorotridecanoic acid	
PFTDA	C14HF27O2	Perfluorotetradecanoic acid	
PFHxDA	C16HF31O2	Perfluoro-n-hexadecanoic acid	
PFOcDA	C18HF35O2	Perfluorooctadecanoic acid	

Table 5: Formulas, names, and structures of PFSA and FTS compounds in the PFAS spiking mix.

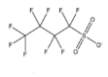
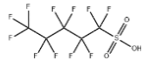
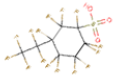
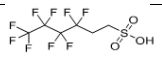
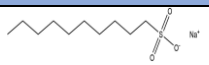
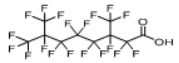
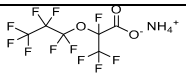
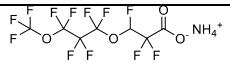
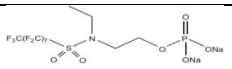
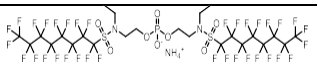
Compound	Formula	Name	Structure
PFBS	C4F9SO3	Perfluorobutanoic acid sulfonate	
PFPeS	C5HF11O3S	Perfluoropentane sulfonic acid	
PFHxS	C6HF13O3S	Perfluorohexane sulfonic acid	
PFHpS	C7F15O3S	Perfluoro-1-heptanesulfonate	
PFOS	C8F17O3S	Perfluorooctano sulfonic acid	
PFNS	C9HF19O3S	Perfluorononane sulfonic acid	
PFDS	C10HF21O3S	Perfluorodecane sulfonic acid	
PFDoDS	C12HF25O3S	Perfluorododecane sulfonic acid	
PFECHS	C8HF15O3S	Perfluoroethylcyclohexane sulfonic acid	
4:2 FTS	C6H5F9O3S	1H,2H-Perfluorohexan sulfonate (4:2)	
6:2 FTS	C8H5F13O3S	1H,2H-Perfluorooctane sulfonate (6:2)	
8:2 FTS	C10H5F17O3S	1H,2H-Perfluorodecan sulfonate (8:2)	
10:2 FTS	C12H5F21O3S	1H,2H-Perfluorododecan sulfonate (10:2)	

Table 6: Formulas, names, and structures of miscellaneous compounds in the PFAS spiking mix.

Compound	Formula	Name	Structure
DecaS	C10H21O3S	Sodium 1- decanesulfonate	
P37DMOA	C10HF19O2	Perfluoro-3,7-dimethyloctanoic acid	
7H-PFHpA	C7H2F12O2	7H-Dodecafluoroheptanoic Acid	
FOSAA	C10H4F17NO4S	Perfluoro-1-octanesulfonamidoacetic acid	
MeFOSAA	C11H6F17NO4S	2-(N-methylPerfluoro-1-octansulfonamido)acetic acid	
ETFOSAA	C12H8F17NO4S	N-ethylPerfluoro-1-octanesulfonamide acetic acid	
PFOSA	C8H2F17NO2S	Perfluorooctane sulfonamide	
MeFOSA	C9H4F17NO2S	Sulfluramid	
EtFOSA	C10H6F17NO2S	N-methylPerfluoro-1-octanesulfonamide	
MeFOSE	C11H8F17NO3S	N-(2-hydroxyethyl)-N-methylperfluorooctane sulfonamide	
EtFOSE	C12H10F17NO3S	N-ethyl-N-(2-hydroxyethyl)-N-methylperfluorooctane sulfonamide	
GenX	C6H4F11NO3	2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate	
ADONA	C7H5F12NO4	dodecafluoro-3H-4,8-dioxanonanoate	
9Cl-PF3ONS	C8ClF16KO4S	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	
SAMPAP	C12H9F17NO6PS	2-(N-ethylperfluorooctane-1-sulfonamido)ethyl phosphate	
diSAMPAP	C24H22F34N3O8PS2	bis[2-(N-ethylperfluorooctane-1-sulfonamido)ethyl] phosphate	

3.3 Analysis

3.3.1 Analysis of Non-polar Compounds CPs (QTOF)

Analysis was performed with a direct injection method to a chloride-anion attachment APCI-QTOF-MS (Synapt G2, Waters, Manchester, UK) operating in full scan mode with a scan range of m/z 250-1200. The collision voltage was set to 0.7 V and cone voltage to 30 V, with a source temperature of 100°C. The resulting resolution was observed at 25,000 FWHM. Detector responses were studied for m/z ratios that corresponded to [M+Cl]- of 129 homologues, ranging from C10Cl3 to C22Cl12. The quantification methodology was based on Tomy et al. (1997) [56]. Here, the sum detector responses of S/M/LCCP homologues were used to quantify the total concentrations of each CP mixture category.

3.3.2 Analysis of Polar Compounds PFAS (UPLC-QqQ)

The method used was adapted from Trimmel et al [57].
Chromatographic separation was performed using an ACQUITY UPLC I Class® system connected to (Waters, Milford, CT, USA) coupled to a triple quadrupole mass analyzer (QqQ; Xevo TQ-S) with a ZSpray ESI ion source (Waters, Milford, CT, USA). A Kinetex C18 column (30 × 2.1 mm, 1.3 µm, 100Å. Phenomenex, Værløse, Denmark) serially connected to a Phenomenex guard column (C18, 10 × 2.1 mm) chromatographic column was used for reverse-phase separation. The column temperature was set to 30°C. The chromatographic separation was carried out using a gradient elution program with 2 mM ammonium acetate in water (A) and MeOH (B) as binary mobile phase with a flow rate of 0.25 µL/min. The gradient elution program is shown in table 7. The injection volume was 4 µL. The electrospray ionization (ESI) was applied at a potential of −2 kV. The cone voltage was set to 25 V and the source offset voltage was set to 40 V. The cone gas (N2) was set at a flow rate of 150 L/h. The desolvation temperature was set at 450 °C and the desolvation gas flow rate at 650 L/h. The nebulizer was set at 6 bar and the source temperature was set at 150 °C. The calibration of the ESI method was verified by injecting solvent calibration standards at concentrations of 0.009–50.0 ng/mL (0.009, 0.05, 0.10, 0.90, 5.00, 20.0, 50.0 ng/mL).

Quantification of the target analytes was accomplished based on the internal standard method and with matrix-matched calibration standards prepared by spiking target analytes into the pooled sediment matrix after extraction. The accuracy (trueness) was evaluated through recovery experiments at the fortified amount of 1 ng of the target PFAS; absolute and relative recoveries percentages were calculated in three replicates (N = 3). The method matrix effects for PFAS analysis were assessed at the same fortification amount in three replicates (1 ng; N = 3). The UPLC-QqQ data was analyzed with MassLynx v4.1 software, TargetLynx (Waters, Milford, CT, USA), and Excel (Microsoft, 2018).

Details regarding parent ions, transitions, structure, and cone voltage for each compound can be found in table A2 in appendix A.

Table 7: Gradient elution programmed using a mobile phase mixture of HPLC-grade water with 2 mM ammonium acetate (A) and methanol (B).

Time (min)	Flow rate (mL/min)	%A	%B
Initial	0.25	80	20
0.1	0.25	80	20
0.2	0.25	50	50
0.8	0.25	30	70
1.5	0.25	20	80
2.8	0.25	15	85
4.5	0.25	0	100
5.5	0.25	0	100
5.6	0.25	80	20
6	0.25	80	20

3.3.3 Non-target Analysis of Polar Extracts (UPLC-QTOF)

The non-target analysis was performed using an ACQUITY UPLC I Class® system connected to a Synapt G2-S Mass spectrometry detector (Waters Corporation, Milford, USA). 200 ng/mL of leucine enkephalin was used as a Lockmass at a flow rate of 10 µL/min to allow correction of exact mass measurements. A Kinetex C18 column (30 × 2.1 mm, 1.3 µm, 100Å. Phenomenex, Værløse, Denmark) serially connected to a Phenomenex guard column (C18, 10 × 2.1 mm) chromatographic column was used for reverse-phase separation. Water with 2 mM ammonium acetate (A) and methanol (B) were used as mobile phase. The mobile phase gradients used in both the 6- and 10-minute methods are described in table 8 and 9. The flow rate was set to 0.25 mL/min and the injection volume was 4 µL. The column was maintained to 30°C. The cone gas (N2) was set at a flow rate of 150 L/h. The desolvation temperature was set at 450 °C and the desolvation gas flow rate at 650 L/h. The nebulizer was set at 6 bar and the source temperature was set at 150 °C. The capillary voltage was set at 2.25 kV (ESI-) and the cone voltage set at 50 V. The full scan spectra were acquired within a range of 50 to 1200 m/z in the 6-minute method, and 50 to 1250 m/z in the 10-minute method.

The UPLC-QTOF-MS data was processed using Masslynx V4.1 and Progenesis QI V2.3 (Waters, Milford, USA).

Table 8: 6-minute method Gradient elution program using a mobile phase mixture of HPLC-grade water with 2 mM ammonium acetate (A) and methanol (B)

Time (min)	Flow rate (mL/min)	%A	%B
Initial	0.25	80	20
0.1	0.25	80	20
0.2	0.25	50	50
0.8	0.25	30	70
1.5	0.25	20	80
2.8	0.25	15	85
4.5	0.25	0	100
5.5	0.25	0	100
5.6	0.25	80	20
6	0.25	80	20

Table 9: 10-minute method Gradient elution program using a mobile phase mixture of HPLC-grade water with 2 mM ammonium acetate (A) and methanol (B)

Time (min)	Flow rate (mL/min)	%A	%B
Initial	0.25	80	20
0.1	0.25	80	20
0.2	0.25	50	50
0.8	0.25	30	70
4.5	0.25	20	80
6.8	0.25	15	85
8.5	0.25	0	100
9.5	0.25	0	100
9.6	0.25	80	20
10	0.25	80	20

4 Results

4.1 Method Development

4.1.1 Target Analysis of Non-polar Compounds Using CPs as Test Chemicals

The linear regressions R2 of the calibration curves for SCCPs, MCCPs, and LCCPs in the calibration solutions were 0.97, 0.97, and 0.98, respectively. The average concentrations of SCCPs, MCCPs, and LCCPs were discovered to be 9.0, 13, and 8.2 ng/g of dry weight in the Barents Sea sediment. The method recoveries of the spiked SCCPs, MCCPs, and LCCPs were 70%, 57%, and 57%, respectively (refer to Table 10 for details). The mean recovery of the labelled internal standard was 66%. SCCPs, MCCPs, and LCCPs were detected in the procedure blanks at an average of 0.4, 0.6, and 0.2 ng/sample, respectively.

Table 10: Overview of results from nontarget screening of SCCPs, MCCPs, and LCCPs in Barents sea sediments.

Class	Native CPs in the sediment ng/g dry weight	Spiked CPs ng/sample	Recovered CPs ng/sample	Method recovery
SCCPs	9.0	4.3	3.4	70%
MCCPs	13	61	35	57%
LCCPs	8.2	21	12	57%

4.1.2 Target Analysis of Polar Compounds using PFAS as Test Chemicals

Fifteen of the 41 compounds in the spike mix were detected in the spiked samples with the targeted screening method. The detected compounds include all PFSAs and FTSs, as well as PFOSA and ADONA. The linear regressions R^2 of the calibration curves of all detected compounds were 0.99 or higher, but the calibration curves had a non-linear section between 1 and 5 ppb. Due to this the calibration curves were split in two sections, one from 0.009 ppb to 1 ppb, and one from 5 ppb to 50 ppb. Both sections of the calibration curves had R^2 >0.995. The matrix effects of the detected compounds were all between -88% and -95%, with the PFOS 13C and 6:2 FTS 13C internal standards having very similar matrix effects of -103% and -102% respectively. The internal standards had absolute recoveries of 74% and 114% respectively. PFSAs and FTSs with C ≤8 had both absolute and recoveries of more than 85%, the larger PFSAs and FTSs had absolute recoveries of 45% or less and relative recoveries of less than 60%. PFOSA and ADONA had absolute recoveries of 32% and 79% respectively. PFOS was used as a stand in IS for PFOSA and ADONA because the intended IS, PFOA 13C, was below the LOD. The relative recoveries of PFOSA and ADONA using PFOS 13C as IS were 44% and 113% respectively. The absolute and relative recoveries as well as the matrix effect of said compounds are presented in table 11. The targeted method had a very high sensitivity to PFSAs, and a high sensitivity to FTSs, PFOSA and ADONA.

Table 11: Matrix effect, and absolute and relative recoveries of compounds in spiked samples from the targeted analysis.

Target data			
Compound	**Absolute recovery (avg, %)**	**Relative recovery (avg, %)**	**Matrix effect (%)**
PFOS 13C	**74**	**100**	**-103**
PFBS	122	169	-88
PFPeS	87	117	-91
PFHxS	100	132	-92
PFHpS	87	117	-91
PFOS	105	148	-94
PFNS	44	57	-90
PFDS	26	37	-90
PFDoDS	11	15	-94
PFECHS	104	141	-92
6:2 FTS 13C	**114**	**100**	**-102**
4:2 FTS	131	114	-93
6:2 FTS	100	88	-91
8:2 FTS	25	22	-91
10:2 FTS	45	41	-95
PFOSA	32	44	-90
ADONA	79	113	-93

The chromatograms of all compounds from the 0.9ppb standard solution, 1ppb matrix match sample, and 1ppb spiked sample 1 are presented in appendix B.

4.1.3 Non-target Analysis Based on Polar Substance Extracts

Of the 41 PFAS compounds used in the spiked samples a total of 29 compounds were detected with either the 6-minute method, 10-minute method, or both. 26 compounds were detected with either method, with MeFOSE only being detected with the 6-minute method, and ADONA and diSAMPAP only being detected with the 10-minute method. DiSAMPAP was being detectable with the 6-minute method due the m/z range. All compounds were confirmed by their fragments, except for the PFOA 13C internal standard which was confirmed by theoretical composition in Progenesis. PFOA and lighter PFCAs were not detected with either method. An overview of detected compounds is shown in table 12.

The method had very a high sensitivity to PFSAs and ahigh sensitivity to FTSs, but a low sensitivity to most other PFAS compounds. Most compounds outside of PFSAs and FTSs were close to the LOD, with PFCAs having the lowest responses. These differences can be seen in the mass spectrums, chromatograms, and complete spectrums of PFOS, 6:2 FTS, and PFOA, which are presented in

figures 7, 8, and 9.

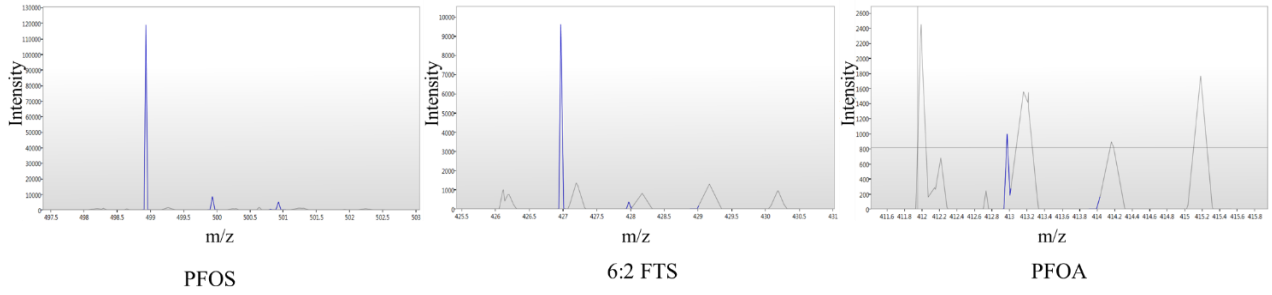


Figure 7: Mass spectrums of PFOS, 6:2 FTS, and PFOA in spiked samples from the 6-minute method. Note the differences in intensity of the signals of the compounds and relative noise.

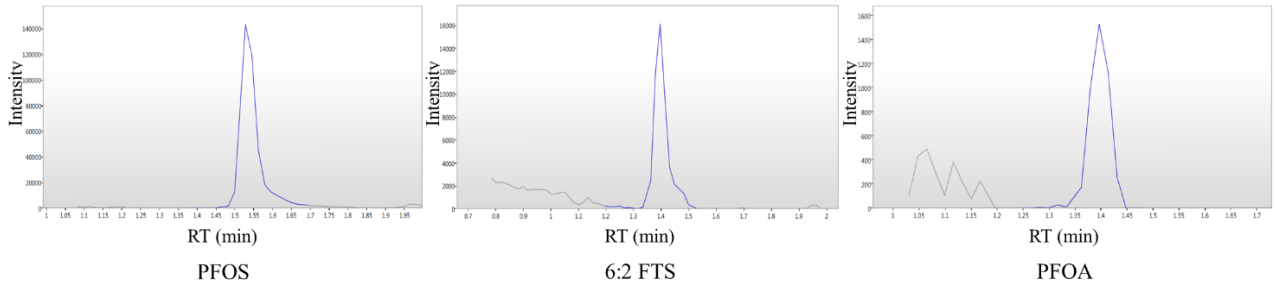


Figure 8: Chromatograms of PFOS, 6:2 FTS, and PFOA in spiked samples from the 6-minute method. Note the differences in intensity and relative noise.

