Norwegian University of Life Sciences
Faculty of Chemistry, Biotechnology
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# Non-target and suspect characterisation of organic chemicals of emerging concern in air and biota

## Ikke-spesifikk karakterisering av organiske forbindelser av økende miljørelevans i luft og biota

Laura Röhler

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Lørenskog, May 2020

# Contents

# List of abbreviations

| | |
|---|---|
| ATE | Allyl 2,4,6-tribromophenyl ether |
| B | Bioaccumulative |
| BAF | Bioaccumulation factor |
| BAS | Bioaccumulation screening |
| BATE | 2-Bromoallyl 2,4,6-tribromophenyl ether |
| BCF | Bioconcentration factor |
| BFR | Brominated flame retardant |
| CAS | Chemical Abstracts Service |
| CEAC | Chemical of emerging Arctic concern |
| CEC | Chemical of emerging concern |
| CMR | Carcinogenic, mutagenic or toxic to reproduction |
| EC10 | Effect concentration at 10 % effect |
| EDC | Endocrine disruptor |
| EEA | European Economic Area |
| GC | Gas chromatography |
| GC×GC | Comprehensive two-dimensional gas chromatography |
| GFF | Glass fibre filter |
| GPC | Gel permeation chromatography |
| HCB | Hexachlorobenzene |
| HPV | High production volume |
| HRMS | High resolution mass spectrometry |
| ISTD | Internal standards |
| $K_{OW}$ | Octanol-water partition coefficient |
| LC | Liquid chromatography |
| LRATP | Long-range atmospheric transport potential |
| LRMS | Low-resolution mass spectrometry |
| LRTP | Long-range transport potential |
| MHC-1 | Mixed halogenated compound 1<br>(1S,2S,4R,5R)-2-Bromo-1-(bromomethyl)-1,4-dichloro-5-[(1E)-2-chloroethenyl]-5-methylcyclohexane |
| MS | Mass spectra |
| NOEC | Long-term no-observed effect concentration |

| | |
|---|---|
| NORMAN | Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances |
| NTS | Non-target screening |
| OCS | Octachlorostyrene |
| OECD | Organisation for Economic Cooperation and Development |
| P | Persistent |
| PAH | Polycyclic aromatic hydrocarbon |
| PBDE | Polybrominated diphenyl ether |
| PeCB | Pentachlorobenzene |
| PFR | Phosphorous flame retardant |
| POP | Persistent Organic Pollutant |
| PUF | Polyurethane foam |
| QuEChERS | Quick, Easy, Cheap, Effective, Rugged and Safe |
| REACH | Registration, Evaluation, Authorisation and Restriction of Chemicals |
| SC | Stockholm Convention |
| SOP | Standard operating procedure |
| STOT RE | Specific target organ toxicity after repeated exposure |
| SUS | Suspect screening |
| SVHC | Substances of very high concern |
| SVOC | Semi-volatile organic compound |
| T | Toxic |
| $t_{1/2}$ | Half-life time |
| TCP | Tricresyl phosphate |
| TSCA | Toxic Substances Control Act |
| vB | Very bioaccumulative |
| vP | Very persistent |

# List of papers

**Paper I:**

Non-target and suspect characterisation of organic contaminants in ambient air, Part I: Combining a novel sample clean-up method with comprehensive two-dimensional gas chromatography.

Röhler, L., Bohlin-Nizzetto, P., Rostkowski, P., Kallenborn, R., and Schlabach, M.

*Atmos. Chem. Phys. Discuss.*, 2020, 1-33, 10.5194/acp-2020-263, 2020.

*Preprint under review.*

**Paper II:**

Non-target and suspect characterisation of organic contaminants in Arctic air, Part II: Application of a new tool for identification and prioritisation of chemicals of emerging Arctic concern in air.

Röhler, L., Schlabach, M., Haglund, P., Breivik, K., Kallenborn, R., and Bohlin-Nizzetto, P.

*Atmos. Chem. Phys. Discuss.*, 2020, 1-33, 10.5194/acp-2020-105, 2020.

*In press.*

**Paper III:**

Non-target and suspect characterisation of organic contaminants in biota, Part III: Selected levels of a marine and freshwater food chains in Norway.

Röhler, L., Bohlin-Nizzetto, P., Rostkowski, P., Kallenborn, R., and Schlabach, M.

*In preparation.*

# Abstract

Persistent organic pollutants (POPs) and other regulated organic chemicals are being monitored in the environment to evaluate the effectiveness of regulations and conventions, spatial and temporal trends as well as a compound`s environmental fate. However, there are hundreds of thousands of chemicals in commerce and new chemicals are continuously being developed. Some of these new chemicals have similar physical-chemical properties as known POPs or regulated chemicals, but their environmental fate is not well documented. Therefore, it is important to screen environmental samples for new potential chemicals of emerging concern (CECs) to detect such CECs at an early stage, preferably before reaching toxic or harmful concentrations for humans and/or the environment. The scientific work of this thesis aims to provide new methods to screen simultaneously for large number of compounds within a wide range of polarity and to identify new potential CECs in air and biota.

One specific aim of the research of this thesis was the development and evaluation of new clean-up methods omitting the use of destructive or very selective clean-up processes in order to keep as many as possible compounds of interest in the clean extract. For high-volume air samples a three-layer liquid chromatography method was established. For biota, this new clean-up method was combined with additional wide scope clean-up steps due to the complexity of biological samples. The evaluation of the new clean-up method found that it could provide sample extracts of similar cleanness and quality, compared to the traditional method using concentrated sulphuric acid, but also including a broader range of compounds (i.e. also acid-labile compounds).

Another aim of the research was the development of data processing workflows for the detection, identification and prioritisation of new potential CECs as well as the development of a wide-scope instrumental method for comprehensive two-dimensional gas chromatography (GC×GC) combined with low-resolution mass spectrometry (LRMS).

The combination of new clean-up methods, comprehensive detection methods, and new data processing workflows, could reveal several new potential CECs in air and biota which were detected for the very first time. It was found that some of the CECs detected in air may undergo long-range atmospheric transport, due to the detection in southern Norway and the Arctic. Furthermore, it was found that some of the detected CECs in

biota may have a bioaccumulation potential. This highlights the importance of screening studies for the early detection of new CECs in the environment. Further research is necessary to evaluate the environmental fate of these found CECs for possible regulatory actions.

# Sammendrag

Persistente organisk miljøgifter (POPer) og andre regulerte organiske forbindelser blir overvåket i miljøet for å evaluere effektiviteten av reguleringer og konvensjoner, romlig og temporale trender så vel som forbindelsers miljøskjebne. Det er likevel hundre tusenvis av kjemikalier i handel og nye kjemikalier blir utviklet for bruk i industrien og daglig bruk. Noen av disse forbindelser har like fysikalsk-kjemiske egenskaper som kjente tungt-nedbrytbare organiske forbindelser (for eksempel POPer) eller regulerte kjemikalier, men deres miljøskjebne er ofte ikke godt nok dokumentert. Det er derfor viktig å kartlegge miljøprøver etter nye potensielle forbindelser av økende miljørelevans (CECer). Dette er også viktig for å oppdage slike CECer på et tidlig stadium, helst før de når toksiske eller skadelige nivåer for mennesker og/eller miljøet. Det vitenskapelige arbeidet i denne avhandlingen har til hensikt å utvikle nye metoder for å analysere et stort antall kjemiske sporstoffer innen et vidt polaritetsområde og identifiserer nye CECer i luft og biota.

Ett mål med dette forskningsarbeidet var også å utvikle og evaluere nye opprensnings-metoder for å unngå bruk av destruktive og veldig selektive opparbeidelsesprosesser. Dette ble gjort for å beholde flest mulig forbindelser i prøveekstrakten. En kolonnekromatografisk metode bestående av tre ulike adsorbentlag ble utviklet for luft prøver med stort volum. Denne nye væske kromatografiske metoden ble kombinert og utvidet med flere ikke-spesifikke opparbeidelsesskritt på grunn av kompleksiteten i de biologiske prøvene. Gjennom evalueringen av den nye opparbeidelsesmetoden vle det bekreftet at metoden produserer ekstrakter med tilsvarende renhet og kvalitet, sammenlignet med den tradisjonelle metoden som benytter konsentrert svovelsyre. Dette gjelder også tilsvarende opparbeidelsesmetoder for analyser av syrelabile sporstoffer.

Basert på denne studien ble det utviklet en standard analyse protokoll (SOP) for detektering, identifisering og prioritering av nye potensielle CECer. Videre ble det utviklet en ikke-spesifikk instrumentell metode for omfattende todimensjonal gass-kromatografi (GC×GC) i kombinasjon med lav oppløsende masse spektrometri (LRMS). Kombinasjonen av de nye prøveopparbeidelsesmetodene, den omfattende deteksjonsmetoden og databearbeidelsesmåten, avslørte flere nye potensielle CECer i luft- og biota-prøver. Det ble oppdaget at noen av CECene som ble detektert i luft

muligens hadde vært utsatt for atmosfærisk langtransport siden de ble detektert i Sør Norge og på Svalbard. I tillegg ble det funnet at noen av de oppdagede CECene i biota kan ha et bioakkumuleringspotensial. Dette påpeker viktigheten av ikke-spesifikke kartlegging av miljøprøver for CECer er ett viktig ledd for en tidlig oppdagelse av nye CECer i miljøet. Videre forskning er nødvendig for å evaluere miljøskjebnen til de oppdagede nye CECene for mulige regulatoriske handlinger.

# 1. Chemicals in the environment and society

The modern way of life comes with a high need for various chemicals to meet the ever-growing demand for consumer products already since the industrial revolution in the 18th century. Together with a rapidly increasing world population, the need for chemicals is continuously growing [1]. A good indicator of the number of chemicals globally is the Chemical Abstracts Service (CAS) registry®, which provides a unique identifier for organic and inorganic chemical substances. This registry has increased with more than 60 % over the last five years, from 100 million registered chemicals in 2015 [2] to over 160 million by May 2020 [3]. It is not known how many of these registered chemicals are in commerce or might have a relevant negative impact on the environment. According to CAS CHEMLIST® by May 2020, over 394 000 chemicals are regulated in key markets worldwide [4]. However, for some organic chemicals like legacy pollutants and priority organic chemicals a relevant negative impact and harm on the environment and/or humans is known. This is acknowledged by international regulatory authorities and for legacy pollutants, as well as priority organic chemicals, international regulations are already in place. Among these, not only the production and use of these legacy pollutants and priority organic chemicals are regulated by international conventions, e.g. Aarhus protocol, Rotterdam convention or Stockholm convention [5-7], but also hazardous waste production and disposal are regulated through international conventions, e.g. Basel convention [8].

## 1.1. New potential chemicals of emerging concern (CECs)

In recent years, more and more organic chemicals are included in international, regional or national regulations or conventions. For example, the initial Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) included 12 POPs in 2004 (the 'dirty dozen'). Through the following years, the SC has been expanded with additional 16 new POPs (status May 2020) and further chemicals are currently under revision [6, 9]. Since these chemicals were restricted in use or banned from the marked, but there might still be a need for their function, the industry is producing replacement chemicals. Through this replacement, new potential chemicals of emerging concern (CECs) may enter the environment in large quantities. Ideally, these replacement chemicals should be less harmful to humans and the environment. However, this is not always the case. As an example, different phosphorous flame retardants (PFRs) were proposed as alternatives

to the banned polybrominated diphenyl ethers (PBDEs) due to their similar use patterns. The chlorine containing PFRs, as well as tricresyl phosphate (TCP), have however been shown to be of environmental concern, due to their toxicity [10, 11] and detection in higher concentrations than PBDEs in environmental samples, also from the Arctic [11, 12].

An additional way that may be used to substitute banned or restricted chemicals is chemical modification. Here, the chemical will be modified by removing the unwanted feature for which it was banned/restricted but keeping its useful function. Consequently, many chemicals with similar functions can be created. Due to the structural difference, these are being handled as individual chemicals by the regulatory authorities, allowing production volumes of each single compound to be kept below the legal thresholds for registration. Thus, the generation of long registration procedures and documentation demands/registration dossiers which should show that a chemical does not have a relevant negative impact on the environment, can be avoided.

Depending on the country, there are different thresholds in production/import quantities for when a chemical requires registration. In the European Economic Area (EEA), the threshold for registration is an annual import or production of ≥ one tonne. This registration is managed by the European Chemical Agency's (ECHA) REACH regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) [13]. In addition to those substituted chemicals, other products will be modified or new additives/other chemicals applied to meet today's quality and functionality requirements. Even though there are many cases where hazardous chemicals were substituted with safer chemicals [14], this might not always be the case, as for example mentioned before for PFRs. In addition, a potentially safe chemical could be classified as more hazardous in the future due to developments in risk assessment and/or scientific studies which propose a potential harmful effect to humans or the environment. Thereby the environment could be exposed to more and more chemicals that might have a relevant negative impact. Furthermore, intermediates of industrial processes are not registered in REACH [15].

Organic chemicals may enter the environment through several pathways, including emission from products and applications, direct application like agrochemical usage or paint, unintended by-products in industrial processes, insufficient waste management or disposal standing in conflict with the Basel convention [8].

Identifying and monitoring relevant organic chemicals at an early stage is an important task to prevent negative impacts on the environment. Depending on how much knowledge exists about negative impacts on the environment, chemicals could be candidates to be included in the previous mentioned conventions, e.g. SC or REACH. But, in many cases, there is not yet enough knowledge about potential impacts on humans and the environment. A chemical that is detected in different environmental matrices and thereby is receiving increasing focus from the scientific community is often referred to as emerging contaminants or CECs. The research, this thesis is based on, is aiming at identifying new CECs that were previously not identified in the respective matrices, and for which very little or no knowledge regarding potential negative impacts on the environment is available. To identify new potential CECs out of hundreds of thousands of chemicals globally in commerce [4], large databases of registered chemicals need to be analysed and theoretical and practical screening studies are necessary.

## 1.2. Risk characterisation of chemicals

The identification, prioritisation and evaluation of organic chemicals is vital for the characterisation of negative impacts on the environment and humans. Such impacts are mainly based on three to four hazardous properties that describe persistent organic pollutants:

1. Persistent (P): The ability of a chemical to remain in the environment over very long time periods without degradation.
2. Bioaccumulative (B): The ability to concentrate in living organisms by bioconcentration and biomagnification. This means an uptake in living organisms through its respiratory media as well as higher concentrations in higher trophic levels through food intake.
3. Toxic (T): The ability to cause harmful effects on humans and/or the environment (depending on concentration).
4. Long-range transport potential (LRTP): The ability to be transported over long distances from the respective sources.

Depending on the regulation or convention, chemicals need to fulfil certain criteria for these hazardous properties to be included. The most relevant regulations for the research, on which this thesis is based, are the Norwegian priority list covering

Norway [16], REACH covering the EEA [13], and the Stockholm convention on POPs [6], a global convention. The Norwegian priority list is using the same criteria as defined by REACH and is not be discussed separately. In addition, there are other regulations and conventions defining different PBT criteria which need to be fulfilled for chemicals to be included in the respective convention/regulation. Examples are the Aarhus protocol on long-range transboundary air pollution on POPs [5] or the US Toxic Substances Control Act (TSCA) of 1976 which was updated in 2016 with the Frank R. Lautenberg Chemical Safety for the 21st Century [17].

A summary for screening criteria for REACH and SC is given in Table 1 and discussed in detail in the following sections.

Table 1: Overview of screening criteria from REACH and Stockholm convention [18, 19].

| | **REACH [13]** | **Stockholm convention [6]** |
|---|---|---|
| Persistent | $t_{1/2}$water fresh/marine ≥ 40/60 days<br>vP ≥ 60 days<br>$t_{1/2}$soil ≥ 120 days<br>vP ≥ 180 days<br>$t_{1/2}$sediment fresh/marine ≥ 120/180 days<br>vP ≥ 180 days | $t_{1/2}$water ≥ 2 months<br><br>$t_{1/2}$soil ≥ 6 months<br><br>$t_{1/2}$sediment ≥ 6 months |
| Bioaccumulative | BCF ≥ 2000<br>vB ≥ 5000 | BCF or BAF ≥ 5000<br>Or log $K_{OW}$ ≥ 5 |
| Toxic | NOEC or EC10 ≤ 0.01 mg/L<br>Or Carcinogen cat. 1A, 1B<br>Or mutagenic cat. 1A or 1B<br>Or reproduction toxic cat. 1A, 1B or 2<br>Or evidence for chronic toxicity<br>STOT RE cat. 1 or 2 | Evidence of adverse effects to human health/environment,<br>Or toxicity/ecotoxicity indicate potential for damage to human health or the environment |
| Long-range transport potential | Not included | Measured levels in distant of source of relevance<br>Or monitoring data showing LRT with potential to transfer to a receiving environment<br>Or environment fate properties/model results that show LRTP: $t_{1/2}$air ≥ 2 days |

$t_{1/2}$: half-life; vP: very persistent; vB: very bioaccumulative; BCF: bioconcentration factor; BAF: bioaccumulation factor; $K_{OW}$ octanol-water partition coefficient; NOEC: long-term no-observed effect concentration; EC10: effect concentration at 10 % effect; STOT RE: specific target organ toxicity after repeated exposure.

### 1.2.1. Persistence (P)

The persistence of an organic chemical is defined by its half-life, $t_{1/2}$. The half-life is the time it takes for the concentration of an emitted chemical to be reduced to half of the original concentration in a specific medium. Both REACH and SC do differentiate between $t_{1/2}$ in the media water, soil and sediment for P classification. In addition to that, REACH has different values for fresh/marine water as well as for

freshwater/marine sediments, with marine water and sediments having prolonged $t_{1/2}$ compared to freshwater/freshwater sediments. As the persistence is depending on temperature as well as the two major degradation processes, photolysis/hydrolysis and biodegradation [20], which all differ geographically and seasonally, there is an uncertainty in exact half-lives. Half-lives might differ from one to another geographic area. It is also difficult to determine half-lives by empirical measurements/experiments, because seasonal variations need to be simulated and experiments need to be carried out over a long time period. Thresholds for $t_{1/2}$ in the respective media which need to get exceeded are presented in Table 1.

A widely used model-software to estimate P, as well as B and LRTP, is the EPIsuite software [21-25]. EPIsuite runs simultaneously different models for the estimation of various physical-chemical and environmental fate properties from one input.

### 1.2.2. Bioaccumulation (B)

Bioaccumulation is the ability to concentrate in living organisms by two processes, bioconcentration and biomagnification. It is a consequence of persistence as the removal (through degradation) is slower than the uptake of a chemical but also other physical-chemical properties (e.g. lipophilicity, hydrophobicity). The uptake of contaminants through respiratory media resulting in higher concentrations in living organisms is the process of bioconcentration. Similarly, biomagnification describes the process of increasing concentrations at higher trophic levels (predators) compared to lower trophic levels (prey) [26]. The higher the lipophilic, i.e. enrichment in lipids/organic tissue, the stronger the bioaccumulation potential. Both REACH and SC do characterise B with the bioconcentration factor (BCF), where BCF ≥ 2000 and 5000 characterise bioconcentration for REACH and SC, respectively. In addition, SC characterises B also by bioaccumulation factor (BAF) and octanol-water partition coefficient ($K_{OW}$), with BAF ≥ 5000 and log $K_{OW}$ ≥ 5 as defined thresholds. For the estimation of B, the same software as for the estimation of P or LRTP, EPIsuite, is widely used [21].

### 1.2.3. Toxicity (T)

As already Paracelsus in the 15th century proposed "*all things are poison, and nothing is without poison; but the dose makes it clear that a thing is not a poison*" [27]. Hence, if a chemical causes adverse effects to living organisms or the environment is a matter of the concentration of that chemical. In the SC, the toxicity is not characterised by defined

values, but rather the premise that a chemical has adverse effects, or that data on toxicity/ecotoxicity suggest a negative impact on human health or the environment. On the other side, REACH has several parameters to characterise T of an organic chemical in aquatic environments, of which minimum one need to be fulfilled. The long-term no-observed effect concentration (NOEC) for marine or fresh water organisms are the highest concentrations of an organic chemical these organisms can be exposed to, without seeing a significant effect compared to the control group, which was not exposed to the chemical in a long-term study. As an alternative, the effect concentration at 10 % effect (EC10) can be used. The EC10 is the concentration at which 10 % of the organisms show an adverse effect. For both, NOEC or EC10, the value needs to be ≤ 0.01 mg/L for marine or freshwater organisms to be classified as toxic. Another parameter under REACH to characterise T are organic chemicals which are carcinogenic, mutagenic or toxic to reproduction (CMRs). A chemical is classified as T if it belongs to one of the following categories: (a) known human CRM based on human evidence (cat. 1A), (b) presumed human CRM based on animal studies (cat. 1B), or (c) suspected reproductive toxicant based on limited evidence from animal studies or/and humans (cat. 2) [28]. In addition, also the specific target organ toxicity after repeated exposure (STOT RE) cat. 1 or 2 can be used to characterise an organic chemicals T under REACH. Here, STOT RE cat.1 is the reliable evidence of adverse effects on organs/systems or systemic toxicity, at which STOT RE cat.2 is the evidence of adverse effects on organs/systems or systemic toxicity [29].