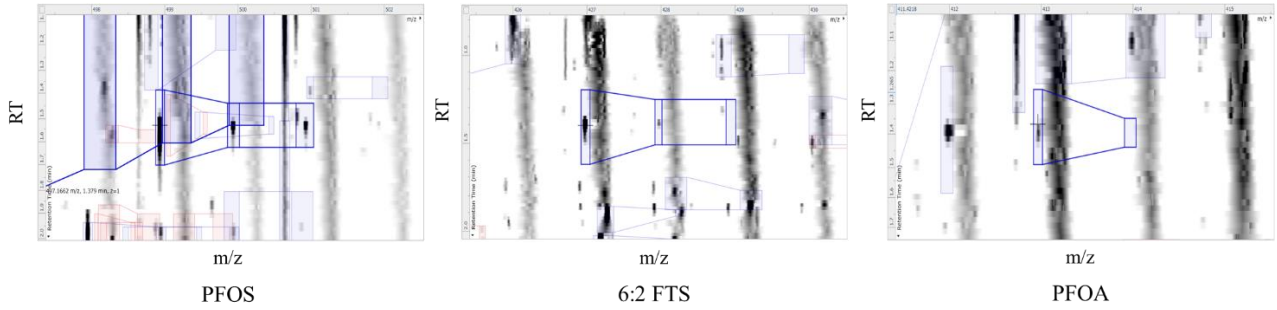


Figure 9: Combined spectrums of PFOS, 6:2 FTS, and PFOA in spiked samples from the 6-minute method. Darker shades represent higher relative intensity, note the differences in intensity and relative noise.

Table 12: Compounds detectable in the spiked samples with the 6-minute and 10-minute methods.

	Detectable with:		Scores and confirmation		
Compound	**6 min method**	**10 min method**	**Score (m/z and RT)**	**Score (Fragmentation)***	**Isotope similarity**
PFOS 13C	X	X	53.6	83.5	86.5
PFBS	X	X	41.5	0	98.5
PFPeS	X	X	55.7	80.4	98.9
PFHxS	X	X	51.6	61.6	97.4
PFHpS	X	X	51.2	0	97.6
PFOS	X	X	52.8	67.2	97.2
PFNS	X	X	59.3	98.5	99.2
PFDS	X	X	59.4	98.6	98.9
PFDoDS	X	X	62.8	83	94.4
PFECHS	X	X	76.1	97	98
6:2 FTS 13C	X	X	58.1	95	96.3
4:2 FTS	X	X	54.9	78.7	99.1
6:2 FTS	X	X	58.4	95.3	98.3
8:2 FTS	X	X	56.2	85.9	96.4
10:2 FTS	X	X	58.8	97.4	97
PFOSA	X	X	71.3	70.2	96.7
ADONA		X	65	62	91.9
PFOA 13C	X	X	37.9	0	91.3
9Cl-PF3ONS	X	X	65.7	99.1	97.5
P37DMOA	X	X	39.5	0	98.5
MeFOSA	X	X	49.7	49.8	98.9
EtFOSA	X	X	53.2	68.4	99.1
EtFOSAA	X	X	39.7	0	98.9
MeFOSE	X		58.3	0	98.4
PFDA	X	X	39.5	0	98.6
PFUnA	X	X	59	96.9	98.9
PFDoDA	X	X	59.1	97.4	98.2
PFTriDA	X	X	58.8	96.2	97.7
PFTDA	X	X	59.1	98.2	97.8
PFHxDA	X	X	58.9	97.7	97.2
PFOcDA	X	X	59.3	99.8	97.3
diSAMPaP	NA**	X	38.6	0	96

*Progenesis occasionally does not assign the correct fragments to a compound, leading to false fragmentation scores of 0, all compounds in this list had their fragments manually confirmed.
**diSAMPAP was not detected with the 6-minute method due to being outside the m/z range.

Although PFOA ^{13}C was detected in the spiked samples, it was barely above the LOD. PFOA ^{13}C had significantly lower intensity in the matrix, and was the only compound not confirmed by its fragments. Figure 10 shows the combined spectrum of PFOA ^{13}C in the standard solution, matrix match, and spiked sample.

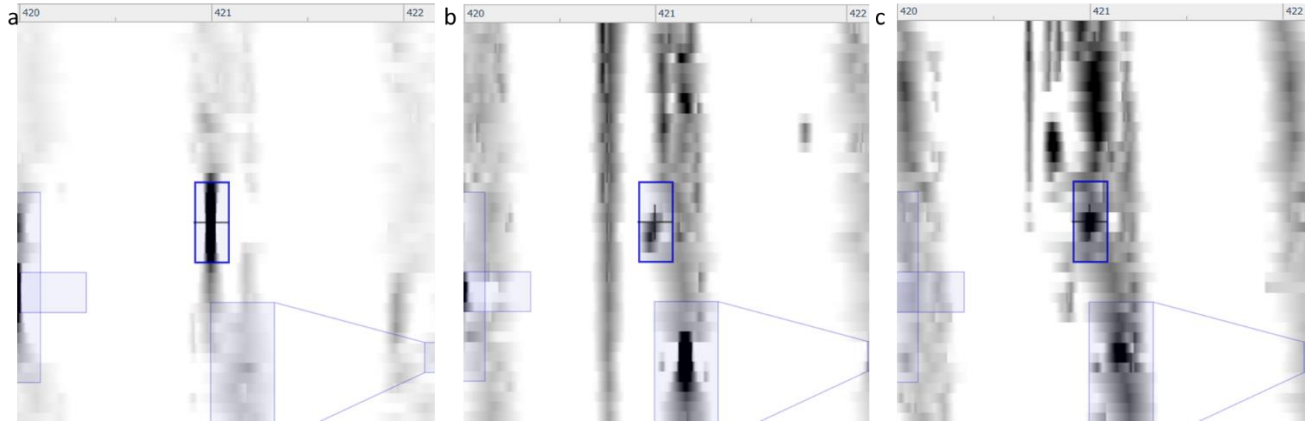


Figure 10: Combined spectrum of PFOA 13C8 in 0.9 ppb standard solution (a), 1 ppb matrix match solution (b), and 1 ppb spiked sample (c), note the difference in noise and peak-shape between the standard solution and the matrix match and spiked sample.

4.2 PFAS detection and non-target analysis in the Arctic sediment samples

A total of 15 compounds were detected in the pooled or individual samples, 7 in the pooled samples, and 11 in the individual samples. The compounds could not be accurately quantified due to the responses falling below the LLOQ or in the non-linear section of the respective calibration curves, the concentrations of PFOS, 4:2 FTS, and 6:2 FTS were estimated by comparing responses in the samples and spiked samples. Three of the seven compounds detected in the pooled samples, PFHxA, Gen X, and 4:2 FTS, had responses comparable to those in the spiked samples, with the remaining four compounds having responses less than half of those in the spiked samples. Three of the eleven compounds detected in the samples from the Kara sea, PFOS, 4:2 FTS, and 6:2 FTS, had responses between ⅕ and ½ of those in the spiked samples, with the remaining 8 compounds having responses close to the LOD. The only compound detected in the Kara sea samples with the non-target method was PFOS, the other compounds were only detected with the targeted method. The Barents sea samples were not analyzed with the targeted method. An overview of the compounds detected is presented in table 13.

*Table 13: Compounds detected in the samples from the Kara and Barents sea. A X indicates higher relative response, a * indicates responses close to the LOD.*

Compound	Barents Sea (pooled sample)	Kara Sea	
	Non-target	Target	Non-target
PFPeS		*	
PFHxS	*	*	
PFHpS		*	
PFOS	*	**X**	**X**
PFNS		*	
PFDS		*	
PFECHS		*	
4:2 FTS	**X**	**X**	
6:2 FTS		**X**	
8:2 FTS		*	
PFHxA	**X**		
PFHxDA	*		
PFOcDA	*		
Gen X	**X**		
ADONA		*	

The highest concentrations of PFOS were detected in the two samples furthest from the mainland (1 and 2), and in somewhat lower levels in the remaining four samples (3, 4, 5, and 6) with the targeted screening method. The data from the non-targeted screening showed similar trends, but with samples 3 and 6 being below the LOD. 4:2 FTS was detected in three of the samples (2, 3 , and 4), with the highest concentrations in the two westernmost samples (3 and 4). 6:2 FTS was detected in all six samples, with the highest concentrations in samples 2 and 3, slightly lower concentrations in samples 5 and 6, and concentrations close to the LOD in samples 1 and 4. An overview of compounds detected in the Kara sea sediments, as well as estimated concentrations, is presented in table 14. It was discovered that samples 1 and 5 had significantly higher levels of noise across all RTs and m/z compared to the other samples when analyzed with the non-target method.

Table 14: Compounds detected in the six samples from the Kara sea. An asterisk indicates detection with the non-target screening at similar responses to the ones in the targeted screening, while an x indicates a response close to the LOD. The concentrations are not accurate as the responses fall in non-linear sections of the applicable calibration curves. The presented concentrations were estimated by comparing the responses in the samples with the spiked samples.*

Compound	Sample					
	1	2	3	4	5	6
PFPeS						x
PFHxS	x			x		
PFHpS						x
PFOS	**0.45 ng/g ***	**0.25 ng/g ***	**0.1 ng/g**	**0.2 ng/g ***	**0.2 ng/g ***	**0.2 ng/g**
PFNS			x			x
PFDS			x			x
PFECHS					x	
4:2 FTS		x	**0.25 ng/g**	**0.4 ng/g**		
6:2 FTS	x	**0.25 ng/g**	**0.3 ng/g**	x	**0.2 ng/g**	**0.2 ng/g**
8:2 FTS	x		x			
ADONA	x	x		x	x	x

The relative concentrations of PFOS, 4:2 FTS, and 6:2 FTS per sample location is presented graphically in figure 11. Concentrations close to the LOD has been included in the figure despite not being quantifiable to illustrate whether the compound was detected at a given location.

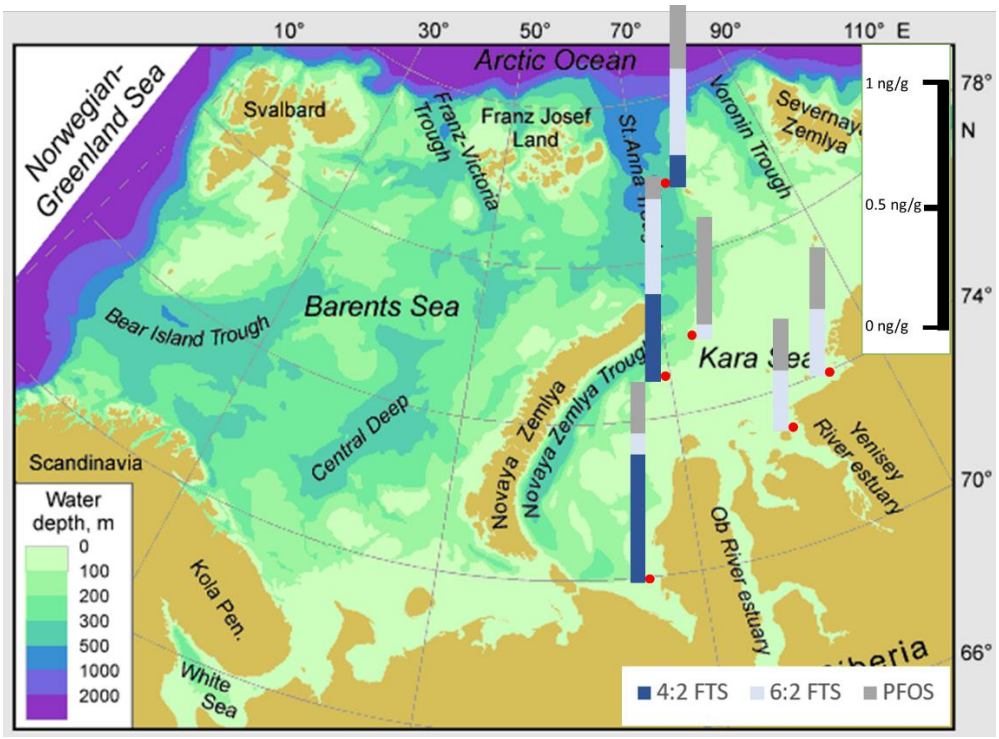


Figure 11: The relative concentrations of PFOS, 4:2 FTS, and 6:2 FTS per sample location. Concentrations close to the LOD has been included despite not being quantifiable to illustrate whether the compound was detected or not. Graphic edited from polarbearscience.com.

A total of 60 features, outside of the 41 compounds in the spiking solution, were detected in the Kara sea samples. Proposed structures or formulas were found for 29 of these 60 by comparing with chemical libraries. The proposed structures and formulas, as well as their m/z, scores, RTs, and fragmentation scores is presented in table C1 in appendix C. The mass errors and isotope similarities for all proposed formulas were <6ppm and >90 respectively. The relative abundances of the twelve features with the highest responses were examined. Some of these features exhibited interesting distributions in the samples. Two of these had significantly higher responses in samples 5 and 6, with one more having a higher response only in sample 5. Both sample 5 and 6 are taken close to shore in the Yenisei and Ob river plumes. The responses of these three features are presented in figure 12.

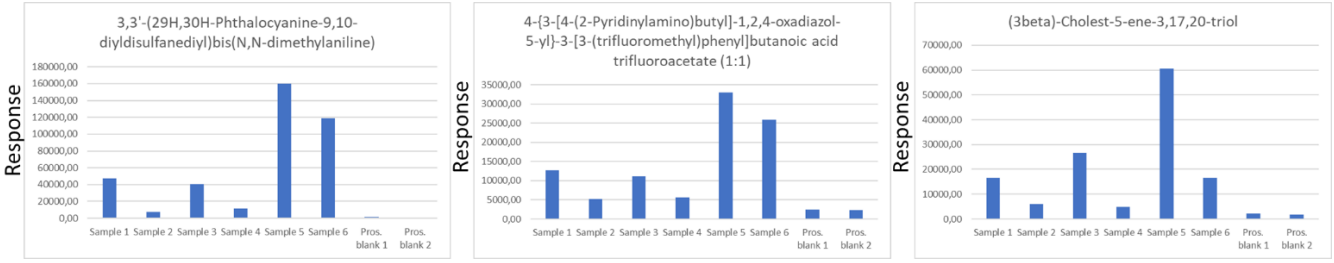


Figure 12: The responses from three of the features identified in the Kara sea sediments. All three have higher responses in sample 5, and two have higher responses in sample 6. Samples 5 and 6 were taken in the Yenisei and Ob river plumes.

Six of the twelve features had the highest response in sample 3, located in the middle of the Kara sea. These six features exhibit different overall trends, with some having somewhat higher responses in the samples taken close to the mainland (4, 5, and 6), while others having similar responses in all the remaining samples. The responses of the six features are presented in figure 13.

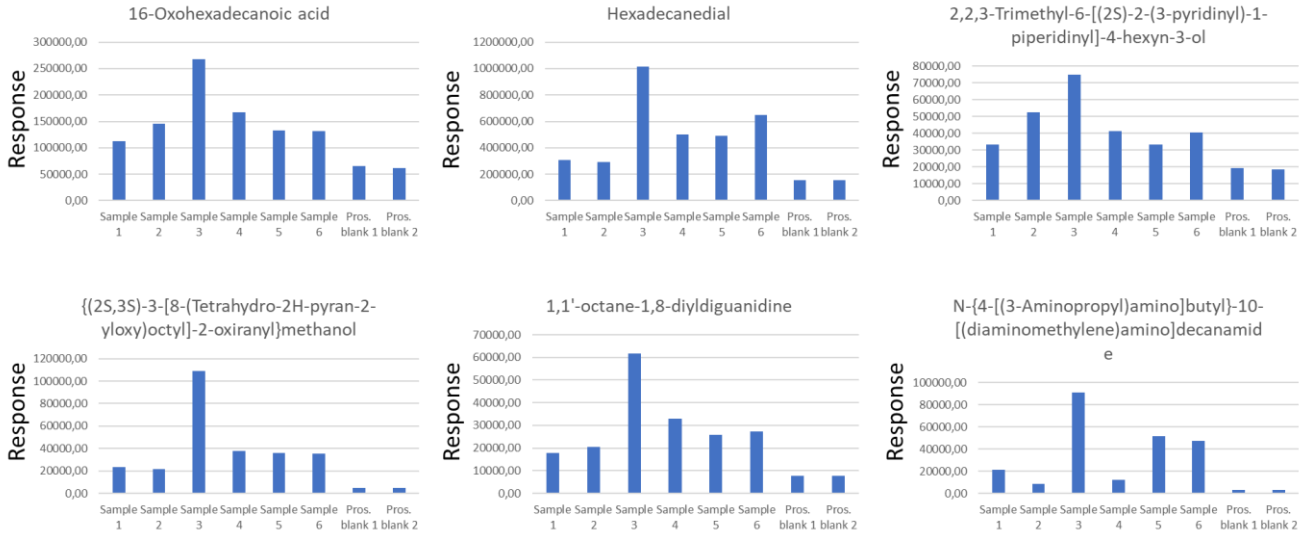


Figure 13: The responses of the six features with the highest response in sample 3.

5 Discussion

The primary goal of this thesis was to test two extraction methods for sediment samples, one for the analysis of polar substances and the other for non-polar substances, and their usefulness in both targeted and non-targeted screenings.

The non-polar extraction performed well and provided reasonable recoveries (57-70%) for all compounds in the spiking mixture (CPs C10-22). The method shows promise as a non-target extraction method for non-polar compounds, offering reasonable and comparable recoveries across a broad spectrum of non-polar CPs, which have log K_{OW} values ranging between 4 and 12 [58]. The method is best suited for non-targeted screenings, as higher recoveries for target analytes are typically desired in targeted screenings.

The polar extraction method performed very well for some compounds in the spiking mixture, providing excellent recoveries (85-130%) for smaller (<C9) PFSAs and FTSs, showing promise as a targeted extraction method for these compounds. The method was also able to detect compounds from many different groups of PFAS compounds using non-targeted screening methods, with 29 of 39 PFAS compounds in the spiking mixture being detectable at concentrations of 1 ng/g.

The polar method provided these recoveries and broad extraction capabilities while using a low amount of sample mass (~1g wet, ~0.5g dry), making it potentially useful in applications where the amount sample material available is limited.

5.1 Limitations and Considerations

One of the primary limitations of this thesis was the sample material. The sediment samples used, both the Barents sea pooled sediment and the Kara sea sediment samples, were originally collected for use in trace metal analysis and therefore collected in accordance with ISO 5667-19 using plastic equipment. This introduces the possibility of contamination of the samples with plasticizer compounds from the plastics used, which might influence the results of the analysis.

The sample size available from the Kara sea was also limited, and only enough for one replicate per location for the polar extraction, and not enough for the non-polar extraction. The possibility for contamination from the sampling methods used, and the lack of multiple replicates leads the significant uncertainties regarding the sample analysis results, which must be taken into consideration when reviewing the results.

Another limitation was the splitting of the calibration curves into two linear regions connected by a nonlinear region. As all compounds detected at levels above the LLOQ fell into or close to the nonlinear region of their respective calibration curves, only semi-quantitative was obtainable.

5.2 Sampling and Treatment Discussion

The samples were collected and treated with trace metal analysis as the main goal, and as such were handled primarily with plastic equipment and stored in plastic containers. This means that the samples may have been contaminated with PFAS or CP compounds from the equipment or containers. This introduces uncertainty to any qualitative and quantitative findings of these compounds from the analysis of the samples from both the Barents and Kara seas.

This potential contamination should however not affect the results of the method development, as the compounds would still need to be extracted with the applicable method, regardless of the compounds origin being contamination during sampling and sample pre-treatment or if the compounds were present in the samples prior to sampling.

5.3 Challenges Encountered During the Extraction Process

The samples for the CP analysis and PFAS analysis method development were extracted by different methods, but were both subsamples of the same pooled sample, and the extraction methods shared some similarities and faced some of the same challenges.

One of these challenges was a yellow discoloration of the samples after the initial extraction, as well as the formation of a brown precipitate during concentration of the samples. The discoloration and precipitate appeared identical in the samples from both methods despite the differences in solvents and methods used. It is suspected that the cause of both the discoloration and the precipitate is related to the sediment matrix, but this was not investigated. The PFAS extraction method included a cleanup step with graphitized carbon, which removed both the precipitate and the discoloration.

The CP extraction did not originally include a cleanup step other than the activated copper treatment, an extra cleanup step with a SPE column was therefore added to the method. The SPE cleanup removed both the discoloration and the precipitate, however it is possible the inclusion of the extra cleanup step and accompanying dilution and re-concentration may lead to a lower recovery overall, and an increased risk of contamination of the samples.

During the copper-cleanup of the non-polar samples, little to no discoloration of the copper powder was observed. This indicates very low levels of sulfur in the sample. The samples from both extraction methods also produced a crystal-like precipitate on the inside of the centrifuge tubes during concentration of the samples. In the samples from the PFAS extraction this occurred at the same time as the formation of the brown precipitate during the first and only concentration step. However, in the samples from the CP extraction method this crystal-like precipitate formed only during the second of three concentration steps, immediately following the SPE cleanup. In both cases the crystal-like precipitate was attached to the inside of the centrifuge tubes and was discarded along with the tubes after the samples were transferred to other containers.

The cause and composition of this crystal-like precipitate is unknown, and to the extent of the authors knowledge and the accessible open literature no other papers have reported this problem; however, some information can be inferred from when and how it formed. Given that it formed in the samples from both the polar and non-polar extractions, it is likely that the precipitate is formed from some compound or part of the matrix that is transferred from the sediments to both polar and non-polar solvents. Additionally, the fact that the crystal-like precipitation did not form when the non-polar samples were initially concentrated with a n-hexane and diethyl ether mix as the solvent, but formed during the second concentration when the solvent was a DCM and n-hexane mix, and the fact that the crystal-like precipitate did not dissolve when acetone was added later might indicate that the crystal-like precipitate is either made up of a compound/mix of compounds more soluble in non-polar solvents like n-hexane, or that it is formed by an interaction between the matrix and more polar solvents like DCM or methanol. Analyzing the chemical makeup of this crystal-like precipitate would be interesting, and it might possibly contain some of the compounds from the PFAS spiking solution that was not detected in the analysis.

5.4 Non-polar Extraction Advantages, Disadvantages, and Improvement Potential

The non-polar extraction method utilized rotation of tubes containing the sample and solvent, instead of the more popular sediment extraction method ASE. The use of rotation instead of ASE has both advantages and disadvantages, with some variation depending on the type of ASE used. Multi-cell or automatic ASE systems negates some of the advantages of the method. The biggest advantage is relative simplicity of the method and the equipment used, making the method more accessible.

One disadvantage compared to ASE is the lower solvent and time efficiency, using both more time and more solvent per sample extracted. The increased time used is however partially negated by the possibility of extracting more samples at the same time, without the need for equipment specialized for handling large numbers of samples at the same time. This is especially true when compared to single cell ASE systems (ASE 150), but not when compared to auto ASE systems capable of extracting samples overnight. The setup used in this thesis used a simple overhead shaker with a universal adapter, which could be used to extract 30 or more samples at the same time. The increased use of solvents compared to ASE will be more of a disadvantage if more expensive or dangerous solvents are used.

Another disadvantage of the sample treatment method used in the current study compared to ASE is the need for a SPE cleanup step, which might reduce overall recovery. This does not appear to be a major issue however, as the recoveries of the CPs used to test the method were reasonably good, but other methods might be worth considering if a higher recovery is necessary, such as in targeted screenings.

One area of improvement for the method is in the liquid-liquid extraction step. The LLE was performed in 50 mL centrifuge tubes with Pasteur pipettes used to transfer the correct phase, due to the relatively low volumes of solvents used. While this approach did work as intended, it proved to be time consuming precision work with a larger likelihood of mistakes, and it is recommended to instead use small separatory funnels if possible.

Overall, the method performed well enough in the lab, with the main area of improvement in regard to time being the LLE. A set of samples extracted with the non-polar extraction method by trained personnel can be ready for analysis in about 2-3 working days, depending somewhat on the type of LLE, SPE and evaporation equipment used, consuming a total of 3 grams of sediments and 50 mL of solvents per sample, not including solvents used during preparation of activated copper.

5.5 Polar Extraction Method Discussion

The polar extraction method performed well, used relatively simple methods and equipment, and used relatively small amounts of both solvents and sample material. This makes the method both very accessible, and useful in situations where the amount of sample material is limited. The method struggled with extracting PFCAs, but it is possible that these compounds can be extracted by varying the amounts of NaOH and HCl added in the extraction to change the pH to ensure the PFCAs are in their deprotonated state.

One possible improvement might be a reduction of the amount of internal standard added, to make the concentration of the standard more similar to the concentration PFAS is typically detected in in sediments, around 1 ng/ml.

A set of samples extracted with the polar extraction method by trained personnel can be ready for analysis in less than a working day, consuming a total of about 10 mL of solvents and 1 gram of sediments per sample.

5.6 Comparing Extraction Techniques: Sample Size Constraints and Results

The non-polar extraction method was designed with a sample mass of 2-3 grams of wet sediment in mind, while the polar extraction method was designed with a sample mass of ~1 gram of wet sediment. Both extraction methods performed well in the method development analysis, but the non-polar extraction method was excluded from the Kara sea sediment analysis because of the higher amount of sediment required per sample and a limited quantity of sample material available. The combined results from the polar analysis of both the Barents and Kara Sea sediments indicate the existence of some interesting trends.

One important detail to note regarding the analysis of the Kara Sea sediments compared to the Barents Sea sediments is that the Kara Sea sediments were freeze dried while the Barents sea sediments were wet. It was noted that the Barents sea sediments were about 50% water by weight, and an equivalent amount of dried sediment from the Kara sea was used for ease of comparison. All concentrations provided in the results and discussion are given as ng/g **wet** sediment.

5.6.1 Discussion on Non-polar Target Screening Results

The results indicate that the extraction method is well suited to extract and analyze CPs, and provided both good R^2 values for the calibration curves as well as reasonable recoveries for all compounds. The method appears promising as the recovery test encompassed a wide range of molecules ranging from C10 to C22. Only the pooled sediment sample from the Barents sea was analyzed, and as such gives no indication of any trends in the geographical distribution of CPs in the Arctic ocean. The samples did indicate levels of 8-13 ppb of CPs in the Barents sea sediments, but these results have significant uncertainty as these samples were collected using plastic equipment with the intention of analyzing metals.

5.6.2 Evaluating Polar Extraction: Insights from Targeted and Non-Target Screening of PFAS Samples

The results from the targeted screening of the PFAS samples from the polar extraction showed a very high sensitivity to PFSAs, and a decent sensitivity to FTSs, ADONA and PFOSA. The method provided both very good R^2 values for the calibration curves as well as high recoveries for most of the compounds and a very consistent matrix effect for all compounds. The targeted method was unable to detect any PFCAs or other classes of PFAS present in the spike mix.

By examining the very limited data available on the various physical and chemical properties of the compounds in the spike mix, the most obvious trend is that almost all the compounds detected are sulfonic acids, and that almost all sulfonic acids were detected. The only sulfonic acid not detected was 9Cl-PF3ONS, and the only non-sulfonic acids detected were PFOSA, a primary sulfonamide, and ADONA.

Other possible trends examined include pK_A and solubility in water. It is possible that pK_A plays some role in extraction, as it determines at which pH different compounds are charged or neutral, and this would explain why PFSAs, with pK_As between -2.6 and -8.6, were extracted but PFCAs, with pK_As between -0.2 and -0.8 were not. However, this does not explain why FTSs, with pK_As around 1.3 were extracted, and pK_A is therefore not likely a major factor determining which compounds are extracted.

Two properties that seem to have had an impact on the extraction is size and water-solubility. In the results from the targeted screening a clear trend in recovery can be seen, with smaller, more water-soluble compounds having better recoveries than larger less water-soluble compounds. This trend is somewhat contradicted however by the results from the non-target screening of the polar PFAS samples, where the larger (C>9) PFCAs were detected in addition to the compounds detected in the

targeted screening, but the smaller PFCAs were not. This difference is probably somewhat related to the difference in the mass spectrometers used in the targeted and non-targeted analyses. The targeted screening with the QqQ using MRM has a very high specificity but a relatively low resolution, and proved to be very sensitive to PFSAs and fairly sensitive to FTSs, while being unable to detect most other PFAS. The non-targeted screening with the Q-TOF had a somewhat lower sensitivity overall, primarily due to the increased levels of noise from operating in full-scan mode, but was able to detect a wider range of PFAS, most likely partially due to the higher resolution compared to the QqQ.

It should also be noted that the PFOA 13C internal standard had significantly lower intensity in any sample containing the sediment matrix, and PFOA 13C was barely above the LOD despite having a concentration of 10ng/ml. The fact that this was a problem with both the spiked samples and the matrix match samples might be an indication that the matrix is the reason for the majority of PFCAs not being detected in, and not necessarily the extraction method itself.

Two versions of the non-targeted screening were tested, one 6-minute and one 10-minute. There were some minor differences in the compounds detected, and in the amount of time required to manually fix some slightly overlapping signals. The difference in data processing time as a result of this was however substantially lower than the difference in time from the analysis itself. Both methods had some issues with high noise levels at lower RTs, with the 10-minute method being slightly better in this regard. Overall, the faster time of analysis of the 6-minute method was evaluated to outweigh the slight benefits of the 10-minute method, unless a slightly higher sensitivity at the lowest RTs is desirable. One interesting difference between the two non-targeted methods and the targeted is the detection of ADONA. ADONA was detected very well, with a strong signal in the spiked samples, in both the targeted and 10-minute non-targeted methods, but not at all, with absolutely no signal in the spiked samples, in the 6-minute non-targeted method. The cause of this is unknown.

The 29 PFAS compounds from the spiking mix that were identified with the non-target analysis were identified with a high degree of confidence, with almost all having scores between 40 and 60, all having fragmentation scores of >50 and most >90, and all having isotope similarities of >90. Some of the compounds had fragmentation scores of 0, but this appears to be an issue with the software, as the fragments of these were confirmed manually.

5.6.3 Insights and Implications from Arctic Sediment PFAS Analyses: Trends, Sources, and Potential Influences

The results from both the targeted and non-targeted analysis of the Arctic sediment samples have a large degree of uncertainty, both from the samples being collected and handled with plastic equipment, and from the lack of multiple replicates. The results do however indicate some interesting trends that might be worth investigating further, and discovered PFAS compounds in similar concentrations to a recently published paper that analyzed PFAS in arctic sediments from the Bering shelf, Lin et al (2020) [59]. A paper published by Kallenborn et al. (2004) [60] reported levels of PFOS in sediments from Iceland of up to 0.11ng/g, as well as the detection of several other PFAS. To the extent of the authors knowledge and the accessible open literature no other papers have analyzed PFAS in Arctic ocean sediments, and this thesis is the first detection of 4:2 FTS and 6:2 FTS in ocean sediments [61].

One of the most interesting trends is that both the legacy PFAS, PFOS, as well as its modern replacement, 6:2 FTS, were detected in all 6 samples from the Kara Sea, but in different concentrations in the different samples. PFOS was detected in the highest concentrations in samples 1 and 2, both samples taken from relatively deep water far from the coast, and in concentrations of about one third of that in the remaining four samples. 6:2 FTS on the other hand was detected in the highest concentrations in samples 2 and 3, both far from the coast, and in almost as high concentrations in samples 5 and 6, both in the plume from the Yenisei and Ob rivers.

These results might indicate that PFOS is stored in deep ocean sediments in higher concentrations than in shallow water, and that the amount of PFOS being introduced from land-based sources is declining. The detection of PFOS in the Barents Sea pooled sample reinforces the hypothesis that PFOS is stored in deep ocean sediment, or that it is transported by ocean currents. The results might also indicate that 6:2 FTS is both being transported to the deep ocean, perhaps by air or ocean currents, and that it is being deposited into the ocean by rivers. 6:2 FTS was not detected in the Barents Sea pooled sediment, which might indicate that air transport or the Yenisei and Ob rivers are the main sources of 6:2 FTS in the Kara Sea.

The fact that PFOS was detected in all samples might also be a result of contamination from the equipment used in the sampling or sample treatment, it is however expected that PFOS is detected in many of not all of the samples given its status as a legacy POP that has seen widespread use over a long period of time. 4:2 FTS was detected in samples 2, 3, and 4, as well as the Barents Sea pooled sample. These are the westernmost samples and indicates that 4:2 FTS is primarily transported from the west, most likely by ocean currents from the Atlantic, and that it is not deposited into the Kara Sea by air or the Yenisei or Ob rivers.

The remaining results from the analysis of PFAS in the Arctic sediment samples is probably more indicative of the differences between the targeted and non-targeted, or more specifically the difference between the QqQ and the Q-TOF mass spectrometry, but seems to indicate that there are more PFSAs and FTSs in the Kara sea and more PFCAs in the Barents sea.