### 1.2.4. Long-range transport potential (LRTP)

The ability to be transported over long distances from the respective sources, LRTP, is defined as a hazardous parameter in the SC, but not within REACH. Chemicals can be transported through air, water or migrating species. LRTP can be shown through measurement or monitoring data of a chemical in a remote environment far away from its sources (e.g. the Arctic/Antarctica), and/or environmental fate properties models. Specifically, for LRTP through air (LRATP), this parameter is defined as: $t_{1/2}$air ≥ 2 days.

### 1.2.5. Additional classifications of high concern under REACH

REACH has, in addition to its PBT classification, additional classifications for chemicals which are of very high concern. Chemicals which are very persistent (vP) and very bioaccumulative (vB), values shown in (Table 1), do not need to be evaluated for T for

being classified as chemicals of very high concern. Other groups of chemicals, namely CRMs, discussed in sect. 1.2.3, and endocrine disruptors (EDCs), which interfere with endocrine or hormonal processes, are also of high concern. REACHs candidate list of substances of very high concern for Authorisation (SVHC list) is containing 205 substances by May 2020, including some inorganic chemicals (e.g. lead, lead oxide, cadmium, cadmium oxide, etc.) [30].

### 1.2.6. Further criteria for risk characterisation under REACH

The risk characterisation of chemicals under REACH does, besides (1) PBT and vPvB assessment also include further characterisations which would classify a chemical as dangerous. This includes (2) physical hazards, e.g. explosives, flammables, oxidising gases, etc., (3) health hazards, e.g. acute toxicity, skin corrosion/irritation, serious eye damage/irritation, etc., and (4) environmental hazard, e.g. hazardous to the aquatic environment, hazardous to the ozone layer [31]. If a chemical is classified as dangerous by meeting the criteria of one of the classes (1)-(4), an exposure assessment is necessary. An exposure assessment is typically conducted for specific chemicals in occupational settings, but the estimation of the risk characterisation for humans and the environment is more complex. In order to do this, information about emissions and exposures during the life-cycle of a chemical is necessary. A first step would be gathering information about more precise production amounts, which then could be used to calculate theoretical emission and exposure values. These are values which are difficult to collect, but the production volume registered in REACH or, as an indicator, the production listing for high production volume (HPV) chemicals from the OECDs (Organisation for Economic Cooperation and Development), in which the European Commission also participates, can be used. The HPV chemical list includes all chemicals which were produced or imported ≥ 1000 tonnes/year in the EEA or at least one member of the OECD. A chemical needs to have large enough production/import or application, since without a large enough emission and thus exposure to a chemical, a negative impact to human health or to the environment cannot occur due to low concentrations in the environment (see also definition of T at sect. 1.2.3).

## 1.3. Supporting strategies

Although many national regulatory authorities have registers in place, the work to classify registered chemicals to classes of high concern is not completed. ECHA was

reporting in 2019 that approximately 40 % of chemicals with a production volume ≥ 100 tonnes/year were classified into classes of high concern, e.g. CMRs, PBT, vPvB or EDCs, which will be followed by the assessment of chemicals with lower production volumes. The assessment of all registered chemicals within REACH is scheduled to be finished by 2027. All chemicals which are not yet classified into classes of high concern, may not have sufficient information in the registration dossier, i.e. chemicals cannot be assigned to a class, or they may are of low priority for further risk assessment [32].

### 1.3.1. Early stage detection of chemicals of emerging concern

The early stage detection of new potential CECs in the environment (e.g. air, biota, sediment, etc.) is an important tool for providing authorities with essential knowledge on a chemicals environmental fate. Such knowledge is crucial for including potential candidates for further regulations. The sooner a chemical is detected the sooner that a chemical can be regulated and the better are humans and the environment prevented from large exposures. Recent candidates for inclusion to the SC, e.g. perfluorohexane sulfonic acid, dechlorane plus and methoxychlor, were not matching totally the parameters for P, B, T and LRTP for inclusion (see Table 2 for theoretical values from EPIsuite), but scientific studies and measurements did show that these compounds do exceed these parameters, which resulted in the suggestion of several parties to include these candidates to the SC [9]. This shows that monitoring and screening studies to detect and monitor new potential CECs are crucial, since the environmental conditions are complex and difficult to predict in models.

Table 2: P, B and LRTP parameter for selected compounds from EPIsuite[21].

| | **Perfluorohexane sulfonic acid** | **Dechlorane plus** | **Methoxychlor** | **Thresholds defined in SC** |
|---|---|---|---|---|
| $t_{1/2}$water | 6 months | 6 months | 6 months | ≥ 2 months |
| $t_{1/2}$soil | 12 months | 12 months | 12 months | ≥ 6 months |
| $t_{1/2}$sediment | 52 months | 52 months | 52 months | ≥ 6 months |
| BCF | 3 | 108 | 1044 | ≥ 5000 |
| log$K_{OW}$ | 3.16 | 11.27 | 5.67 | ≥ 5 |
| $t_{1/2}$air | 76 days | 0.5 days | 0.2 days | ≥ 2 days |

Furthermore, data of such studies can also be used to support the accuracy and to improve environmental fate models [33-36]. Field data are also necessary to highlight

regional limitations of the used models (e.g. low temperature and low atmospheric breakdown during the polar night in the polar regions). Also, publicly accessible production amounts and, ideally, production sites could be of great benefit for further improvement of environmental fate models, since emissions and exposure as well as potential distribution patterns could be calculated. In addition, environmental emissions from products are difficult to estimate by models. This is why field measurements of CECs are of high importance, besides the monitoring of known pollutants, to evaluate if regulations on restricted or hazardous chemicals are effective and if CECs occur in further matrices, sampling sites or regions. In addition to that, measurements, especially in remote areas, can give valuable information on the quality and improvement of environmental fate models. The earlier a chemical is detected in remote areas, the faster regulatory actions can be initiated.

### 1.3.2. Measurements in the environment

There is an increasing incentive to analyse environmental samples for large amounts of known or new potential CECs, but standardised methods applied in monitoring programmes are not directly applicable. The standardised methods often include very compound or compound-group specific targeted sample preparation methods, e.g. analysis of dioxins [37], and are, thus, not suitable for more than the targeted compounds. To avoid in-effective, labour-intensive and expensive developments of one-by-one target method for known or new CECs, new targeted multi-compound analytical methods are being developed [38, 39]. Such methods enable the possibility to detect and quantify many different, often several hundreds, compounds simultaneously. Many CECs often show similar physical-chemical properties as legacy pollutants and other chemicals included in monitoring programmes. However, CECs are often less stable and degrade more easily during destructive sample extraction/clean-up processes (i.e. acid treatment, saponification, lyophilisation, etc.). Such compounds, which are degrading when treated with concentrated sulfuric acid, include some legacy POPs (e.g. dieldrin, aldrin, endrin, endosulfan I/II/sulphate, etc.) and CECs like novel brominated flame retardants (e.g. ATE (allyl 2,4,6-tribromophenyl ether), BATE (2-bromoallyl 2,4,6-tribromophenyl ether),etc.) or cyclic volatile methyl siloxanes [18]. Therefore, novel sample extraction and clean-up methods are necessary to preserve less stable compounds and extend the range of compounds.

### 1.3.3. Multiresidue and wide-scope methods

To screen for chemicals of many different compound classes, or for approaches without any specific target group, non-target screening (NTS), the scope of the sample preparation methods needs to be as wide as possible. In order to achieve wide-scope sample preparation methods, minimal sample preparation is expected to be carried out, in some cases even raw, un-cleaned, extracts are analysed [40, 41].

Recently, some wide-scope sample preparation methods based on the QuEChERS approach (Quick, Easy, Cheap, Effective, Rugged and Safe) have been suggested for organic chemicals. The QuEChERS methods were originally introduced for pesticide residue analysis in fruit and vegetables [42], but have then also been applied to more and more compound groups like pharmaceuticals and veterinary drugs, polycyclic aromatic hydrocarbons (PAHs), dyes or EDCs [43]. These QuEChERS methods are including many compounds, mostly of similar compound classes, and are difficult to adjust for NTS approaches due to the large diversity of compounds for NTS [44]. Hereby, the combination of NTS with suspect screening (SUS), long lists of compounds of interest that are going to be identified and classified, is an often-used approach.

### 1.3.4. Limitations of wide-scope methods for analysis

As a consequence of keeping an extended range of compounds for subsequent analysis by minimal clean-up methods, the sample extracts may contain high amounts of matrix related residues which may affect the chromatographic separation. To compensate for more interfering background, the separation power of the analytical system needs to be increased. Therefore, SUS/NTS analysis are carried out on either ultra-high-resolution liquid or gas chromatographic instruments (LC or GC, respectively), usually in combination with high resolution mass spectrometry (HRMS). These combinations have successfully been applied on various environmental samples for the detection and characterisation of hitherto unknown environmental contaminants [45-52].

Comprehensive two-dimensional gas chromatography (GC×GC), which already has proven its capabilities to detect and characterize new potential CECs in environmental samples [53-59], enhances the separation power of the chromatographic system through its 2D separation. With GC×GC, it is possible to separate compounds which are coeluting on the first separation column, through the different polarity of the second-dimension column (Figure 1).

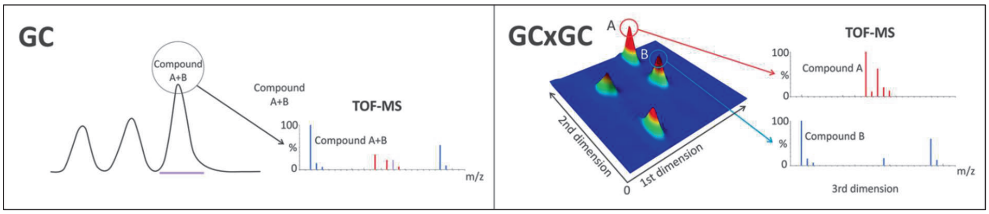



Figure 1: GC separation compared to GC×GC separation [18, 60].

## 1.4. Suspect and non-target screening

While in SUS samples are analysed only for a predefined list of compounds (e.g. CECs identified by scientists, authorities or priority list created by models), in NTS, in theory, all compounds detected in a sample (without a predefined list of compounds of interest) are identified. In practice, however, not all compounds can be identified during NTS data treatment and in literature the two approaches (SUS and NTS) are sometimes confused with each other. In NTS, compounds are identified using their mass spectra (MS) either by matching them to MS libraries (e.g. NIST MS library, Wiley, etc.), reference standards or MS information from shared scientific libraries for SUS (e.g. databases of the NORMAN network including MassBank Europe [61]). In addition to MS information, retention data can be used as identification points by calculating retention indices using retention markers [62].

In contrast to SUS, NTS is also aiming at identifying compounds without match to the used libraries or lists containing suspects. Since the majority of detected compounds in a sample (often more than 20000 compounds per sample) cannot be found in MS libraries, they are only identified by a mass spectrum of interest or unequivocal molecular formula [51]. Hence, intensive, manual investigation of each compound is necessary for further identification of detected compounds. Recently, Schymanski et al. defined a common set of rules on how to communicate SUS/NTS results [52] for a better comparability of SUS/NTS studies (with focus on LC-HRMS). These rules regulate how to communicate the identification confidence by introducing five levels, where level one describes highest confidence (confirmation using a reference standard) and level five describes lowest confidence (only an accurate mass could be determined). The improvement of these rules, and especially the adaption to GC-MS, is a very important task for further improvement of the comparability of SUS/NTS studies.

SUS/NTS approaches provide valuable information for the risk characterisation of CECs and potential new CECs in the environment. For example, a potential B can be assumed if a compound is detected in numerous biota samples of different levels of a food chain, especially if the concentration is rising within the food chain. Furthermore, if a compound can be detected far away from its potential sources in air or biota, a certain P and LRTP can be assumed.

## 1.5. Investigated compounds

The research of this thesis was based on NTS and, hence, not aiming at a specific target group. However, the identification was restricted to organic compounds that could be detected and characterised with the chosen sampling approaches, sample preparation and GC×GC based analysis.

For air samples, the possible compounds to identify are semi-volatile organic compounds (SVOCs) in air which could be sampled with the high-volume active air sampler and sampling material available at the two monitoring sites: (a) Birkenes observatory (southern Norway) for **Paper I** and (b) Zeppelin observatory (Ny-Ålesund, Svalbard) for **Paper II**.

For biota samples in **Paper III**, organic chemicals which had the potential to be present in the investigated food chains from inner Oslofjord or lake Mjøsa were possible compounds to identify.

# 2. Objectives

The overall objective of the research on which this thesis is based on is to reveal new potential CECs in environmental matrices. To achieve that, two major milestones needed to be reached:

(a) Development of a new sample preparation method for air samples and modification of an existing method for biota samples. The aim of this development was to ensure coverage of a broad-range of compounds of interest with an expanded range of polarity and less stable compounds that would degrade during destructive sample preparation.

(b) Development and adjustment of data processing and prioritisation workflows for SUS/NTS on GC×GC coupled to low-resolution mass spectrometry (LRMS) in order to filtrate, identify and prioritise the important findings in very large data sets.

**Paper I:** The main goals of this first publication were the development of novel clean-up method and to develop a simultaneous SUS/NTS data treatment and prioritisation workflow for GC×GC-LRMS data for the identification of CECs. The third goal was obtained by applying the novel clean-up method in combination with the workflow for SUS/NTS data treatment for GC×GC-LRMS data to real high-volume air samples from southern Norway (Birkenes observatory). As a part of this, the novel non-destructive, sulphuric acid free clean-up method for high-volume air samples was quantitatively evaluated with compounds covering a wide range of polarity.

**Paper II:** The main goal of the second publication was to identify known and new potential chemicals of emerging Arctic concern (CEACs) in high-volume air samples from the Arctic. This was obtained by applying the novel sample clean-up and SUS/NTS data treatment strategies from **Paper I** on air samples from the Zeppelin observatory in the Norwegian Arctic (Svalbard). A second goal was to identify CEACs with a possible LRATP, which are not meeting todays accepted criteria for LRATP into polar environments by model calculations.

**Paper III:** The main goal of the third publication was to identify known and new potential CECs in biological samples. This was obtained by modifying an existing extraction and clean-up method for biota and applying this in combination with simultaneous SUS/NTS data treatment strategies on various biological samples. As a

part of this, the SUS/NTS data treatment strategies were expanded with the screening on compounds which occurred in the examined food chains.

# 3. Methods

## 3.1. Samples and experimental design

For the research of this thesis, high-volume air samples were collected at two EMEP background monitoring stations, the Birkenes Observatory **(Paper I)** in southern Norway (Aust-Agder 58° 23' N, 8° 15' E, 190 m.a.s.l) and the Zeppelin Observatory **(Paper II)** on Svalbard (79° 55' N, 11° 53' E, 474 m.a.s.l). The sampling stations were chosen to collect air masses that were minimally affected of local sources, and, thus well suited for the detection of new potential CECs. The detection of CECs in air samples from these sites, far away from source areas, supports the assumption for possible LRTAP and that these CECs have a certain persistency, especially if these compounds can be detected in the Arctic **(Paper II)**. For evaluation of the newly developed clean-up method for high-volume air samples **(Paper I)**, a recovery test was carried out with unexposed glass fibre filters (GFF) and polyurethane foam plugs (PUFs), the same as those used for the real high-volume air sampling in **Papers I & II** as well as in routine air measurements of POPs and other SVOCs [63]. The novel clean-up method was applied to the air samples from Birkenes, in combination with the newly developed SUS and NTS data treatment workflow to detect and prioritise new potential CECs (**Paper I**). To prove the applicability to high-volume air samples, and to reveal CECs with a possible LRATP, this novel clean-up method and SUS/NTS data treatment workflow was applied on the air samples from Zeppelin (**Paper II**).

After this SUS/NTS data treatment workflow showed its applicability on air samples, the SUS/NTS workflow was applied and adjusted to a larger screening study of biota samples (**Paper III**). CECs detected in higher levels of a food chain are a good indicator for a possible bioaccumulation potential and persistency in the environment. These biota samples were collected at different sampling sites at the inner Oslofjord and lake Mjøsa, Norway and covered different levels of the respective food chains (Table 3). Both sampling sites are affected from human activity, e.g. waste water from industry/housing or agriculture, which made these sampling sites well suited to detect new potential CECs with a bioaccumulation potential.

Table 3: Sample types and sample sites of biota samples, used in Paper III.

| Sampling site | Sample type | °E | °N |
|---|---|---|---|
| Inner Oslofjord | Atlantic cod | 10.510-10.603 | 59.810-59.817 |
| | Herring | 10.510-10.603 | 59.810-59.817 |
| | Northern shrimp | 10.510-10.603 | 59.810-59.817 |
| | Krill | 10.510-10.603 | 59.810-59.817 |
| Lake Mjøsa | Brown trout | 10.680 | 60.816 |
| | Smelt and vendace | 11.059 | 60.766 |
| | Zooplankton | 11.04 | 60.69 |
| | Mysis | 11.04 | 60.69 |

## 3.2. Extraction, clean-up and analysis

For SUS/NTS, the extraction and clean-up for all samples, air and biota, should be kept as inclusive as possible. With the applied approaches, a wide-range of compounds could be kept in the extracts for analysis for the detection of as many CECs as possible.

Air samples (**Papers I & II**) were extracted and cleaned according to the novel clean-up method presented in **Paper I**. Briefly, GFFs and PUFs from real high-volume air samples were Soxhlet extracted separately, while GFFs and PUFs of the method evaluation samples were extracted as one combined sample. The individual extracts were cleaned with the novel, custom made three-layer liquid chromatography column clean-up method. Analyses were done with GC×GC-LRMS for air samples and blanks and GC-HRMS for method evaluation samples and their respective blank samples. In addition to GC×GC-LRMS, the air samples from Zeppelin in **Paper II** were also analysed with GC×GC-HRMS for structure elucidation of unknown halogenated compounds without library match.

Biota samples were treated as described in **Paper III**. Briefly, according to the sample's lipid content, aliquots of each sample were extracted with a maximum of 0.25 g lipid/sample. Lipids were frozen out before clean-up with Florisil, followed by gel permeation chromatography (GPC) and the novel clean-up method presented in **Paper I**. Extracts were analysed with GC×GC-LRMS.

### 3.2.1. Development of the final clean-up method for air samples

Different clean-up procedures were tested before the final method, used in **Papers I & II,** was developed for air samples. Four of these introductory clean-up

methods were tested on exposed high-volume air samples (~1000-1500 $m^3$ air collected on GFF and PUF) to simulate real conditions (standardised sampling routines for air samples for POPs) and are presented in details below.

The tested clean-up methods were (a) extracts without clean-up, (b) clean-up using silica fractionation and GPC and (c) clean-up of pooled extracts with two different methods. The extract for (c) was divided in two parts to compare two methods: (c1) clean-up with concentrated sulfuric acid (reference method used for POPs), and (c2) clean-up using GPC and two silica fractionations. Method (c) was applied on pooled extracts of nine air samples, to increase concentrations of possible analytes without the need to analyse too concentrated extracts. Since this method is using many air samples, the method was tested on extracts of samples blanks, GFFs and PUFs without exposure to outdoor air. First after the successful test on sample blanks (GC×GC analysis of these cleaned sample blanks did result in acceptable chromatograms without any mayor contamination of the GC×GC system) the method (c/c1/c2) was applied on pooled extracts of nine air samples.

For all tests, exposed PUFs and GFFs were Soxhlet-extracted separately for 8 h with diethyl ether/*n*-hexane (1:9, v/v). Given the diverse properties of the analytes and the aim of these tests, we did not use internal standards (ISTDs).

For (a) GFF and PUF extracts were reduced to 0.5 mL with a Zymark TurboVap and solvent changed to isooctane. The extracts were further concentrated to approx. 200 µL under a gentle stream of nitrogen gas (5.0, Nippon gases Norge AS, Oslo, Norway).