5.6.4 Detecting and Tracing Non-target Features in Kara Sea Samples

The 60 features detected in the Kara sea samples were the only features with a signal higher than the weakest signal of a detected PFAS, and with higher signals in the samples than in the procedure blanks. 29 of these 60 were given possible identifications by a library search. Multiple libraries were searched, but all proposed identifications are from the ChemSpider library.

The trends of the 12 features with the highest responses were examined, and it was discovered that three of the compounds showed no real spatial trends, three showed significantly higher responses in the samples from the Yenisei and Ob River plume, and six showed the highest response in samples 3 from shallow water in the middle of the Kara Sea. The three features with the highest responses in the samples from the Yenisei and Ob River plume are likely introduced into the Kara Sea primarily by one or both of the rivers, while the source of the remaining nine features is unknown.

The cause of the higher levels of noise detected in samples 1 and 5 is unknown. Sample 5 was collected from the mouth of the Yenisei river, and sample 1 was collected in the middle of the Kara sea in a location directly outwards from the river mouth. It is therefore possible that the increased noise is linked to the Yenisei and Ob rivers but given that the currents in the area flow from west to east, pushing the river plume eastwards, combined with no increase levels of noise observed in sample 6, makes this unlikely. Another possible explanation for the increased noise is human activity or local pollution, but this is also unlikely as several of the other samples are as close to settlements and shipping lanes as sample 1 and 5.

6 Conclusion

This study implemented two different extraction methods, one focused on polar compounds and one on non-polar compounds. The non-polar extraction method provided reasonable recoveries across a wide range of CPs and shows promise as an extraction method for non-targeted screening of non-polar compounds. On the other hand, the polar extraction method provided excellent recoveries for PFSAs and FTSs with C<9 and proved capable extracting compounds from many different sub-groups of PFAS. The polar extraction method shows promise both as a targeted extraction method for C<9 PFSAs and FTSs and as an extraction method for non-target screening of a wide range of polar PFAS.

In samples from the Kara Sea, eleven PFAS compounds were detected, with three of them being semi-quantifiable. PFOS, 4:2 FTS, and 6:2 FTS were detected in concentrations of 0.2-0.45 ng/g of wet sediment. PFOS showed trends indicating storage in deepwater sediments, 4:2 FTS showed trends indicating transport into the Kara Sea from the Barents Sea, and 6:2 FTS showed trends indicating transport into the Kara Sea both by the Yenisei and Ob Rivers and ocean currents from the west.

Furthermore, non-target screening revealed 60 features, with 29 identified through library matches. Spatial trend examination of the twelve most abundant of these showed that three indicated transport into the Kara Sea by the Yenisei and Ob Rivers, six indicated consolidation in the middle of the Kara Sea, and the remaining three showed no trends.

In conclusion, this thesis constitutes a foundational and progressive step in the non-target screening and identification of emerging organic pollutants in the Arctic region.

References

1. Watson, R., et al., *Summary for policymakers of the global assessment report on biodiversity and ecosystem services of the Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services.* Bonn, Germany: IPBES Secretariat, 2019.
2. SDG, U. *UN SDG*. 2019 [cited 2022 29.11].
3. Society, N.G. *Marine Pollution*. 2022 [cited 2022 28.11].
4. Baztan, J., et al., *Breaking Down the Plastic Age*, in *Fate and Impact of Microplastics in Marine Ecosystems*, J. Baztan, et al., Editors. 2017, Elsevier. p. 177-181.
5. Christensen, M.M., et al., *Utlekking av kjemikalier fra plastprodukter i vann*. 2021, NTNU.
6. Council, A. *Adressing Arctic Pollution*. 2022 [cited 2022 28.11].
7. Townhill, B.L., et al., *Pollution in the Arctic Ocean: An overview of multiple pressures and implications for ecosystem services.* Ambio, 2022. **51**(2): p. 471-483.
8. arctic, D.t. *Arctic Pollution*. 2022 [cited 2022 28.11].
9. David Balton, B.J., Halla Hrund Logadóttir, Marisol Maddox, Fran Ulmer, *Policy and Action on Plastic in the Arctic Ocean: October 2019 Workshop Summary & Recommendations*. 2020, Belfer Center for Science and International Affairs: https://www.belfercenter.org/.
10. Polarinstitutt, N. *Pollutants in the Arctic*. 2022 [cited 2022 28.11].
11. CONVENTION, S., *STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS*. 2006.
12. Convention, S.o.t.S. *The Stockholm Convention*. 2019 [cited 2022 28.11].
13. Liu, Y., et al., *Hundreds of Unrecognized Halogenated Contaminants Discovered in Polar Bear Serum.* Angewandte Chemie International Edition, 2018. **57**(50): p. 16401-16406.
14. Al Amin, M., et al., *Recent advances in the analysis of per- and polyfluoroalkyl substances (PFAS)—A review.* Environmental Technology & Innovation, 2020. **19**: p. 100879.
15. Lemal, D.M., *Perspective on fluorocarbon chemistry.* The Journal of organic chemistry, 2004. **69**(1): p. 1-11.
16. Nordby, G.L. and J.M. Luck, *Perfluorooctanoic acid interactions with human serum albumin.* Journal of Biological Chemistry, 1956. **219**(1): p. 399-404.
17. Lewis, C.E. and G.R. Kerby, *An epidemic of polymer-fume fever*. JAMA, 1965. **191**(5): p. 375-378.
18. Renner, R., *Growing concern over perfluorinated chemicals Environ Sci Technol 35: 154A–160A.* Find this article online, 2001.
19. Taniyasu, S., et al., *Analysis of fluorotelomer alcohols, fluorotelomer acids, and short-and long-chain perfluorinated acids in water and biota.* Journal of Chromatography A, 2005. **1093**(1-2): p. 89-97.
20. Joerss, H., et al., *Transport of Legacy Perfluoroalkyl Substances and the Replacement Compound HFPO-DA through the Atlantic Gateway to the Arctic Ocean—Is the Arctic a Sink or a Source?* Environmental science & technology, 2020. **54**(16): p. 9958-9967.
21. Ask, A.V., et al., *Per-and polyfluoroalkyl substances are positively associated with thyroid hormones in an arctic seabird.* Environmental Toxicology and Chemistry, 2021. **40**(3): p. 820-831.
22. Yuan, B., et al., *Chlorinated paraffins leaking from hand blenders can lead to significant human exposures.* Environment International, 2017. **109**: p. 73-80.
23. Obu, J., *How Much of the Earth's Surface is Underlain by Permafrost?* Journal of Geophysical Research: Earth Surface, 2021. **126**(5): p. e2021JF006123.
24. Pörtner, H.-O., et al., *IPCC special report on the ocean and cryosphere in a changing climate.* IPCC Intergovernmental Panel on Climate Change: Geneva, Switzerland, 2019. **1**(3).
25. Monitoring, A., *AMAP Assessment 2016: Chemicals of Emerging Arctic Concern*. 2017: Arctic Monitoring and Assessment Programme (AMAP).
26. Muir, D., et al., *Identifying further chemicals of emerging arctic concern based on 'in silico' screening of chemical inventories.* Emerging Contaminants, 2019. **5**: p. 201-210.

27. Milestone, C.B., et al., *Non-target profiling of bitumen-influenced waters for the identification of tracers unique to oil sands processed-affected water (OSPW) in the Athabasca watershed of Alberta, Canada.* Rapid Communications in Mass Spectrometry, 2021. **35**(3): p. e8984.
28. Plassmann, M.M., S. Fischer, and J.P. Benskin, *Nontarget Time Trend Screening in Human Blood.* Environmental Science & Technology Letters, 2018. **5**(6): p. 335-340.
29. Schlabach, M., et al., *Non-target screening-a powerful tool for selecting environmental pollutants.* NILU OR, 2013.
30. Schlabach, M., et al., *Screening Programme 2017–AMAP Assessment Compounds.* 2018.
31. Schymanski, E.L., et al., *Non-target screening with high-resolution mass spectrometry: critical review using a collaborative trial on water analysis.* Analytical and Bioanalytical Chemistry, 2015. **407**(21): p. 6237-6255.
32. Veenaas, C., et al., *Nontarget Screening and Time-Trend Analysis of Sewage Sludge Contaminants via Two-Dimensional Gas Chromatography–High Resolution Mass Spectrometry.* Environmental Science & Technology, 2018. **52**(14): p. 7813-7822.
33. Washington, J.W., et al., *Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils.* Science, 2020. **368**(6495): p. 1103-1107.
34. EPA, E., *TSCA chemical substance inventory.* Washington DC, 2003.
35. Strempel, S., et al., *Screening for PBT chemicals among the "existing" and "new" chemicals of the EU.* Environmental science & technology, 2012. **46**(11): p. 5680-5687.
36. Timner, M., *Non-target screening of sediment samples fromthe Canadian Arctic: comparing two different gas chromatography – high resolution mass spectrometry (GC-HRMS) techniques*. 2022. p. 36.
37. Peets, P., et al., *MS2Tox Machine Learning Tool for Predicting the Ecotoxicity of Unidentified Chemicals in Water by Nontarget LC-HRMS.* Environmental Science & Technology, 2022. **56**(22): p. 15508-15517.
38. Lundanes, E., L. Reubsaet, and T. Greibrokk, *Chromatography: basic principles, sample preparations and related methods*. 2013: John Wiley & Sons.
39. Poole, C.F., *Chapter 4 - The Column in Liquid Chromatography*, in *The Essence of Chromatography*, C.F. Poole, Editor. 2003, Elsevier Science: Amsterdam. p. 267-429.
40. Poole, C.F., *The essence of chromatography*. 2003, Elsevier.
41. Linscheid, M., *Mass Spectrometry*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2001.
42. Chernushevich, I.V., A.V. Loboda, and B.A. Thomson, *An introduction to quadrupole–time-of-flight mass spectrometry.* Journal of Mass Spectrometry, 2001. **36**(8): p. 849-865.
43. Gross, J.H., *Mass Spectrometry: A Textbook*. 1st edition ed. 2006: Springer Science & Business Media.
44. González, O. and R.M. Alonso, *Chapter 6 - Validation of bioanalytical chromatographic methods for the quantification of drugs in biological fluids*, in *Handbook of Analytical Separations*, G. Hempel, Editor. 2020, Elsevier Science B.V. p. 115-134.
45. Lister, A.S., *7 - Validation of HPLC Methods in Pharmaceutical Analysis*, in *Separation Science and Technology*, S. Ahuja and M.W. Dong, Editors. 2005, Academic Press. p. 191-217.
46. Armbruster, D.A. and T. Pry, *Limit of blank, limit of detection and limit of quantitation.* Clin Biochem Rev, 2008. **29 Suppl 1**(Suppl 1): p. S49-52.
47. *Nomenclature, symbols, units and their usage in spectrochemical analysis—II. data interpretation Analytical chemistry division.* Spectrochimica Acta Part B: Atomic Spectroscopy, 1978. **33**(6): p. 241-245.
48. Malysheva, S.V., et al., *Development and validation of a quantitative UHPLC-MS/MS method for selected brominated flame retardants in food.* Food Addit Contam Part A Chem Anal Control Expo Risk Assess, 2018. **35**(2): p. 292-304.
49. Zhou, W., S. Yang, and P.G. Wang, *Matrix effects and application of matrix effect factor.* Bioanalysis, 2017. **9**(23): p. 1839-1844.
50. Goss, K.-U., *The pKa Values of PFOA and Other Highly Fluorinated Carboxylic Acids.* Environmental Science & Technology, 2008. **42**(13): p. 5032-5032.

51. Rayne, S., K. Forest, and K. Friesen, *Extending the semi-empirical PM6 method for carbon oxyacid pKa prediction to sulfonic acids: Application towards congener-specific estimates for the environmentally and toxicologically relevant C1 through C8 perfluoroalkyl derivatives.* Nature Precedings, 2009.
52. ITRC. *4 Physical and Chemical Properties (of PFAS)*. [cited 2023 26. may]; Available from: https://pfas-1.itrcweb.org/4-physical-and-chemical-properties/.
53. Anzjøn, H., *Mercury in Marine Arctic Sediments*. 2022, NTNU.
54. Nylund, K., et al., *Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge.* Chemosphere, 1992. **24**(12): p. 1721-1730.
55. Powley, C.R., et al., *Matrix Effect-Free Analytical Methods for Determination of Perfluorinated Carboxylic Acids in Environmental Matrixes.* Analytical Chemistry, 2005. **77**(19): p. 6353-6358.
56. Tomy, G.T., et al., *Quantifying C10−C13 Polychloroalkanes in Environmental Samples by High-Resolution Gas Chromatography/Electron Capture Negative Ion High-Resolution Mass Spectrometry.* Analytical Chemistry, 1997. **69**(14): p. 2762-2771.
57. Trimmel, S., et al., *Rapid Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Harbour Porpoise Liver Tissue by HybridSPE®–UPLC®–MS/MS.* Toxics, 2021. **9**: p. 183.
58. Bettina, H., et al., *Effects of Chain Length, Chlorination Degree, and Structure on the Octanol−Water Partition Coefficients of Polychlorinated n-Alkanes.* Environmental Science & Technology, 2011. **45**(7): p. 2842-2849.
59. Lin, Y., et al., *Perfluoroalkyl substances in sediments from the Bering Sea to the western Arctic: Source and pathway analysis.* Environment International, 2020. **139**: p. 105699.
60. Kallenborn, R., *Perfluorinated alkylated substances (PFAS) in the Nordic environment*. 2004: Nordic Council of Ministers.
61. Muir, D., et al., *Levels and trends of poly- and perfluoroalkyl substances in the Arctic environment – An update.* Emerging Contaminants, 2019. **5**: p. 240-271.

Appendix

A: Targeted screenings compound details

Table A1: Compounds used in the standard and spiking solutions, their delivered concentrations, solvents, and suppliers.

Categories	Standard	Solution	concentration ng/uL	Supplier
13C internal standard	**13C-1,5,5,6,6,10-Hexachlorodecane**	**nonane**	**100**	**Cambridge Isotope Laboratories, MA**
13C volumetric standard	**13C-1,1,1,3,10,12,12,12-octachlorododecane**	**nonane**	**100**	**Cambridge Isotope Laboratories, MA**
SCCPs	C10-13, 51.5%Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C14-17, 52.0%Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C16, 45 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C16, 50 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C16, 55 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C16, 60 %Cl	cyclohexane	100,1	Ehrenstorfer GmbH, Germany
MCCPs	C16, 65 %Cl	cyclohexane	100,1	Ehrenstorfer GmbH, Germany
MCCPs	C17, 45 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C17, 50 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C17, 55 %Cl	cyclohexane	99,9	Ehrenstorfer GmbH, Germany
MCCPs	C17, 60 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
MCCPs	C17, 65 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
LCCPs	C18, 40 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
LCCPs	C18, 50 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
LCCPs	C18, 60 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
LCCPs	C20, 40 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
LCCPs	C20, 50 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany
LCCPs	C22, 36 %Cl	cyclohexane	100,6	Ehrenstorfer GmbH, Germany
LCCPs	C22, 50 %Cl	cyclohexane	100	Ehrenstorfer GmbH, Germany

Table A2: the name, CAS, mass, cone voltage, parent ion m/z, and ion transitions of the compounds in the PFAS spiking mixture.