For (b), extracts of GFF and PUF were reduced to 0.5 mL with a TurboVap and solvent changed to cyclohexane. The extracts were filtrated through a Pasteur pipette, packed with cotton and 3 cm sodium sulphate (anhydrous, EMSURE® for analysis, Merck, heated to 450 °C for 8 h), then diluted to 3 mL in GPC mobile phase solvent (cyclohexane/ethyl acetate (1:1, v/v) and injected on a Waters Envirogel GPC system (2 µm Particle filter, 4.6 x 30 mm guard column and 19 x 150 mm + 19 x 300 mm main column). The fraction, typical for POP analysis (approximately 14-30 min), was collected and reduced to 0.5 mL with a TurboVap and solvent changed to *n*-hexane. The extract was further cleaned by silica fractionation. A glass column, 250 mm length and 20 mm inner diameter, was packed with cotton, 8 g silica (dried 130 °C for 24 h, 60 Å, 60-100 mesh, Supelco, Belfonte, PA, USA) in *n*-hexane and a top layer of 1 cm sodium sulphate. The extract was applied in *n*-hexane and two separate fractions were collected. The first fraction was eluted with 48 mL *n*-hexane followed by 50 mL *n*-hexane/ethyl acetate (8:2,

v/v). The second fraction was eluted with 50 mL ethyl acetate. Both fractions were separately reduced to 0.5 mL with a TurboVap and the solvent was changed to isooctane. For analysis, extracts were further concentrated to approx. 200 µL under a gentle stream of nitrogen gas.

For (c), PUF and GFF extracts from 9 samples were pooled to one PUF and one GFF extract, resulting to an air volume of the pooled extract of approximately 10000 $m^3$. The extracts were reduced to 0.5 mL with a TurboVap and solvent changed to *n*-hexane. These extracts were split into two similar parts. One extract part was cleaned with (c1) established methods for legacy POPs using concentrated sulphuric acid clean-up [64]. The other extract part was cleaned by (c2) GPC, silica fractionation as described above at (b), followed by an additional modified silica fractionation for the first fraction [65]. The modified silica column was prepared as described above at (b), but eluted with 50 mL *n*-hexane and 50 mL *n*-hexane/toluene (65:35, v/v). Extracts were reduced to 0.5 mL with a TurboVap and the solvent was changed to isooctane. For analysis, extracts were further concentrated to approx. 200 µL under a gentle stream of nitrogen gas.

All extracts from this introductory clean-up test were analysed with GC×GC-LRMS.

## 3.3. Quality control

For SUS/NTS, quality control and quality assurance are essential to reveal compounds that do not have their origin in the respective sample, i.e. contamination from sample handling. To ensure this, a sufficient number of laboratory blanks are necessary to follow the samples through the whole procedure. Especially for NTS approaches, which do not have a specific target group, a source for numerous false positive findings could be contamination through sample preparation and, e.g. the used laboratory equipment, glassware, solvents or laboratory environment/personal-care products etc.

For air samples (**Papers I & II**), unexposed GFFs and PUFs were used as sample blanks (i.e. laboratory blanks). For biota samples (**Paper III**), clean sodium sulphate was used due to the lack of suitable blank material for each sample type.

In addition to sample blanks, ISTDs were used for quality assurance, sample normalisation and identification of potential contamination/performance issues of the GC×GC-LRMS system for SUS/NTS (**Papers I-III**). ISTDs used in **Paper I** for evaluation of the novel clean-up method were used for target quantification with GC-HRMS.

## 3.4. Identification confidence of SUS/NTS results

The identity of many compounds, detected during SUS/NTS, cannot be sufficiently identified by matches to mass spectra from MS libraries or reference standards. Often, large amounts of detected compounds are only identified by a mass spectrum of interest or a possible molecular formula. In order to harmonise the communication of identification confidence and for better comparability of results, revealed by SUS/NTS studies, Schymanski et al. [52] defined a common set of rules. This level classification concept is currently the gold standard to report results from SUS/NTS. Since this concept was originally developed for LC-HRMS data and not directly applicable on GC-HRMS data [51], it was necessary to adjust the level classification concept and to account for limitations from the used LRMS-data (Figure 2, **Paper I**).

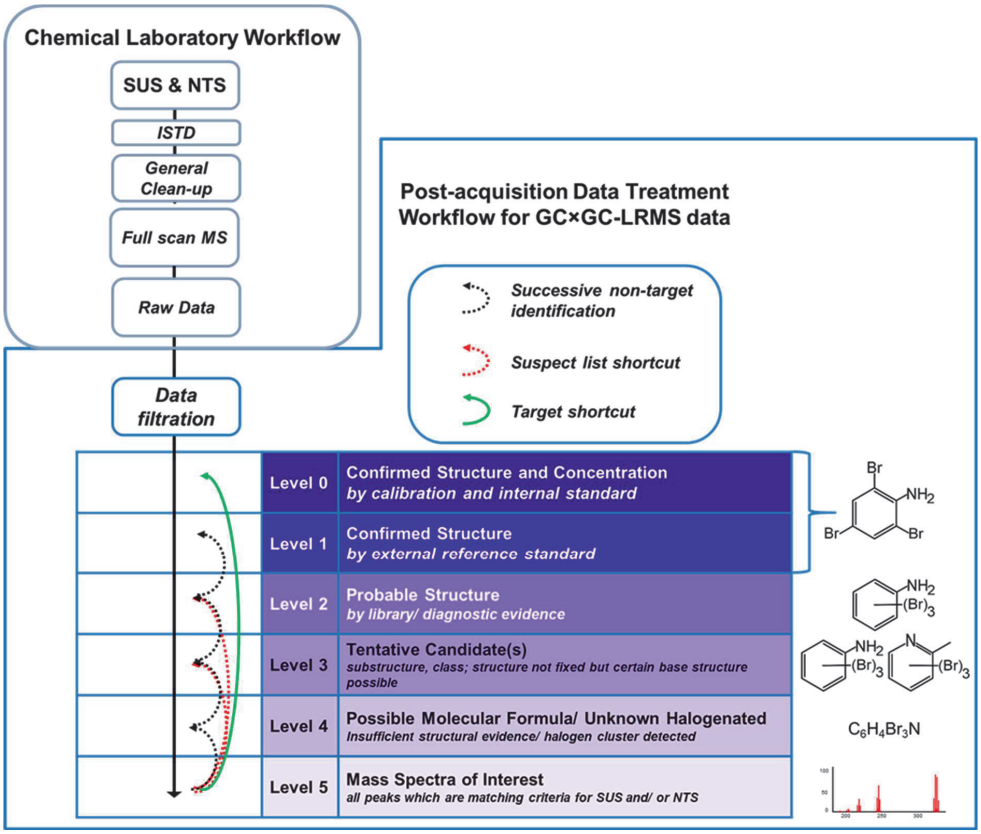



Figure 2: General strategy and levels for identification confidence for GC×GC-LRMS [18]. Adapted from Schymanski et al. [52].

# 4. Results and Discussion

## 4.1. Sample clean-up

### 4.1.1. Initial method considerations

For the wide-scope air sample clean-up method for SUS and NTS approaches, four different sample clean-up methods for GFF and PUF were tested using SUS/NTS workflows. The goal was to find a clean-up method that was keeping a wide range of polarity while avoiding loss of acid-labile compounds. Furthermore, the final extract needed to be as clean as possible to avoid matrix interferences during analysis or heavy contamination of the analytical system.

In the first approach (a), using concentrated extracts of GFF and PUF without clean-up, it was not possible to inject the extract in the needed concentration for the detection of compounds in the low pg/m$^3$ range without heavy contamination of the GC×GC system. This caused problems such as a dirty liner of the injector which had to be exchanged after each injection, a minimum of 10 solvent injections and frequently re-conditioning of the GC columns. The chromatograms of these extracts were also highly affected of sample material matrix. Despite that, it was possible to identify a few known POPs, e.g. pentachlorobenzene (PeCB) and hexachlorobenzene (HCB), tetrachloroveratrole, some PFRs and dichlobenil. Also, the second approach (b) using GPC and silica fractionation caused contamination of the GC×GC system and highly matrix affected chromatograms. The GPC method (b) did remove some matrix compounds, but not sufficiently for the expected low concentrations in air samples. However, these two approaches (a and b) gave valuable information about PUF breakdown products. Often identified structure parts in the mostly non-polar matrix were dioxolane like or glycol ether like structure parts. The two fractions of the silica fractionation after GPC (b) contained different amounts of matrix. The first fraction, eluted with *n*-hexane and *n*-hexane/ethyl acetate, contained the largest part of matrix residues.

Unfortunately, the approaches with pooled extracts of several samples (c) lead also to highly matrix affected chromatograms and did not result in lower system contamination during GC×GC analysis. Furthermore, also the extract cleaned by concentrated sulphuric acid (c1) resulted in highly affected GC×GC chromatograms. This was an unexpected result since the test of this method with unexposed GFF and PUF extracts resulted in less matrix affected GC×GC chromatograms. An additional test with pooled extracts of five

sample blanks, cleaned with concentrated sulphuric acid, also caused highly affected GC×GC chromatograms. As a consequence of this experiments, air samples with a higher sampling volume per samples were necessary, instead of using several air samples to achieve a higher air sample volume and thus, higher concentrations of analytes. In order to omit several fractions per sample for SUS and NTS, other adsorbent materials needed to be tested. SUS and NTS data treatment is very labour-intensive and, hence, analysis of several fractions per sample would be too time consuming. Since analytes could occur in different fractions, fractionation could increase the possibility for analytes to get lost during data processing due to too low concentration and poor signal quality during analysis.

As a final method, the novel three-layer clean-up method presented in **Paper I** was developed. This method provided extracts that were sufficiently clean without major matrix effects of the chromatograms and similar quality than the standardised method.

### 4.1.2. Novel clean-up method

The novel clean-up method for air samples, presented in **Paper I**, could provide cleaned extracts and recovery values of similar quality to the standard clean-up method for compounds included in routine air monitoring (e.g. POPs and brominated flame retardants (BFRs)). Besides these routine monitoring compounds, most of the further evaluated target compounds had recovery values over 50 %. In total, a polarity range of logP 2-11 was covered by the method evaluation. Compared to the standard clean-up method in air monitoring (i.e. treatment with concentrated sulphuric acid) the advantage of the novel method is the possibility of the quantitative determination of acid-labile compounds (62-117 % recovery). These are not detected or detected with low recoveries when extracts are treated with concentrated sulphuric acid. Furthermore, the novel method is more time efficient than the standard method and an extract is ready for instrumental analysis approximately 3-4 hours after extraction, compared to 2-3 days for the standard method.

## 4.2. Data filtration and prioritisation

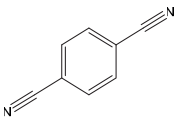
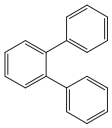
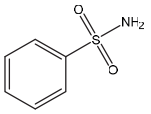
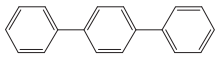
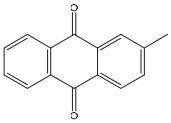
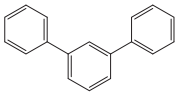
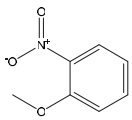
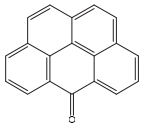
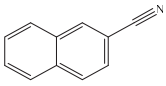
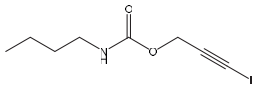
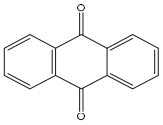
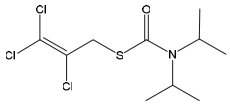
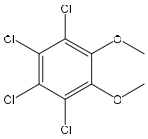
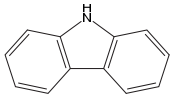
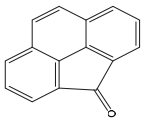
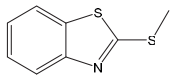
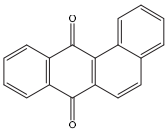
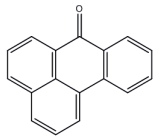
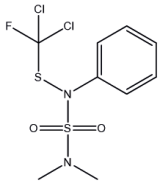
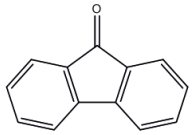
A sound concept for data filtration and prioritisation is, besides a suitable clean-up method for SUS/NTS, a very important but also very difficult task. The developed and applied data processing workflow for air samples (**Paper I & II**) revealed, in combination with the adjusted level classification concept for GC×GC-LRMS, several new

potential CEC which were detected in air samples from the respective areas for the very first time. Such filtration and prioritisation workflows for SUS/NTS are necessary to reduce the number of compounds for manual inspection, since the inspection of often more than 20000 features per sample in a raw dataset [51] would be inefficient and labour-intensive. For **Paper III**, the SUS/NTS workflow from air was adjusted to a larger set of biota samples. Here, a screening for compounds that were present in all samples of a food chain (bioaccumulation screening (BAS)) was included in the SUS/NTS workflow. This SUS/NTS/BAS workflow was able to reveal several known POPs, PFRs and CECs in biota. Furthermore, it was possible to detect contaminants that were present in the examined food chains of inner Oslofjord or lake Mjøsa. It was also possible to detect several new potential CECs for the first time in biota samples from the inner Oslofjord and lake Mjøsa.

## 4.3. Identification of known and new CECs in remote air

By applying the novel sample clean-up method and the developed data treatment workflows to high volume air samples from two Norwegian background monitoring stations, the Birkenes Observatory in southern Norway and Zeppelin Observatory on Svalbard (Artic), it was possible to identify 15 L1 and nine L2 new potential CECs common to both sampling sites. Additional five L1 compounds that are common to both sampling sites, were previously detected in Arctic media but not known in air samples from the Zeppelin observatory (Arctic) or Birkenes observatory (southern Norway). Thus, 20 new potential CECs could be identified as L1 at Birkenes, of which 15 L1 are new potential CECs in the Arctic (Table 4). These compounds are discussed in detail in **Papers I & II** and have various applications and occurrences, e.g. industrial intermediates, pesticides and a pesticide metabolite, combustion oxy-PAHs, etc. Furthermore, 12 legacy POPs, PAHs and known CECs could be identified at both sampling sites. The known CECs have previously been detected in air samples from the national monitoring programme from the same sampling sites [66].

Table 4: Common findings in air samples from southern Norway, Birkenes, and the Arctic, Svalbard.

| Compound name/ CAS/LRATP | Structure | Compound name/ CAS/LRATP | Structure |
|---|---|---|---|
| 1,4-Benzene-dicarbonitrile/ 623-26-7/ With LRATP |  | o-Terphenyl/ 84-15-1/ Without LRATP |  |
| Benzenesulfonamide/ 98-10-2/ With LRATP |  | p-Terphenyl/ 92-94-4/ Without LRATP |  |
| 2-Methyl-9,10-Anthraquinone/ 84-54-8/ With LRATP |  | m-Terphenyl/ 92-06-8/ Without LRATP |  |
| 1-Methoxy-2-nitrobenzene/ 91-23-6/ With LRATP |  | 6H-Benzo[cd]-pyren-6-one/ 3074-00-8/ Without LRATP |  |
| 2-Naphthalene-carbonitrile/ 613-46-7/ With LRATP |  | 3-Iodo-2-propynyl butylcarbamate/ 55406-53-6/ Without LRATP |  |
| 9,10-Anthraquinone/ 84-65-1/ With LRATP * |  | Triallate/ 2303-17-5/ Without LRATP |  |
| Tetrachloroveratrole/ 944-61-6/ With LRATP * |  | Carbazole/ 86-74-8/ Without LRATP |  |
| 4H-Cyclopenta[def] phenanthren-4-one/ 5737-13-3/ With LRATP * |  | 2-(Methylmercapto) benzothiazole/ 615-22-5/ Without LRATP |  |
| 1,2-Benz-anthraquinone/ 2498-66-0/ Without LRATP |  | 1,9-Benz-10-anthrone/ 82-05-3/ Without LRATP * |  |
| Dichlofluanid/ 1085-98-9/ Without LRATP |  | 9-Fluorenone/ 486-25-9/ Without LRATP * |  |

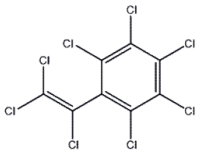
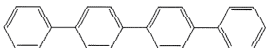
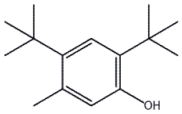
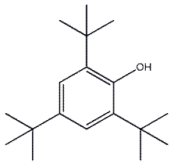
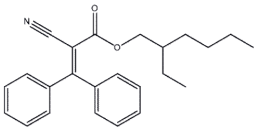
*: previously detected in the Arctic, but not at Birkenes

Of these 15 L1 and nine L2 new potential CECs that occurred in samples from both sites, 10 L1 and four L2 compounds were not meeting todays accepted criteria for LRATP into polar environments ($t_{1/2}$(air) is below 2 days). However, the identification of these compounds at both sampling sites and an adjusted $t_{1/2}$(air) exceeding 2 days **(Paper II)**, reflecting environmental conditions during sampling in the Arctic, is supporting the assumption that these compounds could undergo LRAT (**Paper II**). Besides these common findings and numerous L3 and L4 compounds, additional 45 L1 and L2 compounds were detected in Artic air samples **(Paper II)** as well as 50 L1 and L2 in air samples from Birkenes in southern Norway **(Paper I)**. These compounds were detected in the respective air samples for the very first time. Together with the detection of in total 51 unknown halogenated compounds (MS did not match any on the used MS libraries) this underlines the importance of SUS/NTS studies.

## 4.4. Identification of known and new CECs in freshwater and marine food chains

The screening for CECs in the freshwater food chain of lake Mjøsa and salt water food chain from inner Oslofjord could identify new compounds in the examined food chains. Although the SUS/NTS data treatment was hampered by the study´s design (i.e. no filtration of endogenous/biogenic compounds possible), it was possible to detect suspects from other screening studies and new potential CECs in the here examined food chains. Besides these suspects, it was possible to detect several compounds in the lower and higher levels of these food chain for which the impact on the respective environment is not yet known. Since this study is reporting qualitative data, no assumptions on a potential bioaccumulation could be drawn. Of the detected L0-L2 compounds that previously were not detected in the examined food chains, five compounds have a BCF/BAF or log$K_{OW}$ that would match the bioaccumulation criteria of REACH or SC (Table 5). However, it cannot be excluded that the remaining L0-L2 compounds might have a bioaccumulation potential. This should be followed up by studies using quantitative targeted methods.

Table 5: New potential CECs detected in biota samples from the inner Oslofjord and lake Mjøsa, Norway.

| Compound name/ CAS | Structure | Level | Sample type | BCF | logKOW |
|---|---|---|---|---|---|
| Octachlorostyrene (OCS)/ 29082-74-4 |  | 1 | Brown trout | 7921 | 7.5 |
| Isomer of *p*-quaterphenyl/ 135-70-6 |  | 2 | Vendace<br>Zooplankton<br>Mysis<br>Herring | 9646 | 7.3 |
| 4,6-Di-tert-Butyl-*m*-cresol/ 497-39-2 |  | 2 | Smelt<br>Zooplankton | 2109 | 5.9 |
| 2,4,6-Tris(1,1-dimethylethyl) Phenol/ 732-26-3 |  | 2 | Zooplankton<br>Mysis | 2776 | 6.1 |
| Octocrylene/ 6197-30-4 |  | 2 | Northern Shrimp | 16120 | 6.9 |

## 4.5. Common findings in air and biota samples

Legacy POPs were detected in biota and air samples using the applied NTS/SUS approaches. This was expected since POPs are known to B and undergo LRAT. Known CECs in air like PFRs could also be detected in biota. At which PFRs were already known CECs in the biota samples from the inner Oslofjord, no evidence was found that PFRs were previously detected in biota samples from lake Mjøsa. Four other CECs (L1 and L2) were detected in air and biota. These include *p*-toluenesulfonamide that was detected in air from Birkenes and in herring from the inner Oslofjord for the first time. This compound has a LRATP ($t_{1/2}$(air) ≥ 2 days) but was not detected in the air samples from the Arctic. Even tough *p*-toluenesulfonamide has a BCF and logKOW below the thresholds for B (Table 1), it was detected in herring. Further, octachlorostyrene (OCS), which is regularly detected in Arctic air was identified in brown trout from lake Mjøsa. It is not

known if OCS was previously detected in biota samples from lake Mjøsa, but B of this compound is likely, since BCF and log$K_{OW}$ are exceeding the thresholds for B (Table 1). In air samples from Birkenes and the Arctic, as well as herring from inner Oslofjord and mysis, zooplankton and vendace from lake Mjøsa, one or more isomers of *p*-quaterphenyl were identified. Even tough *p*-quaterphenyl has no LRATP, it was detected in air samples form Birkenes and the Arctic. It is not known if *p*-quaterphenyl was detected previously in biota samples from the inner Oslofjord or lake Mjøsa, but the BCF and log$K_{OW}$ for *p*-quaterphenyl are exceeding the B thresholds (Table 1) and, hence, B could be possible. Finally, the natural halogenated product MHC-1 (mixed halogenated compound 1; (1S,2S,4R,5R)-2-Bromo-1-(bromomethyl)-1,4-dichloro-5-[(1E)-2-chloroethenyl]-5-methylcyclohexane) was detected for the first time in Arctic air and herring from inner Oslofjord, but could not be detected in air from Birkenes. Previously, MHC-1 was detected in various biota samples from Norway [67], but herring or the inner Oslofjord was not content of this study. Since MHC-1 is produced by the seaweed *Plocamium cartilagineum*, it can be expected to be found in biota samples from marine water.