Compound	CAS	Mass	Cone voltage (V)	Parent ion (m/z)	Ion transitions (CE)
PFOS 13C	-	**507.06**	**56**	**506.9**	**506.90 → 79.87 (46)** **506.90 → 171.85 (32)**
6:2 FTS 13C	-	**432**	**26**	**432.96**	**432.96 → 411.959 (24)** **432.96 → 81.901 (30)**
PFOA 13 C	-	**422.01**	**16**	**420.9**	**420.90 → 171.86 (16)** **420.90 → 222.84 (16)**
PFBA	375-22-4	214.04	28	213	213 → 169 (10)
PFPeA	2706-90-3	264.05	20	262.97	262.97 → 219 (8)
PFHxA	307-24-4	314.05	10	312.97	312.97 → 118.95 (18) 312.97 → 269 (8)
PFHpA	375-85-9	364	6	362.96	362.96 → 119 (22) 362.96 → 168.97 (18)
PFOA	335-67-1	414.07	20	412.97	412.97 → 168.90 (18) 412.97 → 369 (8)
PFNA	375-95-1	464.08	20	462.99	462.99 → 219 (16) 462.99 → 419 (10)
PFDA	335-76-2	514.09	10	513.01	513.10 → 219.01 (18) 513.10 → 269.04 (16)
PFUnA	2058-94-8	564.09	12	562.96	562.96 → 268.92 (18) 562.96 → 518.98 (10)
PFDoDA	307-55-1	614.01	26	612.95	612.95 → 168.93 (26) 612.95 → 568.90 (12)
PFTriDA	72629-94-8	664.11	6	662.93	662.93 → 168.90 (24) 662.93 → 618.90 (10)
PFTDA	376-06-7	714.12	20	712.92	712.92 → 168.96 (30) 712.92 → 668.92(14)
PFHxDA	67905-19-5	814.13	36	813.03	813.03 → 168.96 (34) 813.03 → 218.99 (24)
PFOcDA	16517-11-6	914	5	912.09	912.9 → 168.97 (30) 912.9 → 869.02 (15)
PFBS	108427-52-7	299.09	42	298.68	298.90 → 98.96 (28) 298.90 → 82.95 (26)
PFPeS	2706-91-4	350	20	348.98	348.98 → 79.96 (30) 348.98 → 98.96 (26)
PFHxS	355-46-4	390	5	398.09	398.9 → 79.97 (30) 398.9 → 98.97 (30)
PFHpS	146689-46-5	449.12	2	448.97	448.97 → 79.95 (34) 448.97 → 98.95 (34)
PFOS	1763-23-1	499.12	20	498.97	498.97 → 79.96 (20) 498.97 → 98.96 (38)
PFNS	68259-12-1	550	10	548.09	548.9 → 79.97 (40) 548.90 → 98.97 (10)
PFDS	335-77-3	600	10	598.97	598.97 → 79.97 (40) 598.97 → 98.97 (40)
PFDoDS	79780-39-5	700	15	698.09	698.9 → 79.96 (10) 698.90 → 98.91 (40)
PFECHS	335-24-0	461	34	460.97	460.97 → 98.95 (28) 460.97 → 119 (40) 460.97 → 381 (26)
4:2 FTS	757124-72-4	328.15	34	327.01	327.1 → 80.80 (26) 327.1 → 307.15 (18)
6:2 FTS	27619-97-2	428.17	24	427.01	427.10 → 80.93 (26) 427.10 → 407.18 (24)
8:2 FTS	39108-34-4	528.18	40	527.16	527.16 → 80.93 (28) 527.16 → 507.13 (26)
10:2 FTS	120226-60-0	628.02	8	627.03	627.03 → 80.86 (32) 627.03 → 607.07 (32)
DecaS	13419-61-9	221.34	56	221.07	221.07 → 64.98 (22) 221.07 → 79.89 (24)

P37DMOA	172155-07-6	514	44	469	469 →218.7 (24) 469 →269.03 (24)
7H-PFHpA	1546-95-8	346.07	8	345.03	345.03 → 131.03 (24) 345.03 → 281.06 (10)
FOSAA	2806-24-8	557.18	12	555.97	555.97 → 419.05 (24) 555.97 → 497.98 (28)
MeFOSAA	2355-31-9	571.21	6	569.99	569.99 → 419.03 (18) 569.99 → 483 (16)
ETFOSAA	1336-61-4	585.23	76	526.03	526.03 → 168.98 (24) 526.03 → 219.01 (24)
PFOSA	754-91-6	499.14	12	497.97	497.97 → 77.89 (28) 497.97 → 477.58 (26)
MeFOSA	31506-32-8	513.17	42	511.95	511.95 → 111.97 (26) 511.95 → 219 (24)
EtFOSA	4151-50-2	527.02	44	525.09	525.9 → 168.87 (26) 525.9 → 218.80 (26)
MeFOSE	24448-09-7	557.23	24	616.03	616.03 → 58.99 (14)
EtFOSE	1691-99-2	571.25	28	630.03	630.03 → 58.99 (12)
GenX	62037-80-3	347.08	36	284.95	284.95 → 119 (20) 284.95 → 168.97 (10)
ADONA	958445-44-8	395.10	14	376.97	376.97 → 84.96 (30) 376.97 → 251.02 (8)
9Cl-PF3ONS	73606-19- 6	570.67	66	530.97	530.97 → 198.97 (22) 530.97 → 351.05 (20)
SAMPAP	3820-83-5	649	54	650.03	650.03 → 96.94 (30) 650.03 → 123.03 (26) 650.03 → 168.97 (38) 650.03 → 526.06 (24)
diSAMPAP	30381-98-7	1221.50	92	1203.22	1203.22 → 169.02 (66) 1203.22 → 526.09 (40)

Table A3: Compounds used in the spiking solution, their delivered concentrations, and supplier.

Compound	Concentration	Supplier
PFBA	2000 (ng/mL)	Wellington Laboratories
PFPeA	2000 (ng/mL)	Wellington Laboratories
PFHxA	2000 (ng/mL)	Wellington Laboratories
PFHpA	2000 (ng/mL)	Wellington Laboratories
PFOA	2000 (ng/mL)	Wellington Laboratories
PFNA	2000 (ng/mL)	Wellington Laboratories
PFDA	2000 (ng/mL)	Wellington Laboratories
PFUnA	2000 (ng/mL)	Wellington Laboratories
PFDoDA	2000 (ng/mL)	Wellington Laboratories
PFTriDA	2000 (ng/mL)	Wellington Laboratories
PFTDA	2000 (ng/mL)	Wellington Laboratories
PFHxDA	2000 (ng/mL)	Wellington Laboratories
PFOcDA	2000 (ng/mL)	Wellington Laboratories
PFBS	1770 (ng/mL)	Wellington Laboratories
PFPeS	1880 (ng/mL)	Wellington Laboratories
PFHxS	1900 (ng/mL)	Wellington Laboratories
PFHpS	1910 (ng/mL)	Wellington Laboratories
PFOS	1920 (ng/mL)	Wellington Laboratories
PFNS	1920 (ng/mL)	Wellington Laboratories
PFDS	1930 (ng/mL)	Wellington Laboratories
PFDoDS	1940 (ng/mL)	Wellington Laboratories
PFECHS	50 ug/mL K+ (As salt)	Chiron AS
4:2 FTS	50 ug/mL Na+ (As salt)	Cambridge Isotope Laboratories
6:2 FTS	50 ug/mL Na+ (As salt)	Cambridge Isotope Laboratories
8:2 FTS	50 ug/mL Na+ (As salt)	Cambridge Isotope Laboratories
10:2 FTS	50 ug/mL Na+ (As salt)	Cambridge Isotope Laboratories
DecaS	Solid Na+ (As salt)	Sigma-Aldrich
P37DMOA	50 ug/mL	Dr. Ehrenstorfer
7H-PFHpA	Neat	Trc Canada
FOSAA	50 ug/mL	Toronto Research Chemicals
MeFOSAA	50 ug/mL	Chiron AS
ETFOSAA	50 ug/mL	Chiron AS
PFOSA	50 ug/mL	Chiron AS
MeFOSA	50 ug/mL	Chiron AS
EtFOSA	Neat	Sigma-Aldrich
MeFOSE	50 ug/mL	Chiron AS
EtFOSE	50 ug/mL	Chiron AS
GenX	Solid NH4+	Trc Canada
ADONA	50 ug/mL Na+ (As salt)	Wellington Laboratories
9Cl-PF3ONS	50 ug/mL K+ (As salt)	Wellington Laboratories
SAMPAP	50 ug/mL Na+ (As salt)	Wellington Laboratories
diSAMPAP	50 ug/mL Na+ (As salt)	Wellington Laboratories

Table A4: Compounds used in the standard solution, their delivered concentrations, purity, and supplier.

Compound	Concentration	Purity	Supplier
PFOS 13C8	50 ug/mL Na+ (As salt)	99%	Cambridge Isotope Laboratories
PFOA 13C8	50 ug/mL	99%	Cambridge Isotope Laboratories
6:2 FTS 13C2 D4	50 ug/mL Na+ (As salt)	99%	Cambridge Isotope Laboratories

B: Targeted screening chromatograms

Targeted screening (QqQ) chromatograms of all compounds from 0.9ppb standard solution, 1ppb matrix match sample, and 1ppb spiked sample 1.

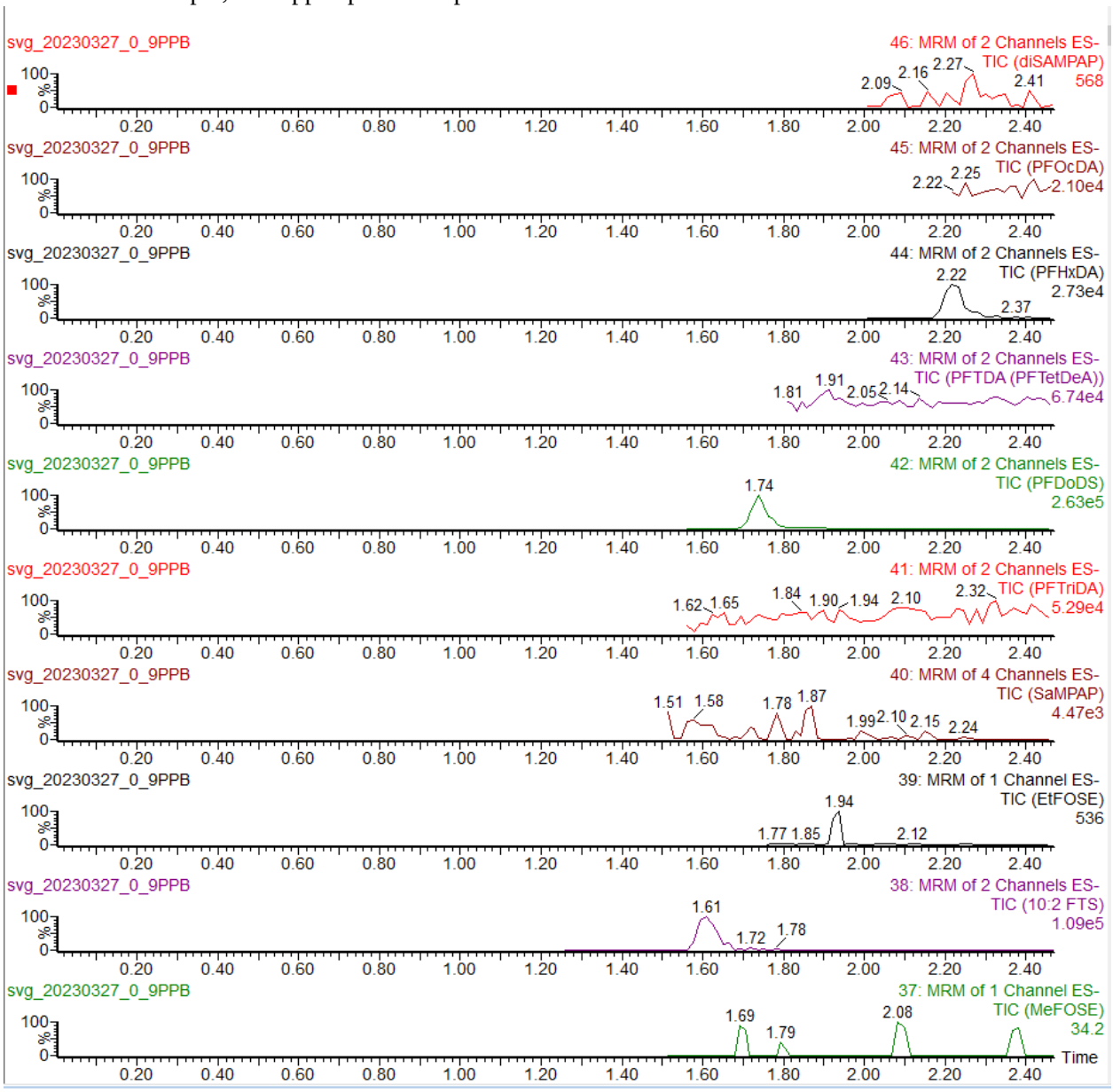


Figure B1: Standard solution 0.9ppb, 1

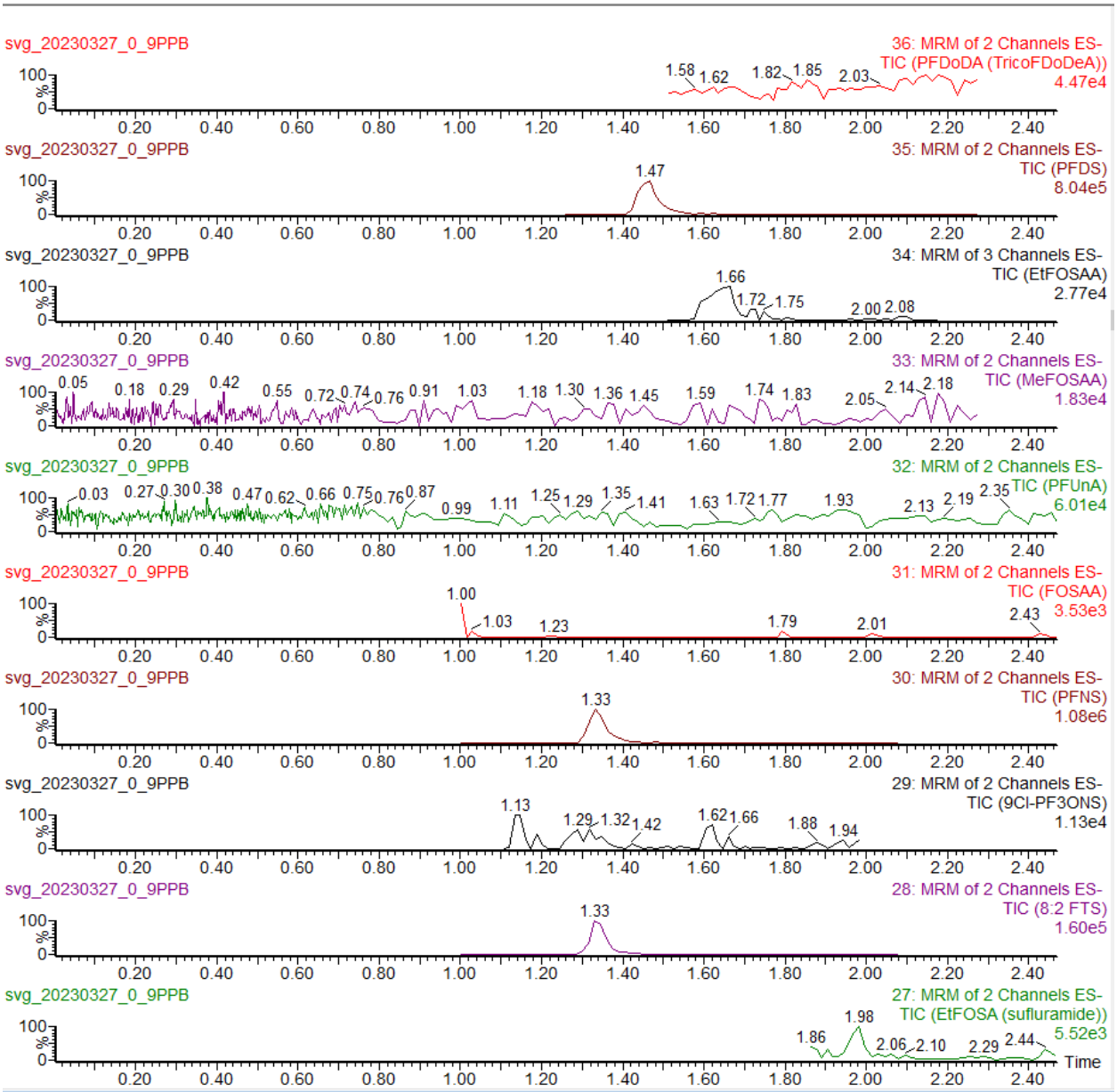


Figure B2: Standard solution 0.9ppb, 2

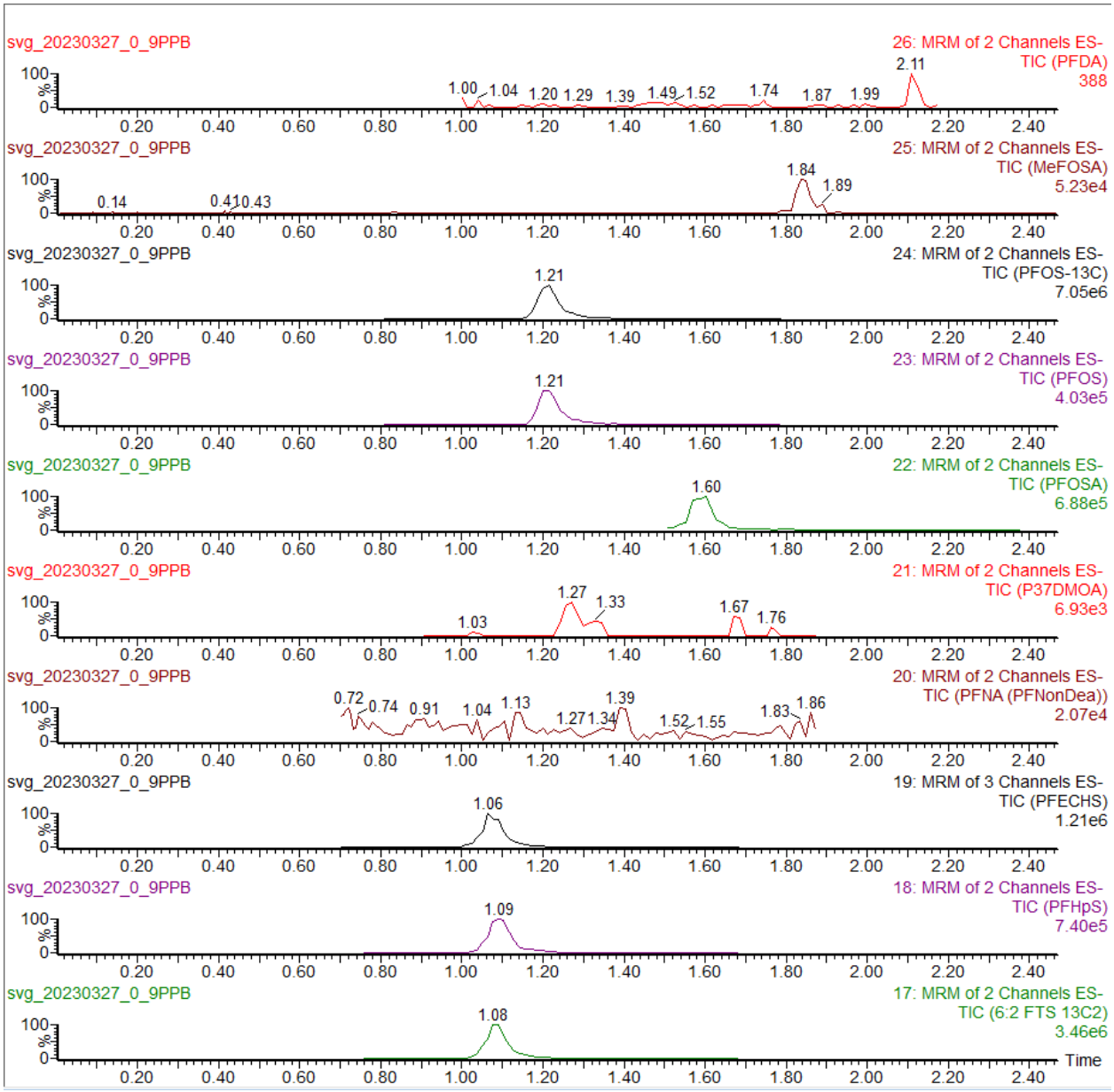


Figure B3: Standard solution 0.9ppb, 3

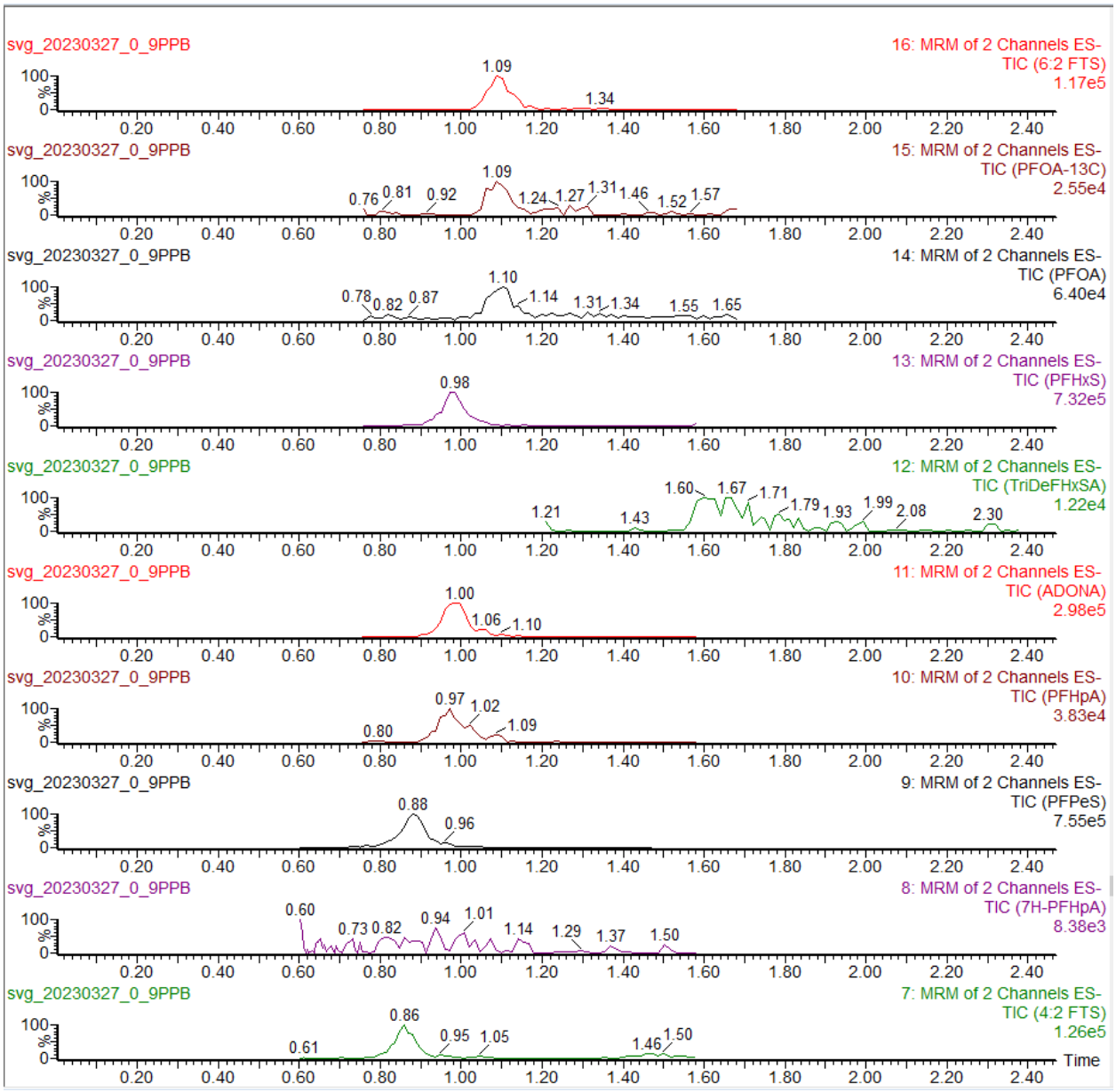


Figure B4: Standard solution 0.9ppb, 4

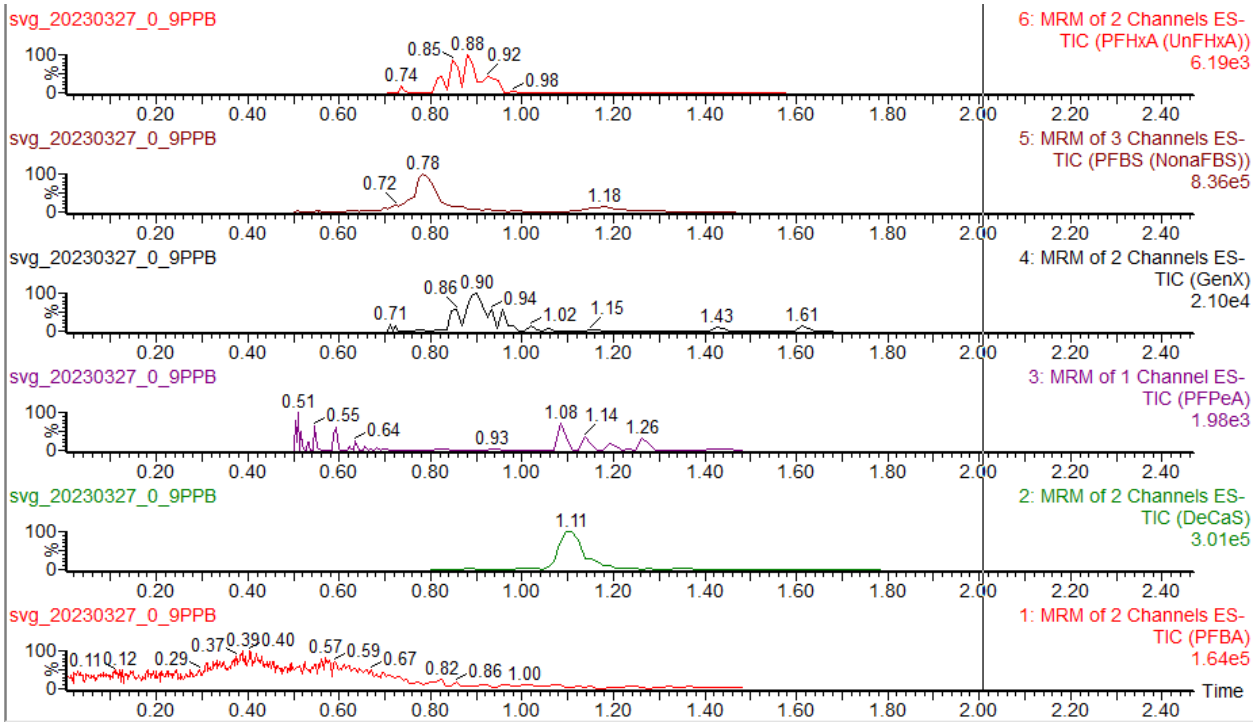


Figure B5: Standard solution 0.9ppb, 5

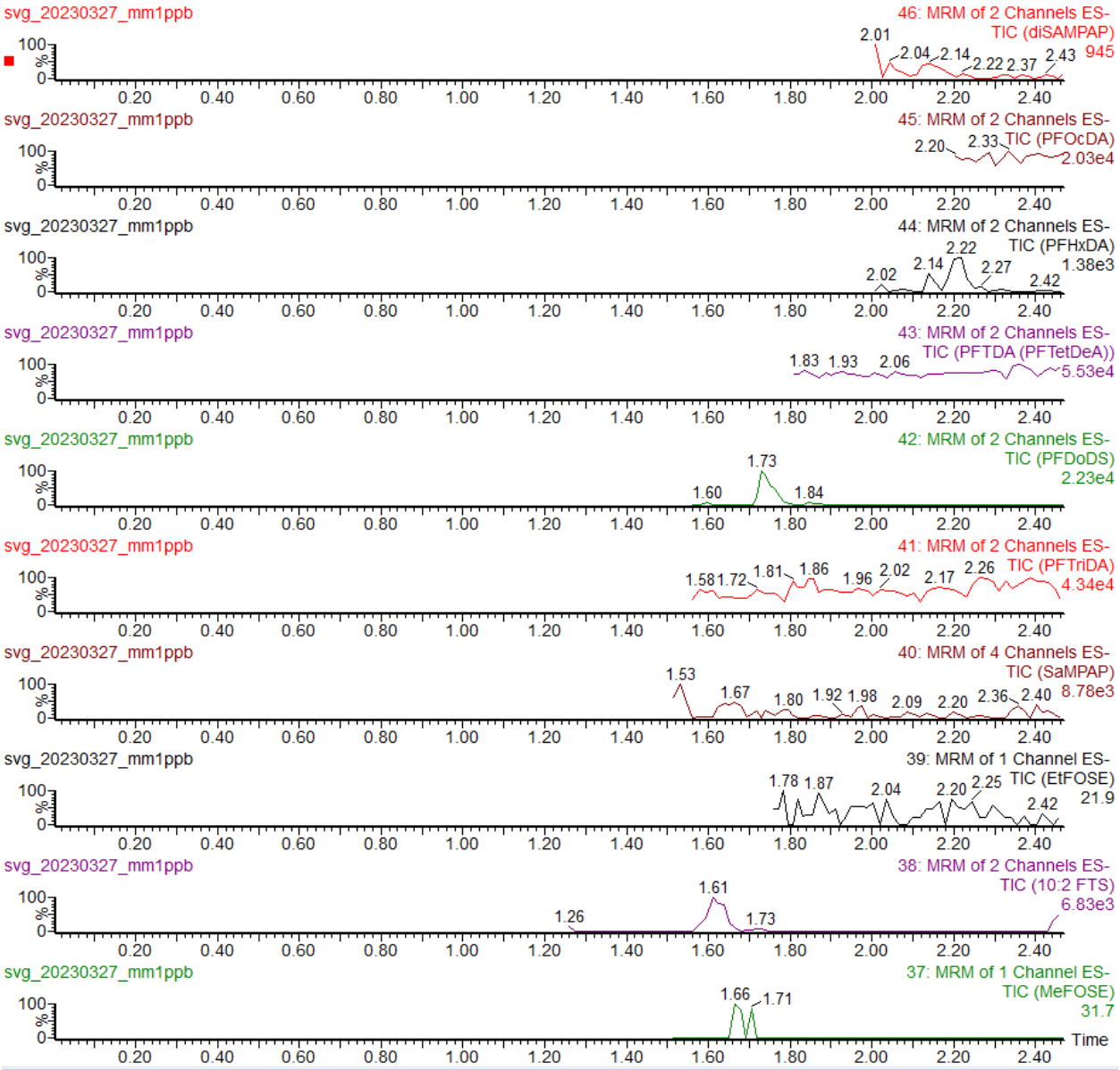


Figure B6: Matrix match 1ppb, 1

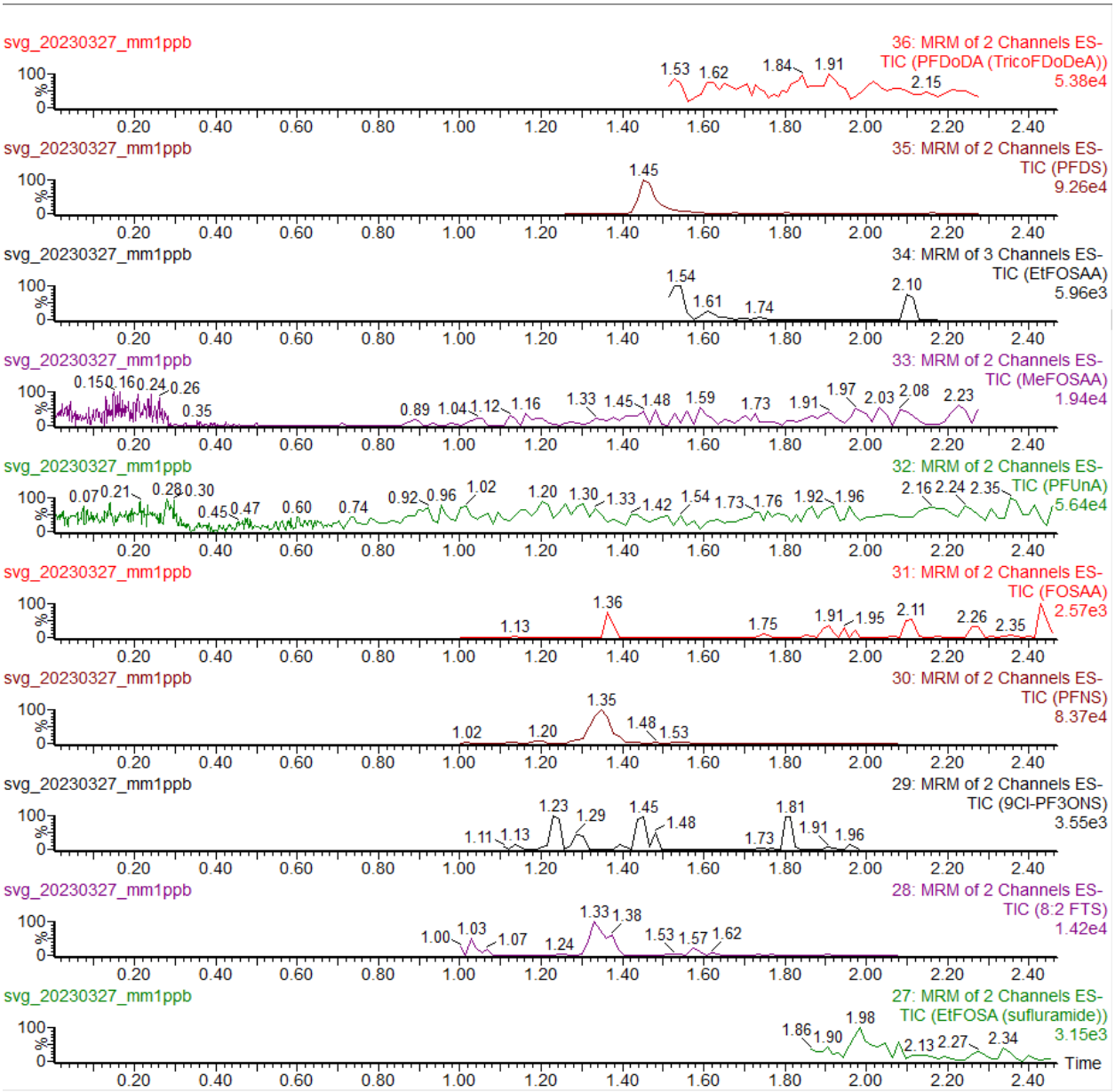


Figure B7: Matrix match 1ppb, 2

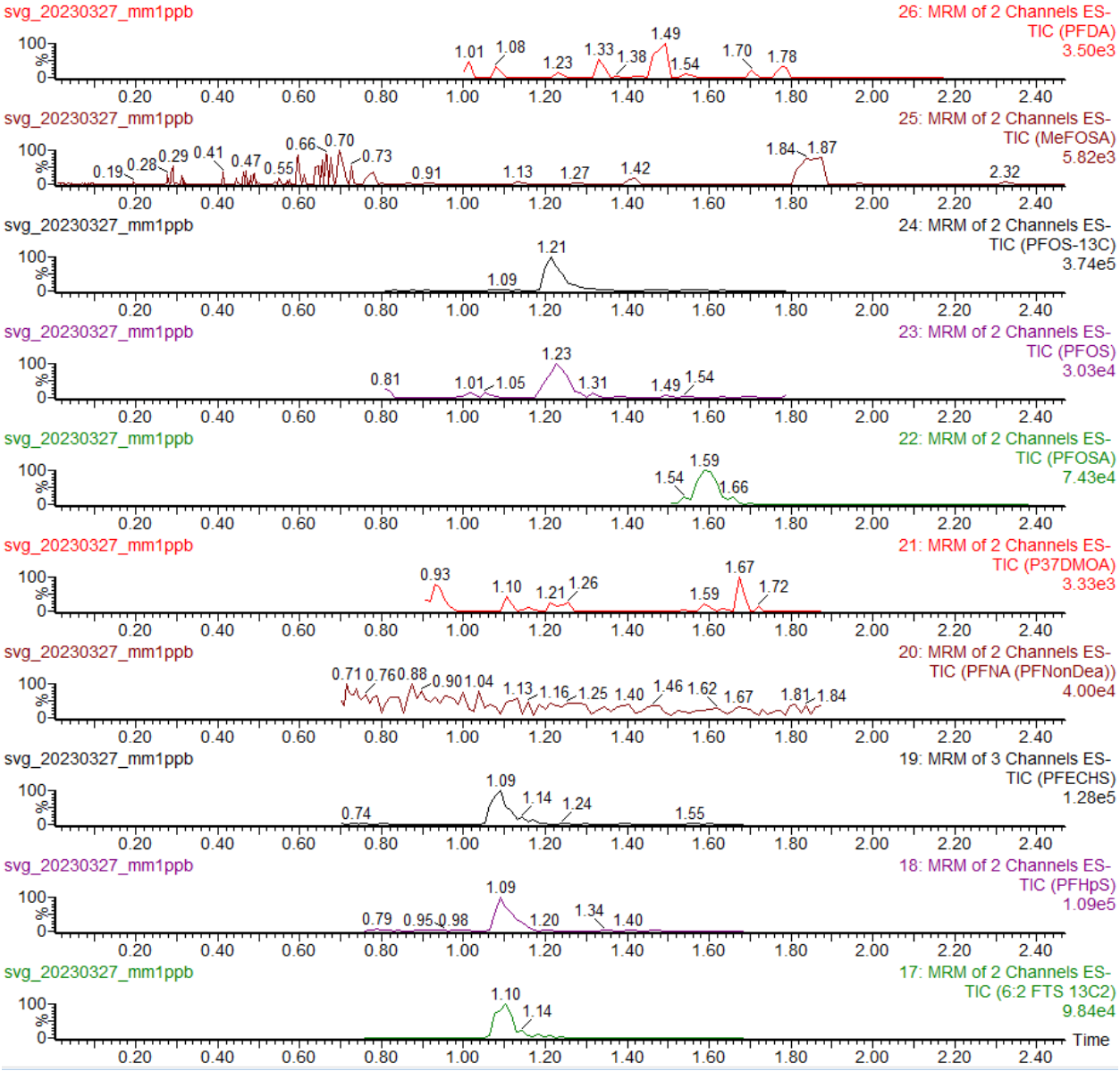


Figure B8: Matrix match 1ppb, 3

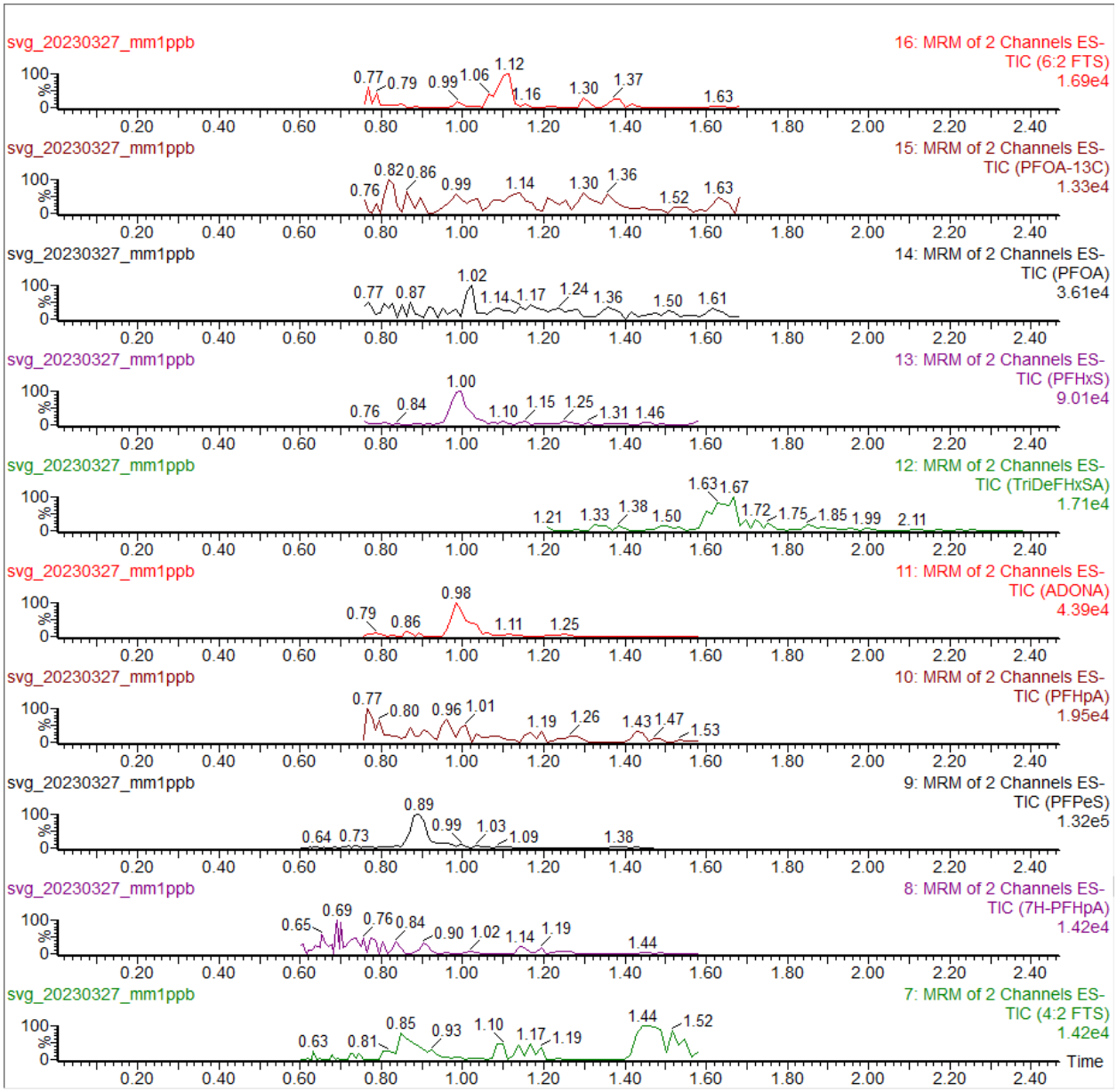


Figure B9: Matrix match 1ppb, 4

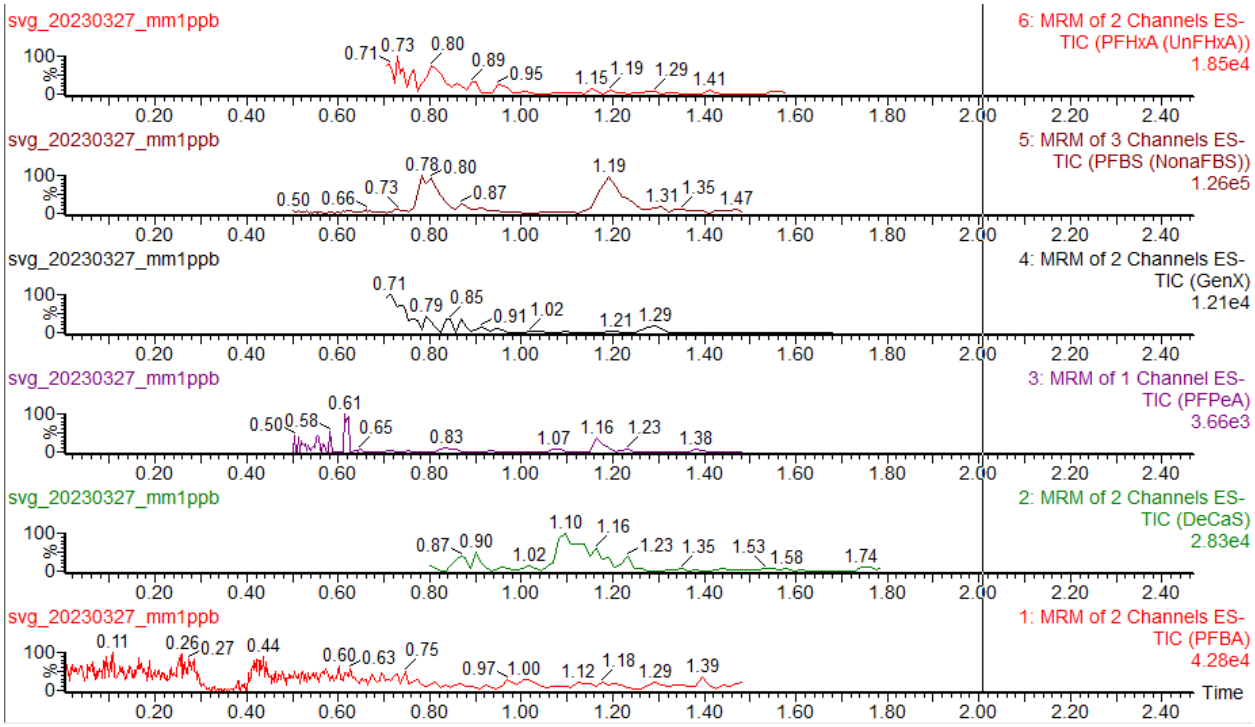


Figure B10: Matrix match 1ppb, 5

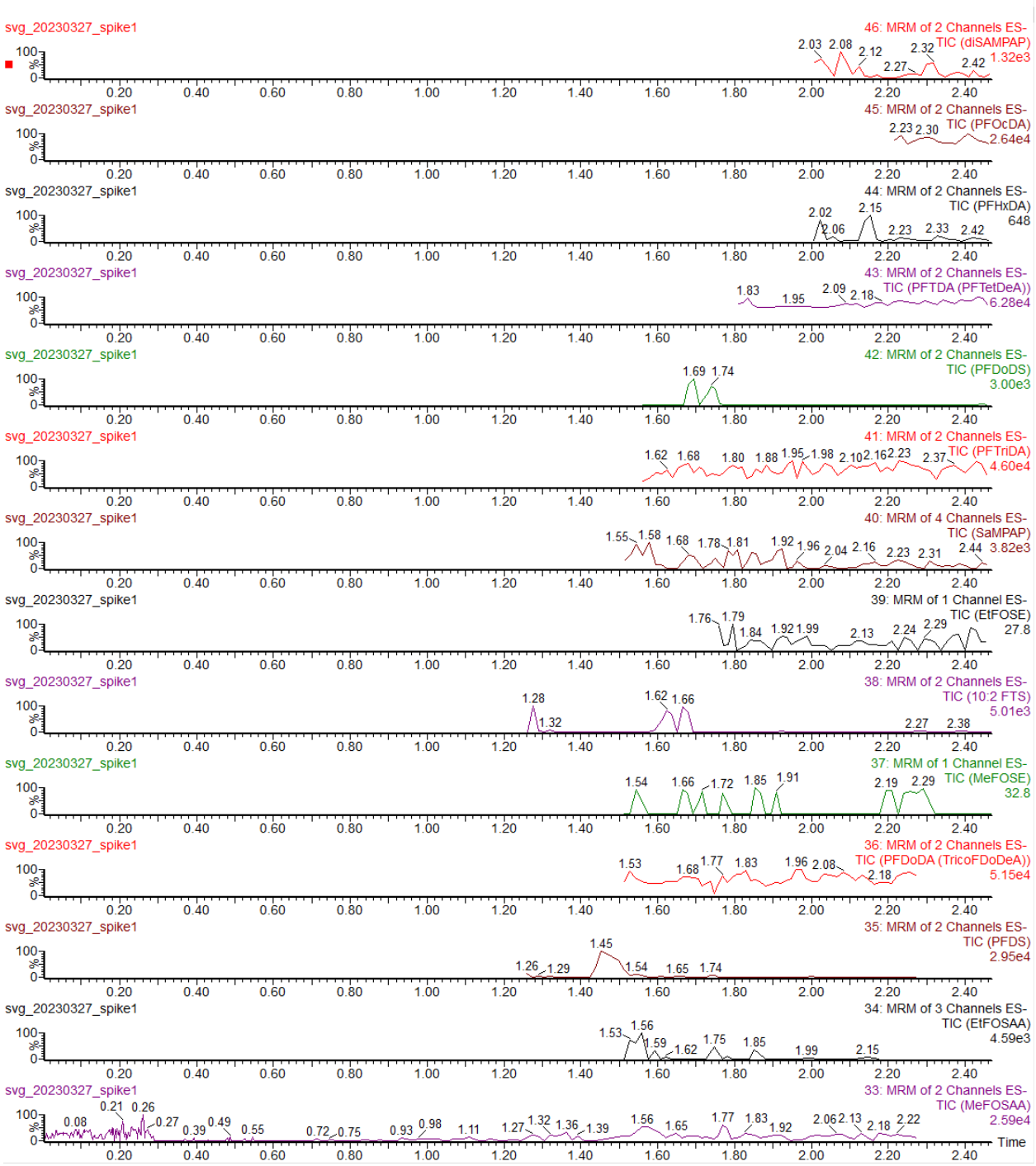


Figure B11: Spiked sample 1ppb, 1

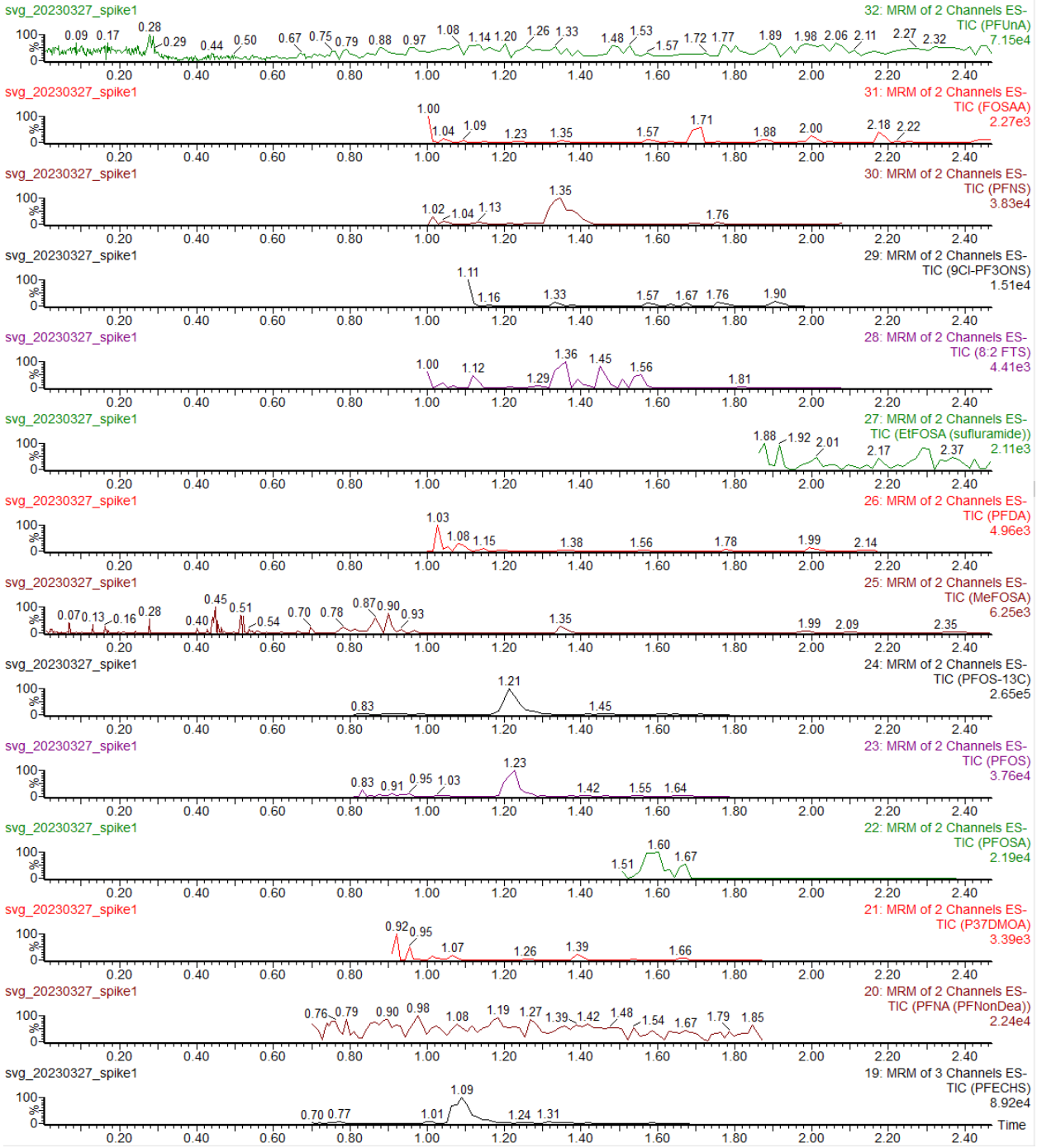


Figure B12: Spiked sample 1ppb, 2

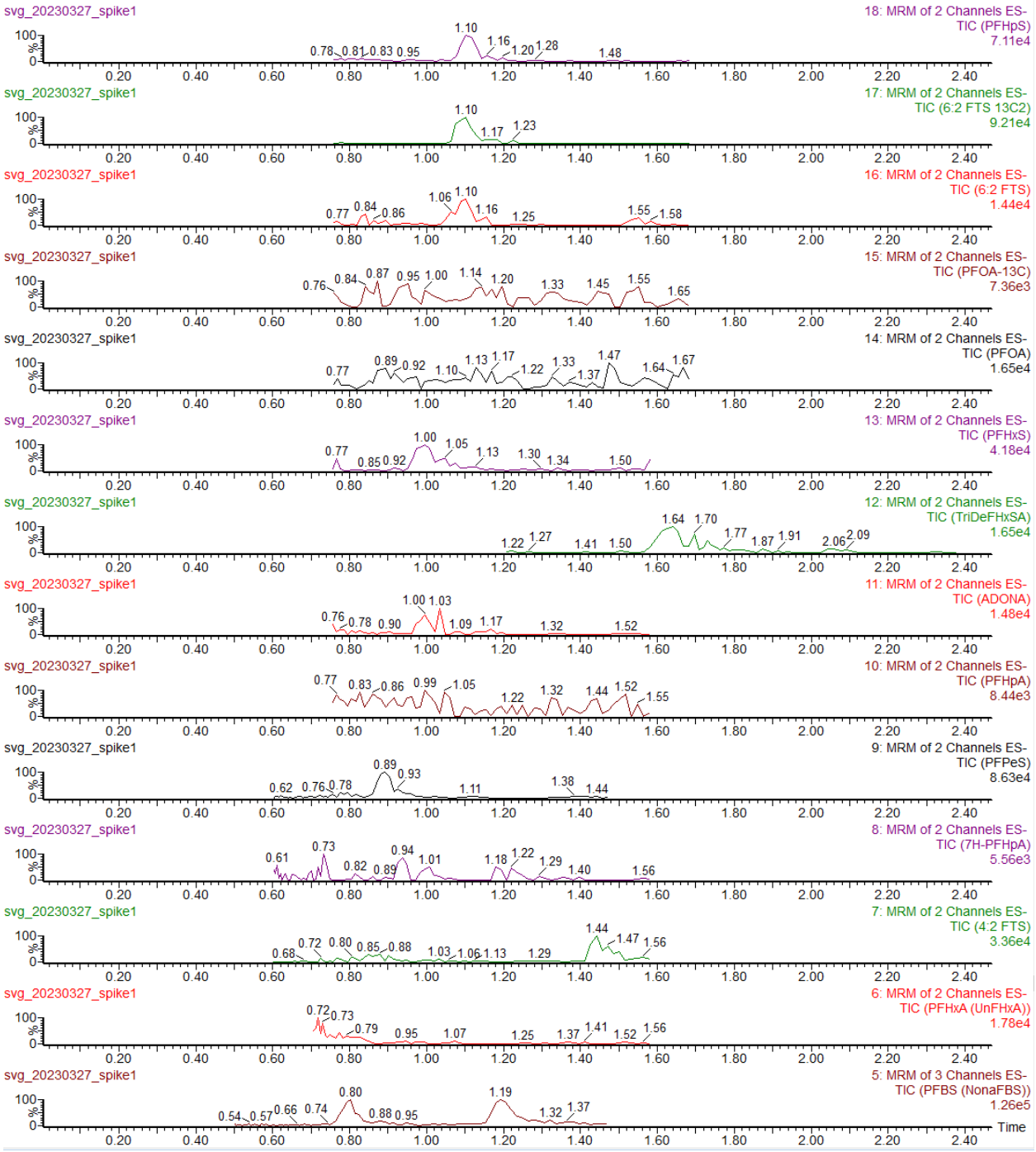


Figure B13: Spiked sample 1ppb, 3

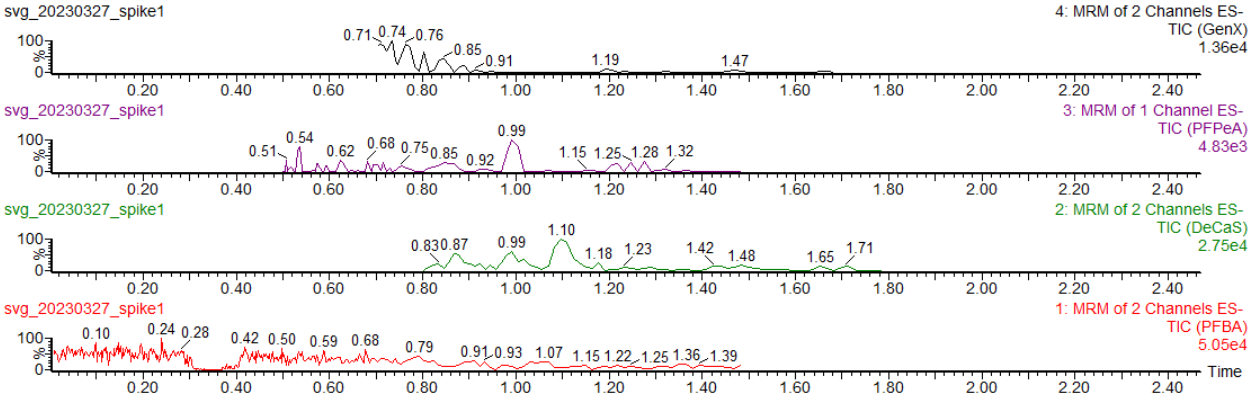
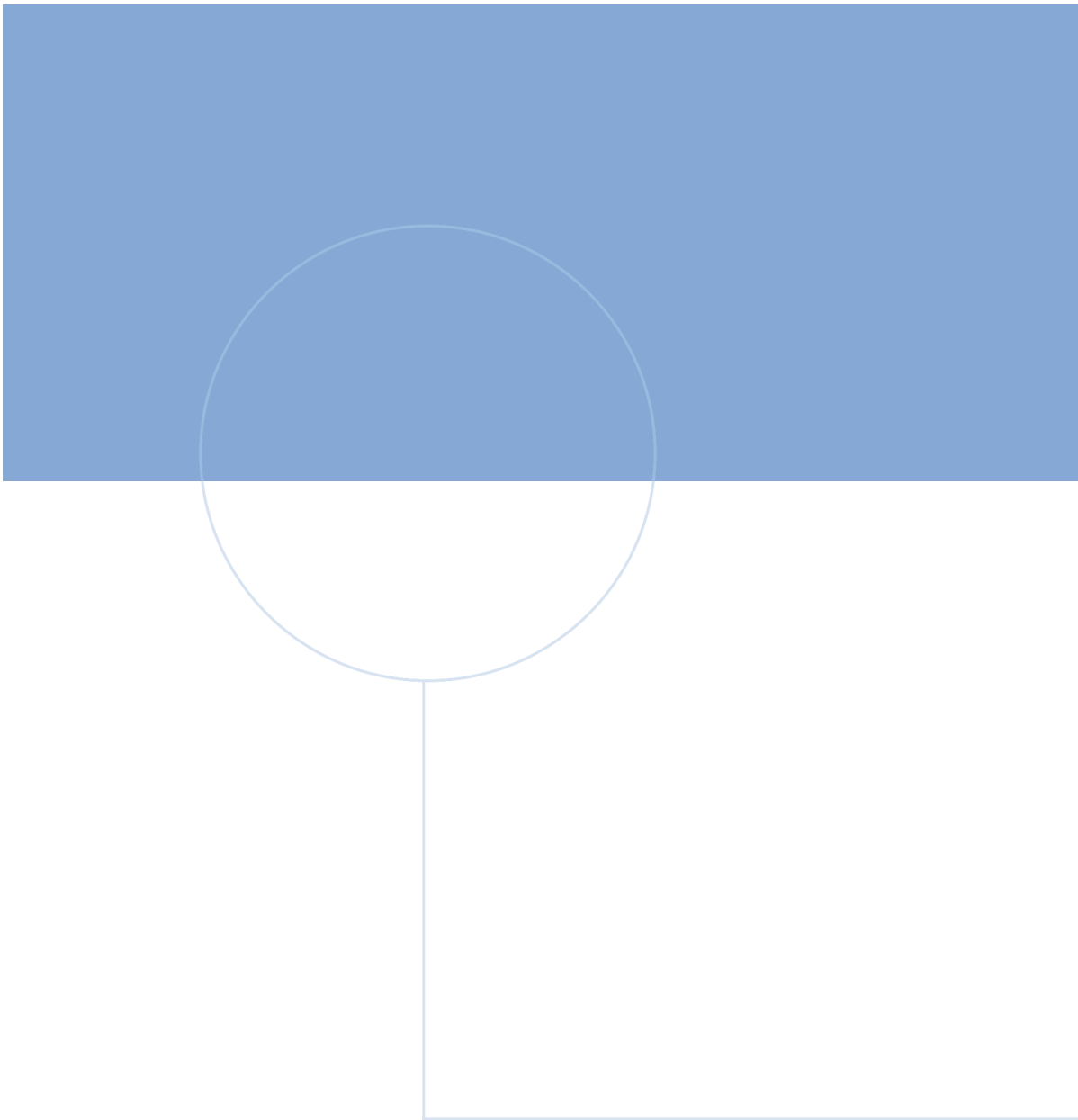


Figure B14: Spiked sample 1ppb, 4

C: Non-target results

Table C1: RT, m/z, proposed formulas and compound names, scores, and fragmentation scores for identified features in the Kara sea samples.

RT	m/z	Proposed Formula	Name	Score	Frag. score