# Conclusions and recommendations for future work

Overall, the newly developed clean-up methods and SUS/NTS identification and prioritisation workflows for air and biota samples identified known and new potential CECs in air and biota. Several CECs could be identified that show a possible LRAT, P or B potential.

A wide-scope, non-destructive sample clean-up method for high-volume air samples based on GFF and PUF has been developed and evaluated. This novel method obtained recoveries for legacy POPs and BFRs of similar quality as the traditional method, using concentrated sulphuric acid. The advantage of the new method was the possibility to quantify also acid labile POPs and BFRs, as well as an extended range of SVOCs (logP 2-11) compared to traditional methods. Furthermore, a SUS/NTS data treatment workflow was developed which included ISTDs for the possibility of simultaneous quantitative target analysis and SUS/NTS. The successful application of the novel sample clean-up method and SUS/NTS workflow to high-volume air samples allowed identification of known and new potential CECs in southern Norway as well as in the Norwegian Arctic (Svalbard). This shows that the clean-up method in combination with the workflow for SUS/NTS can be a useful tool for early identification of CECs in air samples. This in turn will provide regulatory authorities with crucial information on potential for P and LRAT of CECs.

The application and expansion of the SUS/NTS workflow on biota samples from a larger screening study allowed detection of several new CECs in the examined food chains from inner Oslofjord and lake Mjøsa, Norway. Identification of CECs during SUS/NTS data treatment was hampered, since it was not possible to filter the data for endogenous/biogenic compounds. On one side, this was due to the lack of blank sample material for each sample type, on the other side due to the study design. The positive findings from the biota samples do however suggest that the applied methods have a potential for identification of CECs in biota. Further improvements are needed but the potential is there.

The results and conclusions from the scientific work of this thesis show that SUS/NTS on air and biota samples have the potential to be a useful tool for early identification of CECs and thereby proving three of four hazardous properties that describe persistent organic pollutants: P, B and LRTP. The current method can and may even need

improvements to optimise the results. This includes improving (i) the air sampling matrix, (ii) the sampling strategies, and (iii) the instrumental methodologies.

To optimise SUS/NTS studies in air, the high load of matrix related compounds, introduced by the commonly used PUF sampling material should preferably be reduced. Testing a more stable polymer to replace the PUF as gas phase adsorbent is highly needed. This would reduce the load of blank related compounds on the analytical system, enhance the detection limits and positively affect the quality of collected MS spectra. Important for an alternative gas phase adsorbent is also to allow for improved sampling capacity by minimizing the break-through of more volatile compounds. This should be evaluated for further in-depth studies including quantitative estimations of CECs. Not only for higher sampling volumes, but also for higher sampling flows the break-through risk should be evaluated. Increasing sampling volumes and sampling flows might be necessary for higher sample concentrations, detection of compounds in lower concentrations and/or faster collection of air samples (i.e. allowing for shorter sampling time and higher time-resolution). Faster collection of air samples could be beneficial for using the available sampling capacity from a sampling station the optimal way for larger SUS/NTS studies and, more important, to sample air masses which are transported from a specific region.

The matrix related load of compounds was also challenging for NTS/SUS of biota samples and, hence, need to be reduced. This could be realised by testing a different sample extraction procedure which was recently proposed by an expert group of NORMAN [44]. This sample extraction procedure might also shorten the necessary sample clean-up and should, therefore, be considered. An additional important way to reduce blank compounds in the received data set from the analytical system is the study's design (sampling) for SUS/NTS in biota. This should be revised to include the possibility for spatial trend analysis. For this purpose, samples need to be taken from a contaminated site and a non/less contaminated site. Then, endogenous/biogenic compounds can be filtered from the dataset for a more successful SUS/NTS.

Another way to improve future SUS/NTS studies is the use of HRMS instruments. This enables the possibility for structure elucidation of compounds not listed in MS libraries. In addition, a non-polar GC column would enable the use of retention indices, as large

databases of retention indices or retention index prediction are existing for non-polar columns. These indices can help to identify compounds by comparing them to databases. Finally, a more comprehensive suspect library would be of great value, especially for biota for which metabolites and endogenous/biogenic compounds should be included.

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# Paper I

Non-target and suspect characterisation of organic contaminants in ambient air, Part I: Combining a novel sample clean-up method with comprehensive two-dimensional gas chromatography.

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# Non-target and suspect characterisation of organic contaminants in ambient air, Part I: Combining a novel sample clean-up method with comprehensive two-dimensional gas chromatography

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**Abstract.** Long-term monitoring of regulated organic chemicals, such as legacy persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in ambient air provides valuable information about the compounds' environmental fate as well as temporal and spatial trends. This is the foundation to evaluate the effectiveness of national and international regulations of priority pollutants. Extracts of high-volume air samples, collected on glass fibre filters (GFF for particle phase) and polyurethane foam plugs (PUF for gaseous phase), for targeted analyses of legacy POPs are commonly cleaned by treatment with concentrated sulfuric acid, resulting in extracts clean from most interfering compounds and matrices, and suitable for multi quantitative trace analysis. Such standardised methods, however, severely restrict the number of analytes for quantification and are not applicable when targeting new and emerging compounds as some may be less stable to acid treatment. Recently developed suspect and non-target screening analytical strategies (SUS and NTS, respectively) are shown to be effective evaluation tools aiming at identifying a high number of compounds of emerging concern. These strategies, combining high sophisticated analytical technology with extensive data interpretation and statistics, are already widely accepted in environmental sciences for investigations of various environmental matrices but its application to air samples is still very limited. In order to apply SUS and NTS for the identification of organic contaminants in air samples, an adapted and more wide-scope sample clean-up method is needed, compared to the traditional method which is using concentrated sulphuric acid. Analysis of raw air sample extracts, without clean-up, would generate an extensive contamination of the analytical system with especially PUF matrix-based compounds and, thus, highly interfered mass spectra and detection limits which are unacceptable high for trace analysis in air samples.

In this study, a novel wide-scope sample clean-up method for high-volume air samples has been developed and applied to real high-volume air samples, which facilitates simultaneous target, suspect and non-target analyses The scope and efficiency of the method was quantitatively evaluated with organic compounds, covering a wide range of polarities (logP 2-11), including legacy POPs, brominated flame retardants (BFRs), chlorinated pesticides and currently used pesticides (CUPs). In addition, data reduction and selection strategies for SUS and NTS were developed for comprehensive two-dimensional gas

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chromatography separation with low resolution time-of-flight mass spectrometric detection (GC×GC-LRMS) data and applied on real high-volume air samples. Combination of the newly developed clean-up procedure and data treatment strategy enabled the prioritisation of over 600 compounds of interest in the particle-phase (on GFF) and over 850 compounds in the gas-phase (on PUF), out of over 25000 chemical features detected in the raw data set. Of these, 50 individual compounds were identified and confirmed with reference standards, 80 compounds were identified with a probable structure and 774 compounds were assigned to various compound classes. In the here available dataset, 11 hitherto unknown halogenated compounds were detected. These unknown compounds were not yet listed in the available mass spectral libraries.

## 1 Introduction

Air monitoring programmes and case-studies on the environmental fate of anthropogenic pollutants including legacy persistent organic pollutants (POPs) are important tools for environmental risk assessment. Furthermore, data generated in monitoring programmes and case-studies are forming the foundations for integrated modern pollutant regulations as well as the effectivity assessment of international agreements and conventions on POPs (UNECE, 1998; UNEP, 2009a, b; EMEP, 2019). Air measurements of POPs are commonly done using quantitative targeted analytical approaches in combination with highly selective sample clean-up methods often involving destructive sample clean-up with concentrated sulfuric acid ($H_2SO_{4\ conc.}$), sodium hydroxide (NaOH) or other very selective preparation methods for an effective removal of interfering matrix compounds, originating either from the polyurethane foam (PUF) based sampling material or from naturally occurring air compounds. These methodologies are well-proven and appropriate for most legacy POPs, and therefore recommended as standard methods for POPs in the UNECE-EMEP (United Nations Economic Commission for Europe´s European Monitoring and Evaluation Programme) manual for sampling and chemical analysis (EMEP, 2019). The outcome of the established targeted analytical methods for quantitative measurements of important environmental pollutants are, however, limited as they are covering only a minor part of the currently available list of priority substances identified as potential contaminants (Arnot et al., 2011; Breivik et al., 2012; McLachlan et al., 2014; Vorkamp and Rigét, 2014; Reppas-Chrysovitsinos et al., 2017; NORMAN-network, 2019).

The current demand for various chemicals in technical and day-to-day consumer products is steadily expanding leading to a constantly increasing number of new compounds identified as potential environmental contaminants. In the light of the continuously increasing numbers of chemicals in commerce, the development of single compound quantitative analytical methods for each of these new compound groups is today considered as in-effective, time consuming and expensive. Therefore, there is a strong demand to develop targeted multi-compound analytical methods with the potential supplementation with suspect screening and non-target screening strategies (SUS and NTS). Many of potential emerging contaminants are less persistent and therefore rapidly degraded during destructive sample extraction clean-up and processes (i.e. acid treatment, saponification, lyophilisation, etc.). This limitation is a fundamental restriction for quantitative analyses of such labile compounds as well as identification of hitherto unknown potential contaminants with similar physical-chemical properties.

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Hence, there is an obvious incentive for the development of an alternative mild, non-destructive sample clean-up procedure in order to retain the broadest possible range of chemicals and as little as possible interfering matrix in the clean extract. Today, the combination of unspecific sample extraction and clean-up, in combination with high-resolution chromatographic and detection methods is considered a prerequisite for NTS and SUS strategies. In particulate, the application of ultra-high resolution chromatographic methods (either liquid or gas chromatographic) in combination with high resolution mass spectrometry (HRMS) enabled the identification and characterization of hitherto unknown environmental contaminants in different matrices (López Zavala and Reynoso-Cuevas, 2015; Alygizakis et al., 2016; Hernández et al., 2015; Masiá et al., 2014; Al-Qaim et al., 2014; Hernández et al., 2007; Rostkowski et al., 2019; Schymanski et al., 2015). Another advanced analytical tool for non-target specific analysis of environmental samples is comprehensive two-dimensional gas chromatography (GC×GC) coupled to either low-resolution or high-resolution time of flight mass spectrometry (GC×GC-LRMS or GC×GC-HRMS, respectively). Earlier studies have already successfully applied this technology for the identification and characterization of chemical profiles in petroleum product characterisation (Ruiz-Guerrero et al., 2006; Van De Weghe et al., 2006; Arey et al., 2005; van Mispelaar et al., 2005) and in environmental sample analysis (Millow et al., 2015; Ubukata et al., 2015; Mao et al., 2009; Ralston-Hooper et al., 2008; van Leeuwen and de Boer, 2008; Lebedev et al., 2018; Veenaas and Haglund, 2017). As extracts for SUS/NTS analyses will contain a much broader range of compounds compared with extracts prepared for single compound targeted analyses, it is essential to increase the resolution for both associated chromatographic separation as well as the detection technology compared to traditional target specific quantitative analysis. Comprehensive GC×GC allows the two-dimensional chromatographic separation of analytes from interfering matrix in complex samples (Figure 1). However, also in the GC×GC separation, potential matrix interferences will reduce the quality of the chromatographic separation. This will also reduce the quality of the collected mass spectra, making the identification of a compound an even more difficult task. Therefore, sample clean-up needs to be optimised for detection and characterization of substances, often present in ultra-trace amounts.

The overall aim of this study was the development of a wide-scope sample clean-up method for high-volume air samples and to develop SUS and NTS strategies, optimised for GC×GC-LRMS data. This novel sample clean-up method was evaluated by target analytical methods, covering compounds within a wide range of polarities (logP 2-11). The target methods included legacy POPs, brominated flame retardants (BFRs), halogenated agrochemicals, industrial chemicals and currently used pesticides (CUPs). The presented newly developed clean-up method in combination with SUS/NTS strategies was applied on real high-volume atmospheric samples from a background monitoring station in Southern Norway aiming to identify known and new potential chemicals of emerging concern (CECs).

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## 2 Experimental Section

### 2.1 Method evaluation samples and real high-volume air samples

The samples of this study were based on (i), the evaluation of the novel wide-scope clean-up method which was based on a recovery test, covering compounds within a wide range of polarities, using spiked surrogate method evaluation samples and target analysis. And (ii), the application of the novel clean-up method on real high-volume air samples from the Birkenes observatory in combination with the development of SUS and NTS strategies. For both, (i) and (ii), glass fibre filters (GFF; 142 mm in diameter) and PUF plugs (7 cm in diameter, 4 cm in height), commonly used in high volume air sampling (Kallenborn et al., 2013), were used.

For (i), spiked surrogate method evaluation samples (unexposed PUFs and GFFs) were spiked with $^{13}C$ labelled standards representing POPs and CECs analysed within the UNECE-EMEP and AMAP (Arctic Monitoring and Assessment Program) monitoring programmes, as well as native CUPs and pesticide standards, covering a wide range of polarity. A set of three parallel samples of each standard mixture were prepared for quality assurance (POP, Brominated, CUP A, CUP B and CUP C); in total 15 method evaluation samples were prepared (Table 1). A detailed list about all compounds in the used standard mixtures can be found in the SI, Table S2-S5.

For (ii), two dedicated real high-volume air samples were collected during March–April 2015 at an EMEP background monitoring station, the Birkenes Observatory in southern Norway (Aust-Agder 58° 23' N, 8° 15' E, 190 m a.s.l.). The particle phase was collected on GFF (cut-off 10 µm) and the gas-phase on PUF plugs, at a flow rate of ~ 50 $m^3 h^{-1}$. The sampling time was 6 days, resulting in sample volumes of 6100 $m^3$ and 6200 $m^3$ respectively. Details on the GFF/PUF high-volume air sampling methodology can be found in Kallenborn et al. (2013).

### 2.2 Extraction and sample clean-up

**Extraction.** The spiked surrogate method evaluation samples (i), GFF and PUF combined, were Soxhlet extracted for 8 h in acetone/*n*-hexane (1:1, v/v), resulting in one combined extract for GFF and PUF per sample. The extracts were reduced to 0.5 mL with a Zymark TurboVap evaporator and solvent changed to isooctane before clean-up.

The exposed real high-volume air samples (GFF and PUF) from Birkenes (ii) were spiked with internal standard (ISTD) mixture (see SI Table S6 for details) and GFFs and PUFs were Soxhlet-extracted separately for 8 h in acetone/*n*-hexane (1:1, v/v), resulting in separate extracts for PUFs and for GFFs for each sample, respectively. After extraction, the individual extracts were reduced to 0.5 mL and the solvent was changed to isooctane. The same steps were carried out for (i) and (ii) with sample blanks (PUFs and GFFs without exposure to outdoor air) for quality assurance (see sect. 2.6).

**Sample clean-up.** For each extract from (i) spiked surrogate method evaluation samples and (ii) real high-volume air samples from Birkenes as well as sample blanks of (i) and (ii), a custom made three-layer liquid chromatography column was applied for clean-up. The columns consisted of a glass column (l= 250 mm, i.d.= 20 mm), packed with cotton. The bottom layer consisted of a mixture of Z-Sep$^+$ and DSC-18 (2 g each), the middle layer of Florisil (10 g) and the top layer of sodium sulphate

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(1 cm). After conditioning the column with an excessive amount of acetone (1.5 x volume of the column), the column was dried, using a vacuum pump (the columns outlet was connected to a vacuum pump). The individual extracts were applied to the dry column and eluted with 80 mL acetonitrile (ACN)/0.5 % citric acid (w/w). After clean-up, the individual extracts were reduced to 0.5 mL with a TurboVap and further concentrated to approximately 200 µL under a gentle stream of nitrogen gas. After clean-up and prior to analysis, the recovery standard (1,2,3,4-tetrachloronaphthalene, TCN) was added. Details on the used chemicals and equipment can be found in the SI, Table S1.

### 2.3 Target GC-HRMS analysis for method evaluation samples

The samples from part (i) were quantitatively evaluated by target analysis, using GC-HRMS. The detailed quantitative analytical methods applied here are described in Halse et al. (2011) and Kallenborn et al. (2013).

### 2.4 SUS and NTS of real high-volume air samples

The real high-volume air samples (ii) were analysed on a comprehensive high-resolution two-dimensional gas chromatograph coupled to a low-resolution time-of-flight mass spectrometer with unit mass resolution (GC×GC-LRMS, Pegasus® 4D, LECO, St. Joseph, MI, USA system). The GC was equipped with a Restek (Bellefonte, PA, USA) Siltek Guard column (4 m, 0.25 mm), a SGE (Trajan Scientific and Medical, Ringwood, VIC, Australia) BPX-50 (25 m, 0.25 mm x 0.25 µm) first dimension column and an Agilent J&W (Folsom, CA, USA) VF-1ms (1.5 m, 0.15 mm x 0.15 µm) second dimension column. This samples were processed with the here developed SUS and NTS strategies, optimised and developed for GC×GC-LRMS (sect. 2.5 and 3.2)

Further details on chromatographic specifications are given in the SI.

### 2.5 Data processing/Post-acquisition data treatment

LECOs® ChromaTOF® (V 4.50.8) software, including its advanced features Scripts and Statistical Compare, which also controls the GC×GC-LRMS system, was used for data analysing and processing; including automatic peak finding, spectral deconvolution for coeluting peaks, modulation slice combination and mass spectral searching compared to the used mass spectral libraries. In this study, an in-house custom library with mass spectra of reference standards and $^{13}C/^{2}H$ labelled ISTDs was used in combination with the National Institute of Standards and Technology (NIST) 2014 mass spectral library and the Scientific Working Group for the Analysis of Seized Drugs (SWGdrug, Oulton (2019)) mass spectral library. For more efficient suspect screening and flagging of potential suspects during data processing, a customised library, containing selected suspect spectra from NIST14, was created. More details about the chosen suspect lists, creation of the customised library as well as the alignment with the final peak list can be found in sect. 3.4 and in the SI.

An in-house developed post-acquisition workflow for GC×GC-LRMS data of the real high-volume air samples was used for the combined chemical work, target, SUS and NTS (Figure 2 and Figure 3). The level classification concept, developed from Schymanski et al. (2015), describing the levels of classification and identification confidence is currently a gold standard used

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for reporting results from SUS and NTS data evaluation. However, the scheme was developed with the LC-HRMS data in mind, and is therefore not directly applicable to the data produced with a GC-MS based methods (Rostkowski et al., 2019). The combination of columns applied in this study (medium-polar combined with non-polar) had an improved matrix separation from compounds of interest, compared to the most common combination (non-polar combined with medium-polar). However, as stated by Röhler et al. (2020), this column combination is not suitable to use with any available retention indices for further identification confidence. The most comprehensive databases are available for non-polar (5 % phenyl) columns, whereas this study was using a medium-polar column. Limited concepts for retention indices are available for GC×GC, e.g. Mazur et al. (2018) or Veenaas and Haglund (2018), using a non-polar column as first dimension and medium-polar column as second column for GC×GC separation. A new model would be necessary to enable the possibility of retention indices for the column combination used in this study.

### 2.6 Quality control

Laboratory blank samples were included for both sample types (i) and (ii). The blanks consisted of unexposed PUFs and GFFs and were treated as their respective sample type (i) or (ii) regarding extraction, clean-up and analyses. To ascertain that a detected/reported compound has its origin in the sample (i) or (ii), and not occur in the respective laboratory blank samples for (i) or (ii), a compound need to exceed an sample concentration factor $\geq 10$ compared to a blank sample in target analysis for (i) or an area factor $\geq 100$ compared to a blank sample in SUS/NTS for (ii).