1.1	274.9	C6H2Na4O8	Tetrasodium 1,1,2,2-ethanetetracarboxylate	39.1	0
1.2	561.2	C24H21F3N4O5	[2-[4-(furan-2-carbonyl)piperazin-1-yl]-2-oxo-ethyl] 2-[[3-(trifluoromethyl)phenyl]amino]pyridine-3-carboxylate	41.8	21.8
1.3	403.3	C26H41FO2	(2S,4S)-4-([(4beta,5alpha)-8-Fluoropregna-17,20-dien-4-yl]oxy)4-2-pentanol	38.2	0
1.3	287.2	C10H24N6	1,1'-octane-1,8-diyldiguanidine	39.4	4.36
1.4	336.0	C16H7N3O6	3,4,8-Trinitrofluoranthene	38.6	0
1.4	687.5	C40H76O3Si3	(1R,3R,7E,17beta)-1,3-Bis([dimethyl(2-methyl-2-propanyl)silyl]oxy)-2-methylene-17-((2S)-1-[(triethylsilyl)oxy]-2-propanyl)-9,10-secoestra-5,7-diene	38.6	0
1.5	431.3	C18H40N6O2	MFCD00226560	39.4	7.34
1.5	267.2	C16H30O4	((2S,3S)-3-[8-(Tetrahydro-2H-pyran-2-yloxy)octyl]-2-oxiranyl)methanol	44.2	28.5
1.6	561.6	C24H24F6N4O5	4-(3-[4-(2-Pyridinylamino)butyl]-1,2,4-oxadiazol-5-yl)-3-[3-(trifluoromethyl)phenyl]butanoic acid trifluoroacetate (1:1)	39	0
1.6	797.2	C48H36N10S2	3,3'-(29H,30H-Phthalocyanine-9,10-diyldisulfanediyl)bis(N,N-dimethylaniline)	38.7	0
1.7	269.2	C16H30O3	16-Oxohexadecanoic acid	41	10.7
1.7	351.2	C23H30NO2+	(2S,6R)-2-[(2S)-2-Hydroxy-2-phenylethyl]-1,1-dimethyl-6-(2-oxo-2-phenylethyl)piperidinium	41.7	14.5
1.7	299.2	C19H28N2O	2,2,3-Trimethyl-6-[(2S)-2-(3-pyridinyl)-1-piperidinyl]-4-hexyn-3-ol	40.9	10.7
1.8	271.2	C16H32O3	Juniperic acid	40.3	6.43
1.9	444.9	C14H8I2O	4,5-Diiodo-9(10H)-anthracenone	38.2	0