There were no targeted compounds detected in blanks for part (i). ISTDs, used in SUS/NTS of real high-volume air samples (part (ii)) were used for quality assurance and sample normalisation and not for target quantification. Visual comparisons of peak intensity and intensity ratios from ISTDs were used to identify potential contamination/performance issues of the GC×GC-LRMS system. This was done for samples and blank samples from (ii) as well as ISTD mixture analysis, which were analysed in between blank samples and samples from (ii).

## 3 Results and Discussion

### 3.1 Evaluation of the novel sample clean-up method

The application of the novel wide-scope sample clean-up method, with a custom three-layer liquid chromatography method, was quantitatively evaluated with targeted analyses on GC-HRMS of triplicates of unexposed samples (PUFs and GFFs) spiked with a mixture of various compound classes covering a wide range of polarity (logP 2-11). The results show that the novel clean-up method provided extracts of similar cleanness and comparable recoveries for acid-stable POPs as routine methods in monitoring programs for POPs. The recoveries of most of the targeted compounds were over 50 % using the novel clean-up method (Table 2) which is in accordance with the standard QC requirements for this type of analysis. For acid-labile compounds such as dieldrin, endrin, aldrin, isodrin, heptachlor-*exo*-epoxide, endosulfan I/II/sulphate, ATE (allyl 2,4,6-tribromophenyl ether) and BATE (2-bromoallyl 2,4,6-tribromophenyl ether) the recoveries with the novel clean-up method

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were 62-117 % while they are not detected or detected with low recoveries using routine clean-up methods. This shows the advantage of this method to also allow quantitative extraction of acid-labile organic contaminants. More details on recovery of single compounds and relative standard deviations (RSDs) can be found in Table S2-S5 in the SI.

A few of the targeted/spiked compounds had no recorded recovery (i.e. chlorfenvinphos, chlorobenzilate, dichlorvos, endrine aldehyde and etridiazole) or very low recovery (i.e. bromacil and chloroneb). The most probable reason seems to be insufficient elution with the used solvent (ACN/0.5 % citric acid) due to strong/irreversible interactions with Florisil and/or strong Lewis acid/base interactions with Z-Sep$^+$ (Zirconium oxide and C18 coated silica particles).

### 3.2 SUS and NTS identification approach

For compound characterisation, an already reported level classification system for identification confidence by Schymanski et al. (2015) was adopted and optimised for the here used GC×GC-LRMS technique (Figure 2). This level classification is a useful tool to report results from SUS and NTS. The original version was developed for classification of SUS and NTS results from interpretation of LC-HRMS data. This classification strategy provides a suitable platform for a compounds level of identification confidence. The defined confidence levels by Schymanski et al. (2015) are covering identification criteria from accurate mass identification of a compound (Level 5, L5) to direct match with a reference standard (Level 1, L1). As proposed by Rostkowski et al. (2019), the original version of Schymanski et al. is not directly applicable for GC-HRMS, mainly due to different data filtration strategies compared to LC-HRMS. Additionally, in contrast to other previously reported SUS/NTS studies, our work is based on LRMS data, and thus cannot provide accurate masses of compounds of interest. As potential molecular formula and further structural information are not easily available with the here used GC×GC-LRMS technique, we were forced to slightly adjust this level classification scheme for better complying with the needs and limitations of LRMS data treatment. However, our adjusted approach is kept it as close as possible to the original version from Schymanski et al. (2015). An additional Level 0 (L0) was included allowing to distinguish between compounds identified by external reference standards after the original sample analysis (L1) and those compounds identified by ISTDs (L0), added to the sample before sample extraction. Here, direct target quantification of L0 compounds is possible although not further examined in the here reported study. For Level 2 (L2) compounds, a probable structure derived from good library match in combination with a plausible position on the GC×GC 3D surface or an isomer of an available reference standard could be assigned. An example of a L2 compound could be a penta-chlorinated PCB. The mass spectral information is matching well with a penta-chlorinated PCB, however, as there are several possible different penta-chlorinated PCB congeners (n= 47), the individual penta-chlorinated PCB congener could not be identified. For compounds classified as Level 3 (L3), a certain substructure or compound class could be assigned. Here the structure of a compound is not totally clear, but a certain base structure confirmation is possible due to the available information. An example of a L3 compound could be a tentative polycyclic aromatic hydrocarbon (PAH) where the fragment pattern of the mass spectra (MS) was assigned to be a PAH with a possible molecular formula. Since there are too many possible PAHs (n > 100) with various structures matching the given MS and molecular formula, it is only possible to assign a compound class to this compound. Compounds classified as Level 4 (L4) are

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only defined by a possible molecular formula or by characteristic halogen cluster/-s. They do not match any MS in the used MS libraries. All peaks, which were matching the criteria for SUS and/or NTS during DP (Figure 3 before reaching A) were classified as Level 5 (L5), mass spectra of interest.

In comparison to target analysis, developed for the highest confidence level of identification, SUS and NTS results have different confidence levels as described above. In target analysis, isotope dilution analysis with ISTDs is, beside others, a commonly applied technique (EFSA, 2010; European_Commission, 2017). The hereby used specific sample clean-up for those selected compounds removes the bulk of disturbing matrix and other potential deteriorating issues with potential effects on the chromatographic separation, Hence, the results are reported as validated concentration levels in table form for all targets analytes (Figure 2, Level 0). Whereas, for SUS and NTS a more general sample clean-up procedure is necessary which often does not remove all interfering matrix. These SUS/NTS results are identified as extensive lists of relevant peaks (often ≥ 20000 peaks), typically detected via retention time (RT) and full scan mass spectra information (Rostkowski et al., 2019). Usually, the original peak list identified automatically by the analytical software, need to be systematically reduced and categorised according to the above described confidence identification criteria (Figure 2, Level 1-5). Such a data reduction is necessary for a sound interpretation of the results (Figure 3). As described in section 2.5 the instrumental software generates an initial peak list containing 10000s entries. In order to have an efficient data treatment, it is required to priorities properly and reduce the originally long peak lists. This first reduction step is to identify and remove compound signals, which are also occurring in sample blanks. Based on the available software tools a data processing workflow was applied including compound identification with MS libraries, identification of compounds which occur in one or more samples, identification of halogen isotopic clusters or other specific ions (e.g. m/z 149 as base peak for phthalates, etc.). After these automated processes, the received peak list was further reduced by manual or semi-automatic inspections resulting in a shortened peak list, corresponding to previously defined quality thresholds. To increase the level of identification confidence, manual inspection of each peak is necessary. This evaluation step is very time consuming and thus limit the number of compounds for which such semi-automated/manual inspection could be performed.

#### 3.2.1 Automatic blank filtration

The first step in reducing the originally long peak lists produced by deconvolution of raw data is to identify and remove compound signals which are also occurring in sample blanks. Since SUS and NTS at this stage is resulting in qualitative/semiquantitative rather than quantitative results, the exact compound concentration in the collected air samples and blanks is unknown. Therefore, blank compound filtration is based on comparison of signal areas only. In order to compensate for response variation occurring between real sample extracts and method blanks, a high threshold for detection is applied, considerably higher as utilised for traditional target analysis. In our case, a compound in a real sample must exceed an area factor ≥ 100 compared to a blank sample to be confirmed as a detected compound.

After automatic sample blank filtration for NTS/SUS analysis, the peak list of the air samples from Birkenes still covered a large number of compounds also confirmed in sample blanks. This poor efficiency of automated blank filtration can be

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explained by the differences in peak distribution profiles for the different blank samples and for the average of the blank samples compared to the real samples. Only 50-75 % of the identified blank contaminants were identical in the different blank samples. However, the automatic filtration procedure reduced approximately 10 % of the total peak number (reduction from about 26000 to 24000 peaks for PUF sample and 25000 to 22000 peaks for GFFs). Further strategies for peak filtration had to be applied to reduce the number of peaks. Such an effective filtration is necessary providing a suitable platform for priority compound identification (Figure 3, to reach A) and classification of the different confidence levels (Figure 2, L1-L5).

During initial data processing, the here used ChromaTOF® software is automatically finding all relevant signals/peaks, deconvolute coeluting mass spectra, combining modulation slices and comparing this spectral information against the set of chosen MS libraries. Hereby, it may happen that one signal in the chromatogram is associated with several peak markers, e.g. if the peak width is broader than the used specifications for automatic peak finding or peaks are tailing. Unfortunately, the automated deconvolution algorithm from ChromaTOF can mark a single compound with several peak markers, which was shown in a study by Lu et al. (2008). Due to these limitations, the total number of originally detected compounds is usually lower than the number of peak markers. First during comprehensive manual inspection (Figure 3, A) these additional false peak markers will be discovered and peak lists corrected for duplicate peak markers.

### 3.2.2 SUS data processing workflow

In this study, the data processing strategy (DP) was split in two parts, SUS (Figure 3, I) and NTS (Figure 3, II). After the initial automated peak identification, the peak lists from both DP approaches were merged to one L5 list for manual check on identity (Figure 3, A) and further level of identity confidence classification.

During SUS DP (Figure 3, I), all MS of the automatically detected peaks were searched against the MS libraries reference information for SUS (in-house custom libraries of reference standards and ISTDs, customised suspect library as described in sect. 2.5 and SWGdrug Oulton (2019) mass spectral library). Added ISTDs were identified (L0), as well as sample blank compounds. A second blank filtration was performed and only compounds which are exceeding an area of factor ≥ 100 compared to the sample blank were kept for further inspection. As described in the previous section 3.2.1, this high threshold is necessary to compensate for different sample volumes and unknown variation of response between extracts. After blank filtration, all peaks with a forward match of ≥ 70 % to the MS listed in custom suspect libraries for SUS were identified (Figure 3, I: preliminary L5 list). These peaks from "I: preliminary L5 list" (Figure 3) were further processed by including the entire NIST14 MS library in addition to the previously applied custom suspect libraries, to ensure the quality of the library identification procedure (Figure 3, I: L5 list to check manually on identity). Applying this procedure, approx. 600 suspects were identified in the PUF and approx. 400 suspects in the GFF samples. These signals were only identified by MS library matching, without manual check of their identity, the confidence level of identification is here L5 and for found ISTDs and their respective native compound, L0 (Figure 2). In order to improve the confidence level of identification for these compounds, the manual check on right identification is required as the next step (Figure 3, A; in combination with results from NTS).

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### 3.2.3 NTS data processing workflow

For NTS DP (Figure 3, II), LECOs statistical compare® tool for the identification of all compounds occurring in both PUF or both GFF samples was applied. With this approach, it was possible to reduce the peak lists from approx. 30000 to 3800 peaks for PUF and from approx. 25000 to 5000 peaks for GFF samples. After the initial automatic blank filtration (see sect. 3.2.1), DP with the NIST14 and suspect libraries as well as applying NT scripts for the identification of specific compounds of interest (i.e. halogenated etc.) was performed. The resulting peak list was further reduced to approx. 1000 peaks per sample. These NT scripts, written in Visual Basic, were applied during DP to identify brominated and chlorinated compounds based on their isotopic clusters, as well as PAHs, phthalates and nitro compounds with the help of recognizable features in fragmentation patterns (Hilton et al., 2010). These scripts are especially useful to detect compounds which would be overlooked by low MS library match or not listed in the used MS libraries. In addition, a second blank filtration were performed and only compounds which are exceeding an area of factor ≥ 100 compared to the sample blank were kept for further inspection. Like in SUS DP, also during NTS DP it was necessary to reduce the number of peaks for manual inspection. As a final method, all peaks identified with NT scripts and all peaks with a forward match of ≥ 80 % to the MS libraries (NIST14 and suspect libraries) were kept for further processing. Hereby it was possible to identify approx. 550 compounds in the PUF sample and approx. 400 compounds in the GFF sample with NTS DP. Those identified compounds were classified as L5 and ISTDs and their respective native compound, L0 (Figure 3, II: L5 list to check manual on right identity).

Similar to SUS, manual check on the right identity of these NTS L5 compounds is needed in order to increase the level of identification confidence since all confirmations are only based on MS library comparisons or NT script filtrations. For manual inspection of each compound and further level classification, the lists from SUS and NTS were merged to one list for a more effective proceeding (Figure 3, A).

Both DPs, SUS and NTS, were using the forward match percentage to MS library entries to reduce the number of peaks which require manual inspection. In this step, the quality of a MS from a compound is of high importance to match a MS library entry and thus be kept for further processing. The quality of a MS of a compound is not only affected by interferences or S/N ratios, the quality might also be affected from the unit mass resolution of the used GC×GC-LRMS instrument. In particular, the limited unit mass resolution of the used GC×GC-LRMS has negative consequences for MS of compounds with higher mass defects, e.g. brominated, higher chlorinated or mixed halogenated compounds. Even when acquired under optimal conditions, the obtained MS are not identical to reference MS from the NIST14 MS library (Figure 4) and, hence, those compounds would be rejected during DP, due to low match percentage to NIST14 library. The used NT scripts used during DP, developed by Hilton et al. (2010), were specifically developed for MS obtained by LECOs GC×GC-LRMS for the identification of isotopic clusters of brominated and chlorinated compounds and were used as an tool during DP for the identification of compounds of interest for manual inspection.

In addition to the MS quality affected by the unit mass resolution of the ToF-MS detector, lower library match could also be caused by different fragmentation patterns compared to MS from the NIST14 library, which were obtained with quadrupole

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mass filter in electron ionisation mode. Also here it was possible that compounds of interest could be rejected during a DP step due to low match percentage to a NIST14 MS.

Further factors may limit the positive identification of a compound including potential loss during sample clean-up. Our sample clean-up method was optimised for the analysis of compounds covering a wide range of polarity for GC×GC-LRMS analysis. However, the substantial loss of substances purely adsorbing and accumulating on PUF/GFF sampling materials cannot be excluded. Furthermore, compounds may degrade, evaporate or not elute from used adsorbents during sample clean-up. During GC×GC-LRMS analyses, thermolabile substance may degrade in the injector or irreversibly bound/degraded on the chromatographic column. Furthermore, compound specific low sensitivity in the here used positive electron ionisation mode may prevent the positive identification of a possible target compound.

In the here chosen DP strategy, all confirmed compounds need to match all used selection criteria. However, the priority criteria need individual fine tuning for each data set examined for avoiding false positive and false negative listings as well as minimize the occurrence of blank compounds. However, even after following this comprehensive data processing protocol, it cannot be excluded that unconfirmed or excluded substances does not occur in air from Birkenes, southern Norway.

### 3.3 Number of detected and classified compounds

After comprehensive peak filtration from raw data to a reduced peak list for manual inspection, all remaining compounds were initially classified as L5 (mass spectra of interest) (Figure 3: A) and, respectively all compounds, identified with ISTDs as L0. The compounds classified as L5 are further checked manual on their identity to reach a higher level of identification confidence. For some compounds, with high match percentage compared with the reference MS libraries and recognisable m/z pattern/-s in the MS, this check on right identification is a straight forward procedure for classification as L2 or L3 compounds. Others, with less characteristic m/z patterns, or just an identification due to their inherent halogen isotopic pattern, might be classified as L3 or L4 (Figure 2). The procedure for the correct classification of such substances is time consuming and requires comprehensive scientific experience. Before comparing compounds to in-house and/or new reference standards, L2 and L3 compounds were, in addition to the automatic blank filtration during initial data processing, manually checked against sample blanks and ensured that these compounds have an area, which exceeds the area threshold (factor ≥ 100). This manual blank check is essential, since the automatic blank filtration routine during DP may lead to missing compounds (low match factors between the blank and the real sample), partly caused of coelution or matrix related retention time shifts. After this initial step, further characterisation of potential compounds based on sales numbers, inherent physical chemical properties (adsorption, transformation, reactivity), application sources and profiles, seasonal patterns etc, may be beneficial in addition to confidence level determination (L0, L1, L2, L3, L4 or L5).

For the here studied high-volume air samples from the Birkenes observatory, the merged L5 list from SUS and NTS available for manual inspection (Figure 3, A) contain almost 1500 compound suggestions: over 600 compounds from the GFF extracts (particulate phase), and over 850 compounds from the PUF extracts (gaseous phase). More than 50 % of these compounds could be further identified and classified to L4, L3 and L2 during manual inspection of MS. This was possible for 350

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compounds from the GFF and for 655 compounds from the PUF. All L2 and L3 compounds were manually checked against the blank sample before comparison to new and in-house reference standards. For quality assurance, all reference standards were analysed with the same GC×GC-LRMS method as the air samples , as well as analysing a reference mixture of ISTDs to account for retention time shifts (Figure 3, B). Hereby, five compounds were confirmed with ISTDs to L0 (1/4 GFF/PUF) and 45 compounds with reference standards to L1 (12/33 GFF/PUF). In addition, 80 compounds were classified as L2 (21/59 GFF/PUF) and 774 compounds as L3 (290/484 GFF/PUF). The remaining 81 compounds were characterised as L4 (17/64 GFF/PUF) compounds as summarised in Figure 3, C and Table 3.

The L2 compounds include 11 potential PCBs. For those compounds the exact number of congeners might deviate since single reference standards for each PCBs congener were not analysed. Polycyclic aromatic compounds (PAC) was the largest sub-group of L3 compounds (see Figure 6). Unknown halogenated compounds, which did not have any MS library match, were included in L4. An overview about the distribution of L0–L4 compounds in the GFF and PUF can be found in Table 3. The complete peak list of L0–L4 compounds is available in the Excel-SI spreadsheet.

From 45 compounds, classified as L1, 22 compounds are listed in one or more suspect lists, and from 80 compounds, classified as L2, resemble 28 compounds similarity to one or more suspect lists (Table 3). As L2 compounds are not confirmed with reference standards, matches to suspect lists are slightly uncertain and compounds listed as L2 in Excel-SI may also represent different isomers.

The here chosen priority suspect lists were selected for the identification of long-range atmospheric transport potential (LRATP) of CECs and hitherto unidentified CECs. However, the chosen suspects do cover the bulk of legacy POPs, CECs previously analysed at the Birkenes observatory and a large number of CUPs and non-regulated chemicals, especially own measured MS in the customised self-build libraries. The chosen suspects list are considered as relevant for Arctic air samples and suspect prioritisation lists originate from different authors (Reppas-Chrysovitsinos et al., 2017; Brown and Wania, 2008; Coscollà et al., 2011; Hoferkamp et al., 2010; Howard and Muir, 2010; NORMAN-network, 2019; Vorkamp and Rigét, 2014; Zhong et al., 2012) as well as self-build in-house suspect libraries (Table 3). A short summary about data alignment of used suspect lists and findings in our samples can be found in the SI.

The compounds and compound groups identified in the air samples from the Birkenes observatory in this study are grouped in three groups: (i) legacy POPs and PAHs, (ii) known CECs and (iii) new potential CECs not previously reported in southern Norway/Birkenes (status October 2019). In addition to 36 already reported organic contaminants at Birkenes (incl. legacy POPs and known CECs), 92 new potential CECs with match to reference standards (L1) or probable structures (L2) were identified (64 in PUF and 28 in GFF samples). It is interesting to note that 11 chemicals were common to the GFF and PUF sample. 29 of the new potential CECs have a LRATP according to the Stockholm convention (UNEP, 2009a), half-live in air exceeding 2 days, and may, hence, undergo long-range atmospheric transport.

Overall, 39 compounds, identified as L0, L1 or L2, were also detected in high volume air samples from the Zeppelin station (Ny-Ålesund) in Svalbard, using the same analytical approach as in this study (Röhler et al., 2020).

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A complete overview can be found in the Excel-SI spreadsheet, including information on the complementary findings in Arctic air samples, physical-chemical properties, additional information from literature search as well as further parameters on environmental properties (incl. persistence, bioaccumulation and toxicity (PBT) classification by REACH (European Parliament, 2018) and Stockholm convention (UNEP, 2009a), Table S7).

### 3.4 Identified compound groups

As summarised in Figure 5, identified compounds were grouped in different compound classes and arranged as previously detected or previously not detected in air samples at the Birkenes observatory (only including L0, L1 and L2 compounds). For approximately 2/3 of the identified compounds, an application purpose could be identified and are discussed in detail in the following sections.

#### 3.4.1 Legacy POPs and PAHs in air from Birkenes

In total, 23 legacy POPs and PAHs were identified as L0, L1 or L2. The L0 and L1 were hexachlorocyclohexanes ($\alpha$-HCH and $\gamma$-HCH), HCB, *p,p'*-DDE, *p,p'*-DDT, PCB 153, dieldrin, *trans*-nonachlor and a metabolite of heptachlor (heptachloro *exo*-epoxide) and three PAHs, routinely measured at Birkenes, such as biphenyl, fluorene and benzo[*ghi*]fluoranthene (UNEP, 2009a). An extensive list of PAHs was detected showing their presence in air samples from Birkenes, but only a few single PAH reference standards were available for analyses and hamper the identification of individual PAHs. Most of the detected PAHs were therefore classified as L3 (section 3.4.4). In addition, 11 PCB congeners were classified as L2. Besides dieldrin and heptachloro *exo*-epoxide, the remaining legacy POPs are regularly measured using target methods in the Norwegian monitoring programme for long-range transported atmospheric contaminants (Nizzetto, 2016) at the same monitoring station. The detection of those compounds with our novel wide-scope sample clean-up method, combined with SUS and NTS characterisation method in real air samples provides additional confidence for the quality of the here reported comprehensive analytical strategy.

#### 3.4.2 Known CECs

The presence of four known CECs (L0, L1 and L2), recently reported in Birkenes air samples, where also confirmed by the here applied approach (Nizzetto, 2019). These includes BFRs, pentabromotoluene (PeBT, L2) and hexabromobenzene (HBB, L0) as well as OPFRs, triisobutyl phosphate (TBP, L1) and tris(1,3-dichloro-2-propyl)phosphate (TDCPP, L1). In addition to the monitored OPFRs, it was possible to detect nine isomers of previously monitored OPFRs as L2. Two positional isomers of tris(4-isopropylphenyl) phosphate (TiPPP), three isomers of di(isopropylphenyl)phenyl phosphate, one isomer of isopropylphenyl diphenyl phosphate as well as one positional isomer of tris(2-chloroisopropyl)phosphate (TCPP), one isomer of cresyl-diphenyl phosphate and one TBP related isomer as L2. The six isopropylphenyl phosphate congeners are all part of the technical mixture of TiPPP.

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### 3.4.3 New potential CECs

In addition to identification of legacy POPs, PAHs and known CECs in air samples from Birkenes, it was possible to detect 90 new potential CECs that to our knowledge have not been reported previously in air samples from this region. Most of these new potential CECs (n=62), identified with match to reference standards (L1) or probable structure (L2), were detected in the gas phase (PUF) while 28 were detected in the particle phase (GFF).

**Compounds with LRATP.** According to half-life data ($t_{1/2}$(air)) of the AOPWIN model of US EPAs EPIsuite program (U.S.EPA, 2019), 29 of the detected new potential CECs have a LRATP according to the Stockholm convention criteria (UNEP, 2009a), $t_{1/2}$(air) exceeding 2 days.

Of these 29 compounds, 14 were identified as L1 (4/10 GFF/PUF; of those are 4 common to GFF and PUF) and 15 compounds were identified as L2 (4/11 GFF/PUF). Structures, sample, name and CAS for L1 compounds can be found in Figure 4, all further information is available in the Excel-SI spreadsheet.

The four L1 compounds, which were identified both in the GFF and PUF samples were benzenesulfonamide (BSA), p-toluenesulfonamide (pTSA), 2-methyl-9,10-anthraquinone (2-MAQ) and 4H-cyclopenta[def]phenanthren-4-one. BSA and pTSA have similar molecular structures, since BSA is the parent compound of pTSA. BSA is used as an industrial intermediate in the synthesis of widespread products like disinfectants, dyes or photochemical products and pTSA is used as a fungicide in paints and coatings or as a plasticiser (ECHA, 2019b; Naccarato et al., 2014; Herrero et al., 2014). Since BSA and pTSA could be used in many widespread products, a local source cannot be excluded. The identified 2-MAQ is a potential wood combustion product, an intermediate in industrial production of coating products, inks, toners, laboratory chemicals and explosives, and used for the production of plastic products (Czech et al., 2018; Lui et al., 2017; Vicente et al., 2016; ECHA, 2019a). It is also possible that 2-MAQ could be formed through atmospheric reactions (Alam et al., 2014). All three oxy-PAHs, 2-MAQ and 4H-cyclopenta[def]phenanthren-4-one (identified in GFF and PUF) and 9,10-anthraquinone (PUF only), are related to emissions of diesel and petrol vehicles (Karavalakis et al., 2010; Alam et al., 2014, 2013). 4H-Cyclopenta[def]phenanthren-4-one and 9,10-anthraquinone are also identified as oxidation products of PAHs (Singh et al., 2017). The three identified oxy-PAHs are known air contaminants, but to our knowledge never been measured in Norwegian background air samples before. To understand the origin of these oxy-PAHs, further research is necessary, e.g. diagnostic ratios to distinguish between different sources (Alam et al., 2013).

The remaining five L1 compounds (only detected in PUF) were two intermediates, 1,4-benzenedicarbonitrile (terephthalonitrile) and 1-methyl-2-nitrobenzene (2-nitrotoluene), the biodegradation product tetrachloroveratrole as well as two combustion products, 1-methoxy-2-nitrobenzene (2-nitroanisole) and 2-naphthalenecarbonitrile. Terephthalonitrile might be an intermediate for the production of the pesticide dacthal (Meng, 2012) and was detected together with two isomers of terephthalonitrile (probably positional isomers), which were classified as L2. 2-Nitrotoluene is used as an intermediate for the production of azo dyes and other dyes, rubber chemicals, agriculture chemicals, pharmaceuticals and explosives (IARC, 2013; ECHA, 2008). The presence of 2-nitrotoluene may also be a degradation product of explosives like TNT (trinitrotoluene)

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(Mohsen et al., 2013). A possible local source could be a shooting range (6 km south-westerly) or military training areas, which is approximately 30 km south-westerly from the Birkenes observatory (NOU, 2004). The pesticide metabolite, or bacterial biodegradation product tetrachloroveratrole is formed during bleaching of wood pulp or chlorination of wastewaters in the pulp and paper industry (GovCanada, 2019; Su et al., 2008; Arinaitwe et al., 2016). Tetrachloroveratrole is a known priority pollutant, found and monitored even in the Arctic (Su et al., 2008), but previously not reported in southern Norway background air. 2-Nitroanisole is mainly derived from combustion processes but can also be formed by atmospheric reactions (Stiborova, 2002). Large quantities of 2-Nitroanisole were released into the atmosphere in the course of an accident at the Hoechst plant, Germany in 1993 (Weyer et al., 2014). 2-Naphthalenecarbonitrile is related to plastic combustion, e.g. ABS (acrylonitrile-butadiene-styrene) plastic or polyester fabrics (Moltó et al., 2009; Watanabe et al., 2007; Wang et al., 2007; Moltó et al., 2006) but can also be used for the bluing of steel surfaces (Stefanye, 1972). The corresponding isomer 1-naphtalenecarbonitrile was classified as L2. Other compounds identified as L2 can be found in the Excel-SI spreadsheet.

**Compounds without LRATP.** The other group of new potential CECs detected in this study (n=61) do not have LRATP, according to the Stockholm convention criteria (UNEP, 2009a), $t_{1/2}$(air) need to exceed 2 days. The origin of these compounds is still considered to be through LRAT as Birkenes is a background monitoring station where background air is being measured. The presence of these compounds at Birkenes is therefore itself an evidence for LRAT of these compounds. It shows a limitation of modelling calculations for LRATP. The results of this study can be compared with data from the Zeppelin observatory on Svalbard (Arctic background air samples) reported earlier (Röhler et al., 2020). In brief, 16 of 17 L1 compounds without LRATP (all compounds in Table 5, except 3,6-Dimethylphenanthrene) from the Birkenes dataset were also confirmed in the Arctic air samples, further confirming LRATP of these compounds. For more details see Excel-SI.

Overall, 61 new potential CECs without LRATP were classified in Birkenes air samples, 17 compounds were identified as L1 (5/12 GFF/PUF; 4 are common to GFF and PUF) and 44 compounds classified as L2 (15/29 GFF/PUF; 3 are common to GFF and PUF). For L1 compounds, CAS, name, sample and structure are listed in Table 5, and further information on all compounds identified can be found in SI Excel-SI.

Four oxy-PAHs, 1,2-BAQ, BPone, BAone, 9-Fone, and one PAH, 3,6-DMPH, have previously been detected in particle related samples from three southern European cities, with highest concentrations during winter (Alves et al., 2017), but to our knowledge have not been previously measured in south Norwegian air samples. 3,6-DMPH and 9-Fone were found in the PUF, BPone in the GFF and 1,2-BAQ as well as BAone in the GFF and PUF sample. The identified PAH and four oxy-PAHs were all previously detected in wood combustion experiments (Czech et al., 2018) and a local sources cannot be excluded. A further group of compounds, consisting of three terphenyl isomers (*o,m,p*), were previously detected during pyrolysis and combustion experiments of polyether fabric (Moltó et al., 2006). The commercial mixture of all three terphenyl isomers is used for heat transfer and storage agent in industrial processes. Also applications as textile dye carriers and as intermediate of non-spreading lubricants are reported (Netherlands, 2002). All three terphenyl isomers were identified in the PUF sample and m-terphenyl was in addition to that, also detected in the GFF sample. The terphenyls were to our best knowledge never before analysed in air samples from southern Norway but were part of a larger screening study from Oslo in 2018. In that study,

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terphenyls were found in indoor air, sewage water and sediment samples, indicating their widespread emission to the environment (Schlabach, 2019).

Carbazole may mainly be used in carbazole containing polymers (PVK, poly(-N-vinylcarbazole)), which could be used in photovoltaic devices or in semiconducting polymers (Zhao et al., 2017; Grazulevicius et al., 2003). This compound is also used in the production of various pharmaceuticals (Zawadzka et al., 2015). Carbazole was identified in both GFF and PUF sample. For two identified wood preservatives, dichlofluanid and IPBC, a local source cannot be excluded. IPBC is also used in cosmetics and personal care products (ECHA, 2019c, d). Both compounds were detected in the PUF sample. Triallate, which was detected in PUF sample, is used as agriculture pesticide (herbicide). While never being detected in air samples from southern Norway, there was a previous finding in air samples from Manitoba (Canada) during winter, suggesting relatively high persistence in air and possibly LRATP (Messing et al., 2014). A major methylation product of 2-mercaptobenzothiazole (2-S-BTH), 2-Me-S-BTH, could be identified in the PUF sample. 2-S-BTH is used as vulcanisation accelerator in rubber of car tires, shoes, cables, rubber gloves and toys (Herrero et al., 2014; Leng and Gries, 2017). Due to its widespread use, the finding of 2-Me-S-BTH could be affected by local sources.

#### 3.4.4 Summary for Level 3 compounds

A large number of L3 compounds (tentative candidates; n=774) were identified. After grouping those L3 compounds in classes, the largest groups of compounds are PACs (polyaromatic compounds), carbonic acid esters and phthalates. Other detected esters and a few halogenated compounds were two minor groups. All further compounds were grouped as miscellaneous (Figure 6). The list of L3 compounds can be found in the SI Excel-SI.

#### 3.4.5 Summary for Level 4 compounds

In the group of L4 compounds, 81 possible molecular formula and unknown halogenated compounds could be detected. Of these, 11 were classified as potential unknown halogenated compounds (2/9 GFF/PUF) and the other 70 compounds only with possible molecular formula (15/55 GFF/PUF; 2 are common to GFF and PUF). The detected unknown halogenated compounds did not match MS from NIST14 or in-house MS libraries. It was, however, possible to extract a potential content of chlorine and/or bromine, a potential molecular weight and structural fragments from the given LRMS spectra. For further identification, to receive more structural information or a potential molecular formula, investigation on HRMS instruments is required. The list of detected L4 compounds can be found in SI Excel-SI.

## 4 Conclusions

A comprehensive sample clean-up method is one of the key factors for successful SUS and NTS approaches. An ideal method removes interfering matrix and in the same time keep a maximum number of compounds of interest in the extract. In this study, a novel sample clean-up method has been developed and tested on spiked samples and real air samples. The results demonstrate

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that this method is promising in target as well as SUS and NTS analyses of regulated and emerging organic compounds in air samples. The recoveries for legacy POPs and BFRs were comparable to those obtained with the traditional acid clean-up method, but with the possibility to quantify an extended range of compounds including the acid-labile POPs and BFRs. The GC×GC-LRMS analyses in combination with the newly developed SUS/NTS data evaluation strategies on real air samples resulted in the identification of 90 new potential CECs, here detected in southern Norway for the first time. With the application of ISTD to SUS and NTS, we extended the SUS and NTS approach into potential quantitative target analysis.

In order to increase the effectiveness of future SUS and NTS studies in air, expanding the suspect library with entries of relevant airborne contaminants is considered as essential. GFF and PUF-based high volume air sampling is a widely used air sampling technique, but the polyurethane polymer used in the foams generates a massive load of PUF related matrix (often more than 20 000 compounds) which need to get removed during sample clean-up or during post acquisition data filtration. Reducing this load by developing cleaner PUFs or replacing PUF with another adsorbent is an important next step in further development of SUS/NTS methods for air samples. In future work, the application of GCxGC-HRMS would be an important step for further improvement of the presented SUS/NTS method as it enables structure elucidation of CECs not yet present in MS libraries. In addition, the application of retention indices and retention index prediction data would provide additional information for the selection of the most likely compound structure.

**Competing interests**

The authors declare that they have no conflict of interest.

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Compound structures were created using ChemOffice19 (PerkinElmerInformatics, 2019).
LogP and logD values were created using JChem for Excel (ChemAxon, 2019).

**Author contribution**

LR, MS, PBN and RK developed the idea behind this study.
LR performed chemical work, analysis, created the figures and wrote the paper.
MS and PBN provided guidance and contributed to the paper preparation
PR provided guidance for Z-Sep$^{+}$/C18 method development and paper preparation
RK provided financial support from internal NMBU funding, academic guidance and contributed to the paper preparation
All authors read and approved the submitted manuscript.

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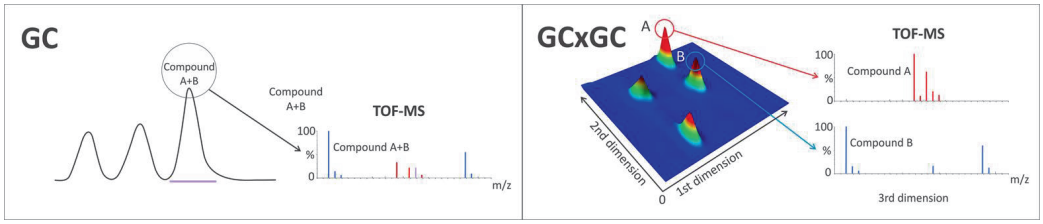


**Figure 1: GC separation compared to comprehensive GC×GC separation (Röhler et al., 2014).**

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**Table 1: Spiked standard mixtures for method evaluation samples.**

| Sample type (Set of 3 parallels) | Standard mixture native compounds | Standard mixture $^{13}$C-labelled compounds |
|---|---|---|
| POP | - | POP |
| Brominated | BFR | BFR |
| CUP A | Mix 1 | - |
| CUP B | Mix 2 | - |
| CUP C | Mix 3 | - |

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**Table 2: Summary of average recovery rates [%] for legacy POPs, BFRs, CUPs and CECs.**

| Compound class | Average recovery from 3 parallels [%] | Number of compounds |
|---|---|---|
| POPs | 50 – 117 | 40 |
| BFRs | 45 – 92 | 19 |
| CUPs and CECs | <20 | 2 |
| | 20-50 | 11 |
| | >50 | 31 |

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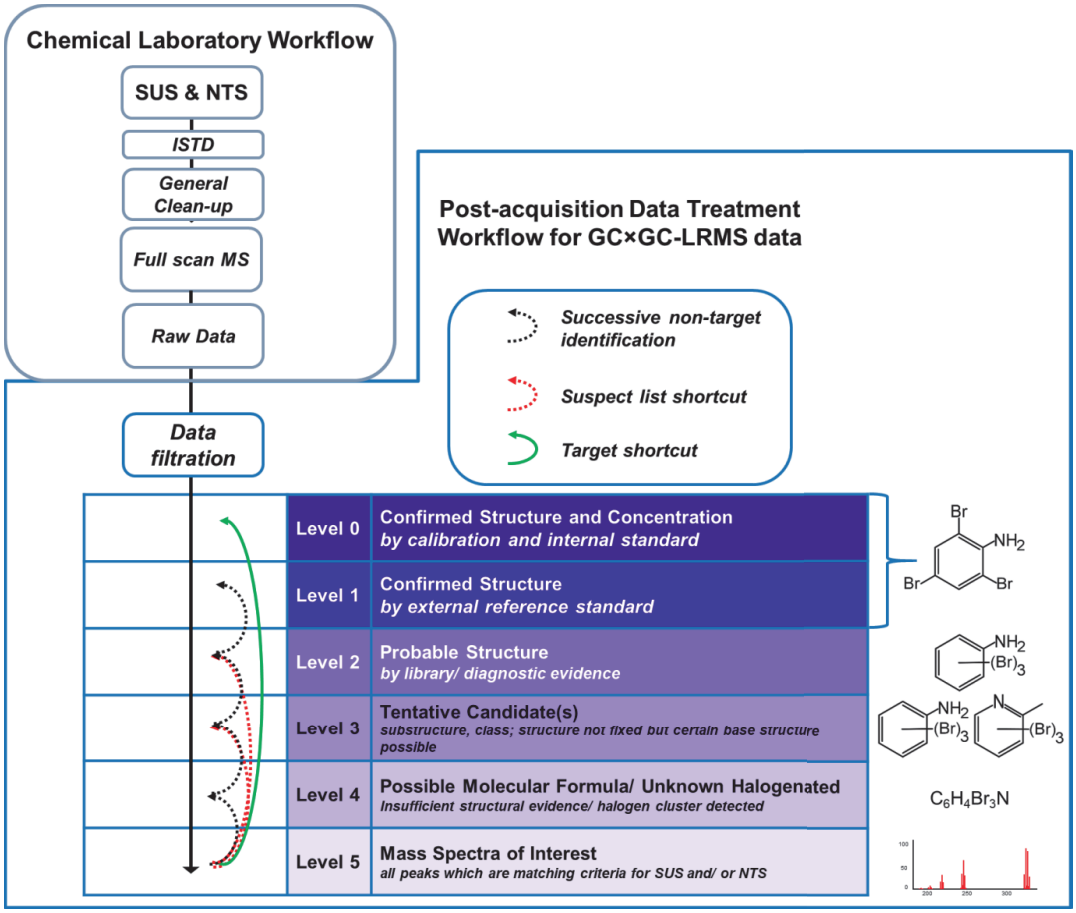


**Figure 2: General strategy and levels for identification confidence for GC×GC-LRMS. Adapted from Schymanski et al. (2015).**

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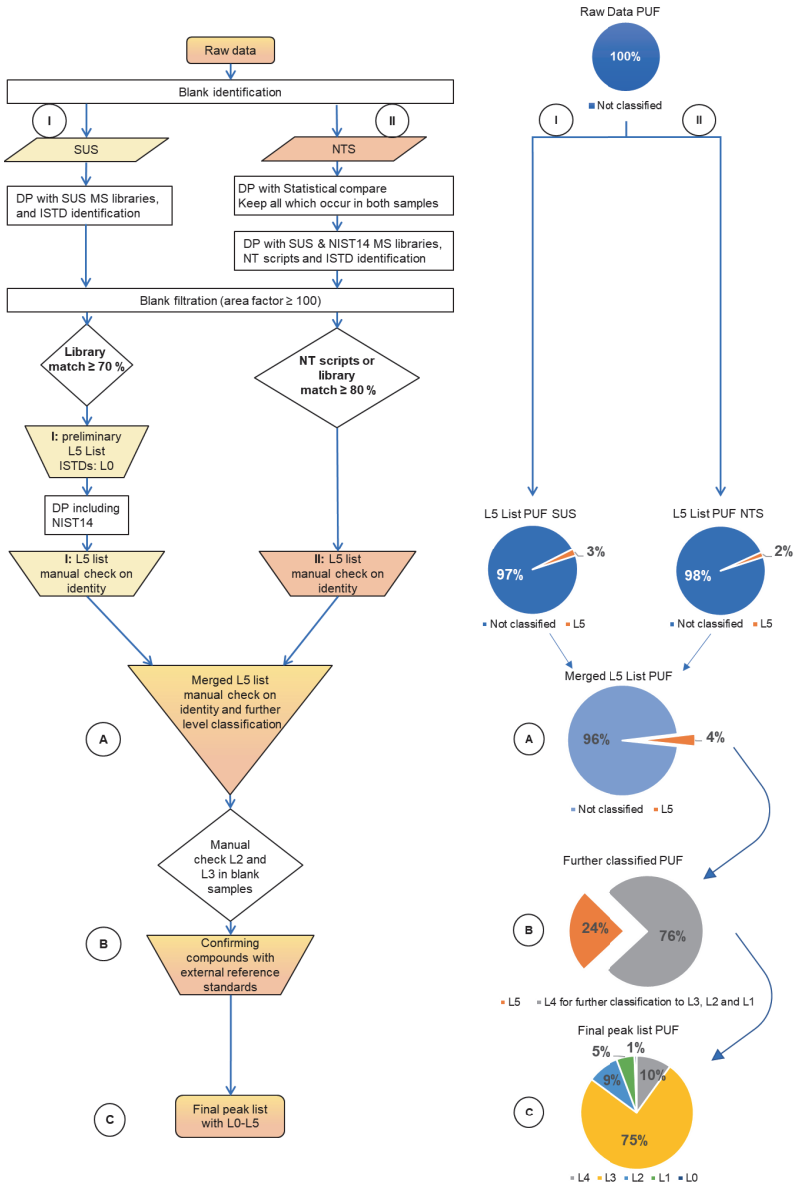