1.9	365.2	C22H32N4O2	N-Cyclohexyl-N-[2-(dimethylamino)ethyl]-2-(3-ethyl-4-oxo-3,4-dihydro-1-phthalazinyl)acetamide	49.8	57.3
2.1	379.3	C23H34N4O2	2-[4-([2-(4-Methoxyphenyl)-5-pyrimidinyl]methyl)-1-(3-methylbutyl)-2-piperazinyl]ethanol	42.4	18.6
2.4	1145.7	C57H91FN6O13	"(2R,3S,4R,5R,8R,10R,11R,13S,14R)-11-[(3-([2-(1-((1R,2S)-1-[4'-(Aminomethyl)-4-biphenylyl]-3-fluoro-1-methoxy-2-propanyl)-1H-1,2,3-triazol-4-yl)ethyl](methyl)amino)-3,4,6-trideoxy-beta-D-xylo-hexopyran	39.8	5.93
2.5	301.2	C20H32O3	osyl)oxy]-2-ethyl-3,4,10-trihydroxy-3,5,6,8,10,14-hexamethyl-15-oxo-1-oxa-6-azacyclopentadecan-13-yl 2,6-dideoxy-3-C-methyl-3-O-methyl-alpha-L-ribo-hexopyranoside"	42.6	21.6
2.5	369.2	C23H32O5	Tridecyl salicylate	47.9	50.9
2.6	253.2	C16H30O2	cannogenin	42.7	16.7
2.6	253.3	C17H40N2+2	Hexadecanedial	38.7	0
2.6	529.4	C28H50N6	N,N,N,N',N',N'-Hexamethyl-1,11-undecanediaminium	37.6	0
2.8	455.4	C30H50O4	2-[Bis(3-cyclohexyl-1-pyrazolidinyl)methyl]-5-cyclohexyl-2,3-dihydro-1H-pyrazole	41.6	22.7
2.8	303.2	C20H34O3	Bryodulcosigenin	42.4	27.6
3.1	477.4	C27H46O3	1-[5-(Tetradecyloxy)-2-furyl]ethanone	42.8	21
3.2	355.3	C18H40N6O	(3beta)-Cholest-5-ene-3,17,20-triol	51.4	65.1
3.2	423.3	C25H45O3P	N-(4-[(3-Aminopropyl)amino]butyl)-10-[(diaminomethylene)amino]decanamide	38.4	0
3.5	479.3	C26H44O2S	Benzyl hydrogen octadecylphosphonate	38.5	5.88



NTNU

Norwegian University of
Science and Technology