**Figure 3: Data processing workflow and peak reduction during level classification.**

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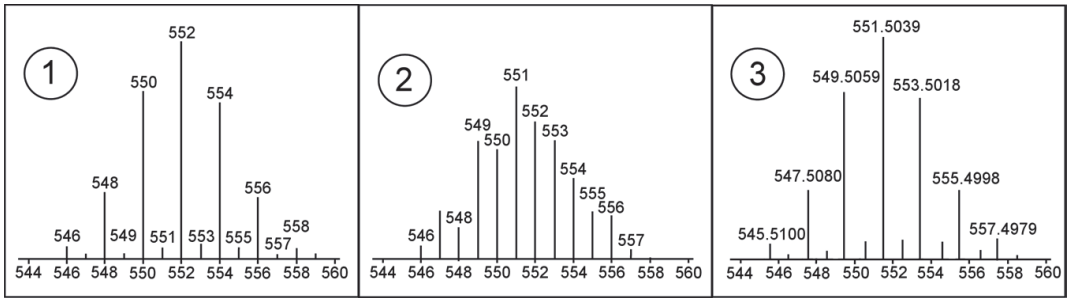


**Figure 4: 1: Isotope cluster of hexabromobenzene (HBB) in NIST14, 2: own measured HBB on GC×GC-LRMS and 3: HRMS isotope cluster HBB.**

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**Table 3: Overview of the L0 – L4 compounds, classified in air samples from Birkenes (southern Norway).**

| Level | Compounds classified | PUF samples | GFF samples | Common to PUF and GFF | Found in suspect lists |
|---|---|---|---|---|---|
| **L0** | 5 | 4 | 1 | 1 | 4 |
| **L1** | 45 | 33 | 12 | 10 | 22 |
| **L2** | 80 | 59 (11 PCBs) | 21 | 4 | 28[a] |
| **L3** | 774 | 484 | 290 | -[b] | -[b] |
| **L4** | 81 | 64 (9 unknown halogenated) | 17 (2 unknown halogenated) | 2 | -[b] |

a: showing similarity to suspect lists, isomer not confirmed; b: not applicable

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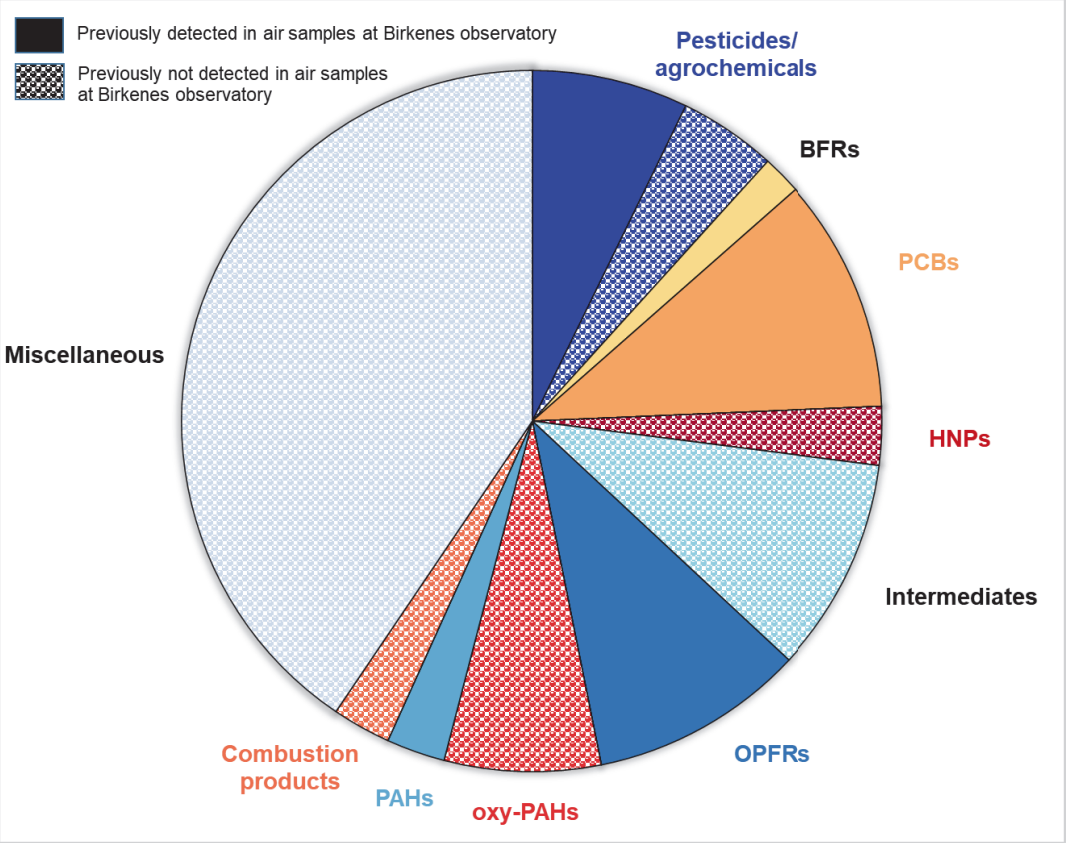


**Figure 5: Overview of detected compounds confirmed with reference standards (L0 and L1) and probable structures (L2).**

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**Table 4: Structure overview of L1 compounds, classified as new potential CECs with LRATP.**

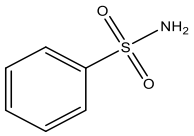
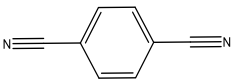
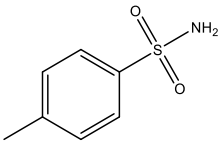
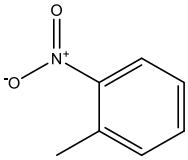
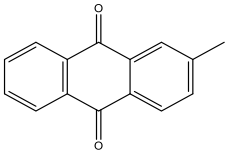
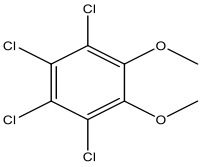
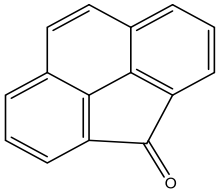
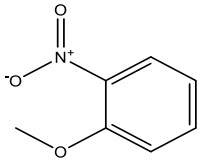
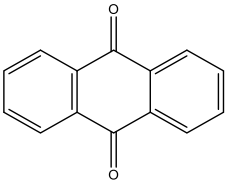
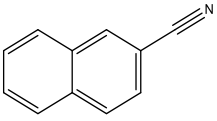
| Name/ CAS/ Sample | Structure | Name/ CAS/ Sample | Structure |
|---|---|---|---|
| Benzenesulfonamide (BSA)/ 98-10-2<br>GFF (particle phase) and PUF |  | 1,4-Benzenedicarbonitrile (Terephthalonitrile)/ 623-26-7<br>PUF (gas phase) |  |
| p-Toluenesulfonamide (pTSA)/ 70-55-3<br>GFF (particle phase) and PUF |  | 1-Methyl-2-nitrobenzene (2-Nitrotoluene)/ 88-72-2<br>PUF (gas phase) |  |
| 2-Methyl-9,10-Anthraquinone (2-MAQ)/ 84-54-8<br>GFF (particle phase) and PUF |  | Tetrachloroveratrole/ 944-61-6<br>PUF (gas phase) |  |
| 4H-Cyclopenta[def] phenanthren-4-one/ 5737-13-3<br>GFF (particle phase) and PUF |  | 1-Methoxy-2-nitrobenzene (2-Nitroanisole)/ 91-23-6<br>PUF (gas phase) |  |
| 9,10-Anthraquinone/ 84-65-1<br>PUF (gas phase) |  | 2-Naphthalenecarbonitrile/ 613-46-7<br>PUF (gas phase) |  |

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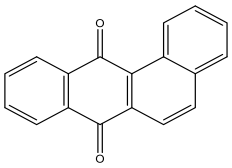
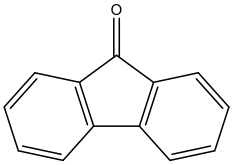
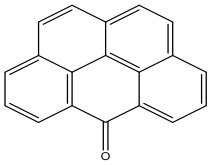
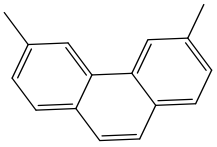
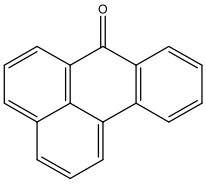
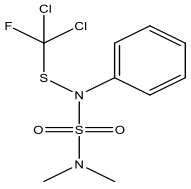
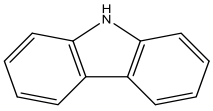
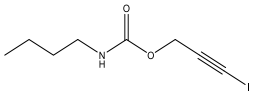
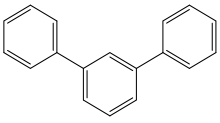
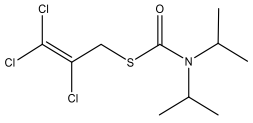
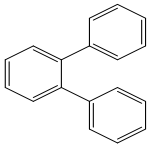
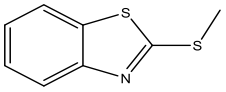
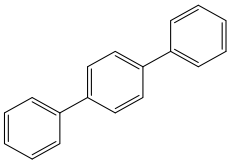
**Table 5: Structure overview of L1 compounds, classified as new potential CECs without LRATP.**

| Name/ CAS/ Sample | Structure | Name/ CAS/ Sample | Structure |
|---|---|---|---|
| 1,2-Benzanthraquinone (1,2-BAQ)/ 2498-66-0<br>GFF and PUF |  | 9-Fluorenone (9-Fone)/ 486-25-9<br>PUF (gas phase) |  |
| 6H-Benzo[*cd*]pyren-6-one (BPone)/ 3074-00-8<br>GFF (particle phase) |  | 3,6-Dimethylphenanthrene (3,6-DMPH)/ 1576-67-6<br>PUF (gas phase) |  |
| 1,9-Benz-10-anthrone (BAone)/ 82-05-3<br>GFF and PUF |  | Dichlofluanid/ 1085-98-9<br>PUF (gas phase) |  |
| Carbazole/ 86-74-8<br>GFF and PUF |  | 3-Iodo-2-propynyl butylcarbamate (Iodocarb, IPBC)/ 55406-53-6<br>PUF (gas phase) |  |
| *m*-Terphenyl/ l92-06-8<br>GFF and PUF |  | Triallate/ 2303-17-5<br>PUF (gas phase) |  |
| *o*-Terphenyl/ 84-15-1<br>PUF (gas phase) |  | 2-(Methylmercapto)-benzothiazole (2-Me-S-BTH)/ 615-22-5<br>PUF (gas phase) |  |
| *p*-Terphenyl/ l92-94-4<br>PUF (gas phase) |  | | |

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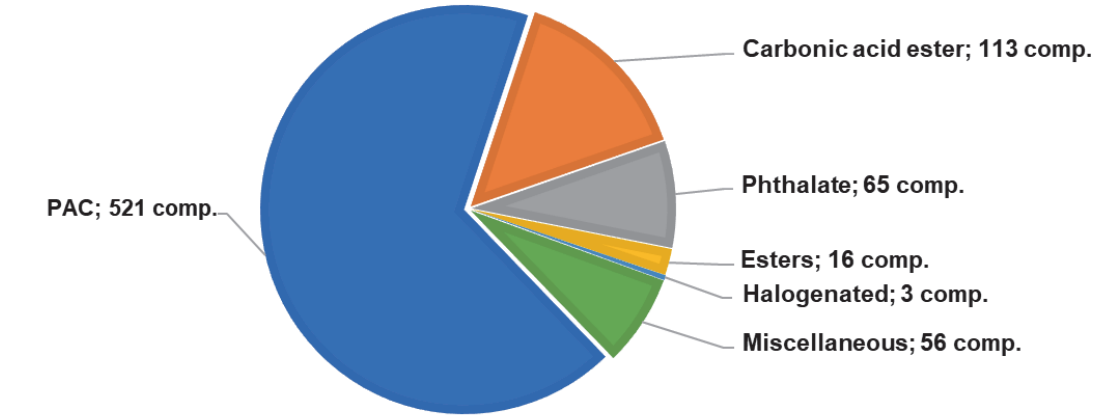


**Figure 6: L3 compounds.**

# Supplementary Material ACP-2020-263

The Excel-SI document for ACP-2020-263 can be found on ACPs webpage:

https://www.atmos-chem-phys-discuss.net/acp-2020-263/

## Used chemicals and equipment

**Table S1: Used chemicals and equipment.**

| Chemical/ Equipment | Purchased |
|---|---|
| Aceton | VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway |
| *n*-Hexane | VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway |
| Cyclohexane | VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway |
| Acetonitrile | LiChrosolv, isocratic grade for LC, Merck, Darmstadt, Germany |
| Toluene | EMSURE® for analysis, Merck, Darmstadt, Germany |
| Isooctane | EMSURE® for analysis, Merck, Darmstadt, Germany |
| Extran® | Merck, Darmstadt, Germany |
| Sodium sulphate | anhydrous, EMSURE® for analysis, Merck, Darmstadt, Germany |
| Discovery DSC-18 | Supelco, Bellefonte, PA, USA |
| Supel™QuE Z-Sep$^{+}$ | Supelco, Bellefonte, PA, USA |
| Florisil® 60-100 Mesh | Sigma Aldrich Chemie GmbH, Germany |
| Citric acid | anhydrous, puriss., Sigma Aldrich Chemie GmbH, Germany |
| Cotton | Mediq Norge, Norway |
| Polyurethane foam (PUF) plugs (7 cm in diameter and 4 cm in height) | Sunde Skumplast A/S, Gan, Norway |
| Glass fibre filters (150 mm in diameter) | GF/C standard, Whatman®, GE Healthcare Life Sciences, Oslo, Norway |
| KNF vacuum pump | Laboport, N86KT.18, Village-Neuf, France |
| Nitrogen gas | 5.0 quality, Nippon gases Norge AS, Oslo, Norway |

All used glassware was washed with Extran®, heated to 450 °C for 8 h and rinsed with acetone prior use.

Florisil, glass fibre filters and sodium sulphate were heated to 450°C for 8 h prior use.

Cotton was Soxhlet extracted with n-hexane for 24h, rinsed with acetone and dried prior use.

PUF plugs were pre-cleaned by Soxhlet extraction prior use: 8 h with acetone followed by 8 h with cyclohexane.

**Standards used for spiked surrogate method evaluation samples**

$^{13}C/^{2}H$-labeled and native standards for used for standard mixtures 'POP' and 'BFR' were purchased from Wellington Laboratories, Guelph, ON, Canada.

Native standards for mixtures CUP A-C were purchased from AccuStandard, New Haven, CT, USA.

**Table S2: Overview of spiked compounds, recovery and RSD for method evaluation samples 'POP', spiked with 'POP'.**

| Target compound | Native/ $^{13}C/^{2}H$ - labelled | Spike [ng] | POP ($n$ = 3) | |
|---|---|---|---|---|
| | | | Rec [%] | RSD [%] |
| Dieldrin | $^{13}C$ | 24 | 112 | 12 |
| Aldrin | $^{13}C$ | 12 | 63 | 3 |
| Endrin | $^{13}C$ | 9 | 95 | 6 |
| Mirex | $^{13}C$ | 15 | 92 | 2 |
| Isodrin | $^{13}C$ | 46 | 74 | 4 |
| Trifluralin | $^{13}C$ | 2 | 70 | 10 |
| *Cis*-Chlordane | $^{13}C$ | 1 | 82 | 3 |
| *Trans*-Chlordane | $^{13}C$ | 1 | 76 | 3 |
| Oxychlordane | $^{13}C$ | 13 | 78 | 4 |
| *Trans*-nonachlor | $^{13}C$ | 1 | 81 | 3 |
| *Cis*-nonachlor | $^{13}C$ | 1 | 81 | 2 |
| Heptachlor | $^{13}C$ | 14 | 67 | 4 |
| Heptachlor *exo* epoxide | $^{13}C$ | 16 | 81 | 4 |
| Endosulfan sulphate | $^{13}C$ | 1 | 117 | 5 |
| Endosulfan I | $^{13}C$ | 2 | 90 | 5 |
| Endosulfan II | $^{13}C$ | 3 | 105 | 5 |
| α-HCH | $^{13}C$ | 20 | 96 | 4 |
| β-HCH | $^{13}C$ | 4 | 48 | 17 |
| γ-HCH | $^{13}C$ | 20 | 91 | 3 |
| *p,p'*-DDE | $^{13}C$ | 6 | 59 | 4 |
| *o,p'*-DDD | $^{13}C$ | 6 | 78 | 4 |
| *p,p'*-DDT | $^{13}C$ | 7 | 83 | 10 |
| δ-HCH | $^{13}C$ | 9 | 65 | 8 |
| PCB-28 | $^{13}C$ | 5 | 80 | 4 |
| PCB-52 | $^{13}C$ | 5 | 91 | 3 |
| PCB-101 | $^{13}C$ | 5 | 68 | 3 |
| PCB-105 | $^{13}C$ | 5 | 62 | 3 |
| PCB-114 | $^{13}C$ | 5 | 63 | 3 |
| PCB-118 | $^{13}C$ | 5 | 62 | 4 |
| PCB-123 | $^{13}C$ | 5 | 64 | 3 |
| PCB-138 | $^{13}C$ | 5 | 59 | 3 |
| PCB-153 | $^{13}C$ | 5 | 65 | 3 |
| PCB-156 | $^{13}C$ | 5 | 57 | 3 |
| PCB-157 | $^{13}C$ | 5 | 57 | 4 |
| PCB-167 | $^{13}C$ | 5 | 63 | 4 |
| PCB-180 | $^{13}C$ | 5 | 61 | 2 |
| PCB-189 | $^{13}C$ | 5 | 55 | 11 |
| PCB-209 | $^{13}C$ | 5 | 55 | 4 |
| HCB | $^{13}C$ | 2 | 83 | 5 |
| PeCB | $^{13}C$ | 2 | 58 | 6 |

**Table S3: Overview of spiked compounds, recovery and RSD for method evaluation samples 'Brominated', spiked with 'BFR'.**

| Target compound | Native/ $^{13}C/^{2}H$ - labelled | Spike [ng] | Brominated, BFR ($n$ = 3) | |
|---|---|---|---|---|
| | | | Rec [%] | RSD [%] |
| PBDE-28 | $^{13}C$ | 5 | 48 | 11 |
| PBDE-99 | $^{13}C$ | 5 | 59 | 16 |
| PBDE-47 | $^{13}C$ | 5 | 62 | 4 |
| PBDE-153 | $^{13}C$ | 5 | 85 | 4 |
| PBDE-197 | $^{13}C$ | 5 | 92 | 11 |
| PBDE-183 | $^{13}C$ | 5 | 92 | 7 |
| EHTBB | $^{2}H$ | 2 | 46 | 14 |
| γ/δ-TBECH | native | 48 | 57 | 6 |
| PBBZ | $^{13}C$ | 2 | 60 | 2 |
| BTBPE | $^{13}C$ | 2 | 60 | 7 |
| α-TBECH | native | 25 | 63 | 12 |
| β-TBECH | native | 25 | 61 | 10 |
| TBP-AE (ATE) | native | 49 | 62 | 9 |
| BEHTBP | native | 98 | 70 | 25 |
| DPTE | native | 49 | 74 | 5 |
| BATE | native | 50 | 74 | 4 |
| PBEB | native | 49 | 81 | 5 |
| PBT | native | 49 | 82 | 5 |
| HBB | $^{13}C$ | 2 | 80 | 3 |

**Table S4: Overview of spiked compounds, recovery and RSD for method evaluation samples CUP A, spiked with 'Mix 1'.**

| Target compound | Native/ $^{13}C/^{2}H$ - labelled | Spike [ng] | CUP A, Mix 1 ($n$ = 3) | |
|---|---|---|---|---|
| | | | Rec [%] | RSD [%] |
| Alachlor | native | 50 | 90 | 13 |
| Atrazine | native | 1012 | 50 | 5 |
| Bromacil | native | 51 | 14 | 46 |
| Carbophenothion | native | 50 | 129 | 16 |
| *Cis*-chlordane (α-Chlordan) | native | 51 | 108 | 5 |
| *Trans*-chlordane (γ-Chlordan) | native | 51 | 109 | 5 |
| Chloroneb | native | 50 | 19 | 10 |
| Chlorothalonil | native | 50 | 46[a] | 141[a] |
| Chlorpyrifos | native | 100 | 88 | 18 |
| Chlorpyrifos-methyl | native | 98 | 59 | 15 |
| Chlorthal-dimethyl (Dacthal or DCPA) | native | 51 | 78 | 3 |
| *cis*-Permethrin | native | 40 | 169 | 8 |
| Cyanazine | native | 152 | 86 | 27 |
| Diazinon (Dimpylate) | native | 50 | 50 | 14 |
| Dieldrin | native | 49 | 103 | 3 |
| Endine | native | 10 | 131 | 12 |
| Endrin ketone | native | 10 | 139 | 5 |
| Ethion | native | 98 | 261 | 21 |
| Fenitrothion | native | 99 | 98 | 13 |
| Heptachlor *exo*-epoxide | native | 5 | 104 | 6 |
| Malathion | native | 50 | 108 | 14 |
| Methidathion | native | 49 | 200 | 21 |
| Methoxychlor | native | 25 | 103 | 10 |
| Metolachlor | native | 50 | 127 | 16 |
| Metribuzin | native | 25 | 79 | 18 |
| *p,p'*-DDT | native | 49 | 110 | 5 |
| Pentachloronitrobenzene (PCNB or Quintozene) | native | 49 | 41 | 0 |
| Phosalone | native | 99 | 103 | 11 |
| Pirimiphos-methyl | native | 48 | 26 | 23 |
| Propachlor | native | 51 | 32 | 6 |
| Simazine | native | 1019 | 56 | 9 |
| Tecnazene (TCNB) 2,3,5,6-Tetrachloronitrobenzene | native | 49 | 29 | 4 |
| trans-Permethrin | native | 59 | 157 | 15 |
| Trifluralin | native | 55 | 51 | 6 |
| Chlorfenvinphos | native | 49 | 0 | - |
| Chlorobenzilate | native | 51 | 0 | - |
| Dichlorvos | native | 99 | 0 | - |
| Endine aldehyde | native | 10 | 0 | - |
| Etridiazole | native | 51 | 0 | - |

[a]: This recovery is not sure, 2 samples with no recovery and one sample with 139 % recovery

**Table S5: Overview of spiked compounds, recovery and RSD for method evaluation samples 'CUP B' and 'CUP C', spiked with 'Mix 2' and 'Mix 3'.**

| Target compound | Native/ $^{13}C/^{2}H$ - labelled | Spike [ng] | CUP B, Mix 2 ($n = 3$) | | CUP C, Mix 3 ($n = 3$) | |
|---|---|---|---|---|---|---|
| | | | Rec [%] | RSD [%] | Rec [%] | RSD [%] |
| Octachlorostyrene | native | 46 | 43 | 9 | - | - |
| 2,3,5,6-Tetrabromo-*p*-xylene | native | 52 | 64 | 16 | - | - |
| Musk ketone | native | 81 | 83 | 58 | - | - |
| Musk xylene | native | 44 | 44 | 3 | - | - |
| Tonalide | native | 50 | 29 | 18 | - | - |
| Galaxolid | native | 20 | - | - | 27 | 8 |
| 1,2,3,5,8-Pentachloronaphthalene (PCN 53) | native | 20 | - | - | 110 | 8 |
| 1,2,3,5,6,7-Hexachloronapthalene (PCN 67) | native | 19 | - | - | 135 | 8 |
| 1,2,3,4,5,6,7-Heptachloronaphthalene (PCN 73) | native | 20 | - | - | 155 | 5 |
| 1,2,3,4,5,6,7,8-Octachloronaphthalene (PCN 75) | native | 20 | - | - | 120 | 51 |

**Standards used for real high-volume air samples**

Internal standards were used for method quality control.

$^{13}$C-labeled standards were purchased from Wellington Laboratories, Guelph, ON, Canada.

$^{2}H_{10}$-labeled phenanthrene was purchased from Chiron AS, Trondheim, Norway.

1,2,3,4-Tetrachloronaphthalene was purchased from Ultra-Scientific, North Kingstown, RI, USA.

**Table S6: Spiking amounts ISTDs for real high-volume samples.**

| Internal standard | Spiking amount [ng] |
|---|---|
| $^{2}H_{10}$ phenanthrene | 2.08 |
| $^{13}C_{6}$ HCB | 4.78 |
| $^{13}C_{12}$ *p,p'*-DDT | 16.12 |
| $^{13}C_{12}$ PCB-153 | 12,20 |
| $^{13}C_{6}$ HBB | 21.14 |
| $^{13}C_{12}$ PBDE-28 | 5.28 |
| $^{13}C_{12}$ PBDE-47 | 5.22 |
| $^{13}C_{12}$ PBDE-99 | 5.30 |
| Recovery standard | |
| 1,2,3,4-Tetrachloronaphthalene (TCN) | 7.96 |

**GCxGC-LRMS analysis**

Three microlitre (µL) of each extract was injected into a PTV (programmed temperature vaporiser) inlet, operating in solvent vent mode.

PTV solvent vent mode with 30 sec solvent vent time, 50 mL min$^{-1}$ solvent vent flow at 0 psi, with a Gerstel PTV injector. Initial inlet temperature was 50 °C with a duration of 0.55 min, ramped with 200 °C min$^{-1}$ to 280 °C with a duration of 6 min and ramped with 100 °C min$^{-1}$ to 320 °C with a duration of 2 min.

The temperature program of the primary GC column was set as follows: 45 °C (hold time 0.55 min), ramped with 50 °C min$^{-1}$ to 80 °C (hold time 1.5 min) and ramped with 4 °C min$^{-1}$ to 300 °C (hold time 8 min). The secondary oven temperature was programmed 105 °C (hold time 2.25 min) and ramped at 4 °C min$^{-1}$ to 315 °C (hold time 10.5 min). Modulation period was set to 4.5 s with 0.54 s hot pulse time and 19 °C modulator temperature offset relative to the primary oven temperature. Liquid $N_2$ (Nippon gases Norge AS, Oslo, Norway) was used as coolant for the GC×GC modulator. The ion source and the transfer line temperatures were set to 200 °C and 300 °C, respectively and the MS was operated in electron ionisation (EI) mode with an electron energy of 70 eV. A data acquisition rate of 100 spectra s$^{-1}$ was used in combination with an acquired mass range

of *m/z* (mass to charge ratio) 45 – 1000. Autotuning was performed by using the *m/z* 219 perfluorotributylamine (PFTBA) ion instead of the default *m/z* 69 ion. In order to avoid system contamination and memory effects, clean solvent (Toluene followed by Acetonitrile) was injected after each sample run.

**Data alignment for suspect lists, which MS are to find in NIST 14/customised self-build libraries and how to highlight findings of suspects in peak lists**

This study applied pre-defined suspect lists with components relevant as potential Arctic atmospheric contaminants (Reppas-Chrysovitsinos et al., 2017; Brown and Wania, 2008; Coscollà et al., 2011; Hoferkamp et al., 2010; Howard and Muir, 2010; NORMAN-network, 2019).

In order to account for different CAS numbers and/or different names of compounds in the used suspect lists and available MS libraries, compound names from the suspect lists were transformed to CAS numbers and compared to the original CAS number in the suspect list. In case the transformed CAS number derived for the respective original CAS number stated in the chosen publications, a manual search was performed in SciFinder to identify the correct CAS number for a compound. After all compounds were assigned with corrected CAS numbers, SMILES stings were created of each compound, using JChem for Excel (ChemAxon, 2019).

Conditional formatting in Excel was used to create a merged suspect list, including the information from which list a suspect is originating (e.g. AMAP list or NORMAN list etc.).

To identify which of those suspects might be listed in the used MS libraries, all entries of the used MS libraries were exported to Excel (Name, CAS and molecular formula).

With conditional formatting in Excel, all suspects, of which a MS is available in the used MS libraries, were highlighted and copied to a separate column.

The mass spectra of these suspects were manually copied from the used MS libraries to a separate, customised self-build library.

This customised MS library, containing the selected mass spectra, was used beside other self-build MS libraries for suspect screening. During suspect screening, the first library search was only performed with self-build libraries. Here all peak markers in ChromaTOF were highlighted as suspects before further data processing and classification. The final peak list, L0–L2 compounds, was cross checked with the initial suspect list and the origin list of a suspect was included.

**Table S7: Summary of PBT criteria.**

| | REACH (European Parliament, 2018) | Stockholm convention (UNEP, 2009) |
|---|---|---|
| **Persistent (P)** | $t_{1/2}$water fresh/marine ≥ 960/1440 h (40/60 days)<br>(vP[1] ≥ 1440 h (60 days))<br>$t_{1/2}$soil ≥ 2880 h (120 days)<br>(vP[1] ≥ 4320 h (180 days))<br>$t_{1/2}$sediment fresh/marine ≥ 2880/4320 h (120/180 days)<br>(vP[1] ≥ 4320 h (180 days)) | $t_{1/2}$water ≥ 2 months (1440 h)<br>$t_{1/2}$soil ≥ 6 months (2880 h)<br>$t_{1/2}$sediment ≥6 months (2880 h) |
| **Bioaccumulative (B)** | BCF[2] ≥ 2000 (vB[3] ≥ 5000) | BCF[2] ≥ 5000 |
| **Toxic (T)** | NOEL or EC10 ≤ 0.01 mg/L<br>Or Carcinogen 1A, 1B or 2<br>Or mutagenic 1A or 1B<br>Or reproduction toxic 1A, 1B or 2<br>Or evidence for chron. Tox. STORE cat. 1 or 2 | Evidence of adverse effects to human health, or toxicity or ecotox. indicate potential damage to human health or the environment |
| **Long-range transport potential (LRTP)** | -[4] | Measured levels in distant of source of relevance<br>Or monitoring data showing LRT with potential to transfer to a receiving environment<br>Or environment fate properties/model results that show LRTP: $t_{1/2}$air ≥ 2 days |

[1] vP: very persistent; [2] BCF: Bioconcentration factor; [3] vB: very bioaccumulative; [4] not applicable

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# Paper II

Non-target and suspect characterisation of organic contaminants in Arctic air, Part II: Application of a new tool for identification and prioritisation of chemicals of emerging Arctic concern in air.

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# Non-target and suspect characterisation of organic contaminants in Arctic air, Part II: Application of a new tool for identification and prioritisation of chemicals of emerging Arctic concern in air

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**Abstract.** The Norwegian Arctic possess a unique environment for the detection of new potential chemicals of emerging Arctic concern (CEACs) due to remoteness, sparsely populated and the low number of local contamination sources. Hence, a contaminant present in Arctic air is still considered a priority indication for its environmental stability and environmental mobility. Today, legacy persistent organic pollutants (POPs) and related conventional environmental pollutants are already well-studied since their identification as Arctic pollutants in the 1980s. Many of them are implemented and reported in various national and international monitoring activities including the Arctic Monitoring and Assessment Program (AMAP). These standard monitoring schemes, however, are based on compound specific quantitative analytical methods. Under such conditions, the possibility for identification of hitherto unidentified contaminants is limited and randomly, at the best. Today, new and advanced technological developments allow a broader, unspecific analytical approach as either targeted multi-component analysis or suspect and non-target screening strategies. In order to facilitate such a wide range of compounds, a wide-scope sample clean-up method for high-volume air samples, based on a combination of adsorbents was applied, followed by comprehensive two-dimensional gas chromatography separation and low-resolution time-of-flight mass spectrometric detection (GC×GC-LRMS). During the here reported study, simultaneous non-target and suspect screening were applied. The detection of over 700 compounds of interest in the particle phase and over 1200 compounds in the gaseous phase is reported. Of those, 62 compounds were confirmed with reference standards and 90 compounds with a probable structure (based upon mass spectrometric interpretation and library spectrum comparison). These included compounds already detected in Arctic matrices and compounds not detected previously (see also Figure 1). In addition, 241 compounds were assigned tentative structure or compound class. Hitherto unknown halogenated compounds, which are not listed in the used mass spectral libraries, were also detected and partly identified.

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## 1 Introduction

A high number of organic chemicals is used today in large quantities. By 2019, the Chemical Abstracts Service (CAS) registry[SM], contained more than 156 million unique inorganic and organic chemicals. This is 50% more than in 2015, when CAS was celebrating 100 million registered compounds (Wang, 2015). For the effective regional control of chemicals in commerce, the REACH register was introduced in the EU-region (Regulation (EC) No 1907/ 2006 of the European Parliament and of the Council concerning the registration, evaluation, authorisation and restriction of chemicals) managed by the European Chemicals Agency (European Parliament, 2018). REACH has only classified about 2000 substances (about 40 % of chemicals registered with a production volume above 100 tonnes per year) into classes of high concern. Such chemicals were identified as carcinogenic, mutagenic, toxic for reproduction (CMRs), persistent, bioaccumulative and toxic (PBT), very persistent and very bioaccumulative (vPvB) and/ or endocrine disruptors (EDCs) (data status May 2018, (ECHA, 2019b)). The assessment of chemicals with lower production volumes will follow. A considerable amount of organic chemicals is released into the environment by various pathways including insufficient waste management, direct application (e.g. agriculture, structure treatment), unintended by-products from largescale production lines and primary emission/ releases from products and applications. Some of these organic chemicals are persistent and can migrate over long distances, ultimately reaching remote areas, such as the Arctic (Lebedev et al., 2018; Macdonald et al., 2000; Macdonald et al., 2005; Genualdi et al., 2011; Barrie et al., 1992). An important pathway for long-range transport of persistent organic chemicals is via the atmosphere (Xiao et al., 2012; Genualdi et al., 2011; Hung et al., 2010; MacLeod et al., 2005; Koziol and Pudykiewicz, 2001; Barrie et al., 1992). Environmental persistence and long-range atmospheric transport potential (LRATP) (Zhang et al., 2010; Czub et al., 2008) are two hazard criteria which characterise persistent organic pollutants (POPs). POPs are today considered as priority pollutants and their use and production is regulated through international agreements, such as the Stockholm Convention on POPs and the Aarhus protocol on POPs under the Convention on Long-range Transboundary Air pollution (CLRTAP) (UNEP, 2009b; UNECE, 1998). In order to evaluate the effectiveness of these agreements aiming at reducing human and environmental exposure to POPs (Fiedler et al., 2019), air monitoring strategies for legacy POPs have been established on national, regional and global levels. Examples are the European Monitoring and Evaluation Programme (EMEP, 2019) for the Aarhus protocol on POPs (UNECE, 1998), the Global Monitoring Plan (GMP) for the Stockholm Convention (UNEP, 2009a) and the Arctic Monitoring and Assessment Programme AMAP (2019) for the Arctic. Within these, air monitoring of POPs in remote areas including the Polar Regions are used to study the long-range atmospheric transport of POPs to remote areas and such knowledge is considered vital for the understanding of the environmental behaviour of POPs and further international POP regulation. Recently, chemicals of emerging Arctic concern (CEACs) (AMAP, 2017) including new flame retardants, plasticizers, per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), current use pesticides (CUPs) and more, have received increased attention within AMAP. Selected CEACs have already been included in some of the national and regional air monitoring programmes in the Arctic (AMAP, 2009, 2017). Measurements of CEACs in the Arctic provide authorities with crucial knowledge supporting adequate policy measures and, if necessary, national or

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international regulations to come into place. In addition, it is important to identify new CEACs in the Arctic at an early stage. While this is often accomplished using biotic matrices there is also a need for measurements in abiotic matrices like air as not all CEACs bioaccumulate but still are persistent and transported over long distances. Non-target and suspect screening (NTS and SUS) approaches represent promising strategies for identification of so far unidentified CEACs. However, standard sampling and analytical methods used for targeted monitoring of POPs in air are not necessarily suitable for non-target analyses and methodological challenges remain to be solved. For example, some CEACs may have similar properties to legacy POPs while others might be less stable under certain conditions, such as being acid labile (e.g. some flame retardants, cyclic methyl siloxanes as well as some legacy POPs like dieldrin and related compounds) (Röhler et al., 2020). It is, therefore, important to develop non-destructive sample clean-up procedures, e.g. without sulfuric acid, to preserve an expanded range of compounds for SUS/ NTS strategies in atmospheric samples. As a natural consequence of a wide-scope sample clean-up method, the resulting analytical extracts contain a larger load of interfering background matrix. It is therefore essential to increase the separation power of the instrumental analysis. This could be achieved by high-resolution chromatographic separation and/ or high-resolution mass separation, i.e. high-resolution mass spectrometry (HRMS) methods.

In this study, a new, non-destructive wide-scope sample clean-up procedure and a powerful instrumental analysis method was applied on high-volume air samples, from an Arctic background monitoring station, aiming at identifying regulated POPs, known CEACs and emerging or new CEACs. The final separation and detection method was comprehensive two-dimensional gas-chromatography (GC×GC), which offers enhanced peak capacity as compared to conventional GC and a better separation of matrix residues from analytes, and low resolution time-of-flight mass spectrometry (LRMS) (Röhler et al., 2020). New potential CEACs were evaluated by comparing them to the PBT classification of the Stockholm Convention (UNEP, 2009b) with a focus on long-range atmospheric transport potential (LRATP).

## 2. Experimental Section

### 2.1 Air sampling and sample clean-up

Two air samples were collected at the Zeppelin Observatory, on Svalbard (78° 55' N, 11° 53' E, 474 m a.s.l.) in December 2015. Zeppelin is a Norwegian background station providing environmental monitoring data including organic environmental pollutants to many national authorities and international monitoring programmes; EMEP, AMAP and GMP. The particle phase of the air samples was collected on glass fibre filters (GFFs; 142 mm i.d.; cut-off 10 µm) and the gas phase were collected on polyurethane foam (PUF) plugs (11 cm in diameter, 5 cm in height) using high volume air samplers (average 25 $m^3$ $h^{-1}$). The sampling time was 4-5 days resulting in sample volumes of 2700 m³ and 3500 m³. Details on the sampling methodology can be found in Kallenborn et al. (2013).

Before extraction, the PUFs from the two air samples were combined in one Soxhlet extractor and spiked with internal standards (ISTDs, details in Table S1, SI). The same was done for GFFs from the two air samples. PUFs and GFFs were Soxhlet extracted separately for 8 h in acetone/ *n*-hexane (1:1 v/v). This resulted in one pooled PUF extract and one pooled

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GFF extract. The individual extracts were reduced to 0.5 mL with a Zymark TurboVap and solvent exchanged to isooctane. For clean-up, three-layer liquid chromatography columns were used, with the bottom layer consisting of a mixture of Z-Sep$^+$ & DSC-18, the middle layer of Florisil, and the top layer of sodium sulphate. Samples were applied in isooctane and eluted with acetonitrile (ACN)/ 0.5 % citric acid (w/w). Detail about the sample clean-up can be found in the and in the Supplementary Information (SI) and Röhler et al. (in preparation, (2020)).

### 2.2 GC×GC-LRMS Analysis

The samples were analysed using a LECO Pegasus® 4D, St. Joseph, MI, USA) GC×GC-LRMS system, operating in EI mode. The GC was equipped with a Restek (Bellefonte, PA, USA) Siltek Guard column (4 m, 0.25mm), a SGE (Trajan Scientific and Medical, Ringwood, VIC, Australia) BPX-50 (25 m, 0.25 mm, 0.25 µm) first dimension column and an Agilent J&W (Folsom, CA, USA) VF-1ms (1.5 m, 0.15 mm, 0.15 µm) second dimension column. Helium (5.0 quality, Nippon gases Norge AS, Oslo, Norway) was used as carrier gas with a constant flow of 1 mL min$^{-1}$. Three microliter (µL) of each extract was injected into a PTV (programmed temperature vaporiser) inlet, operating in solvent vent mode. For identification of unknown halogenated compounds (see sect. 3.7), the samples were also analysed using a LECO GC-HRT GC×GC-HRMS instrument, operating under the same conditions described above for the GC×GC-LRMS analyses. Details on chromatographic conditions can be found in the SI.

### 2.3 Quality control

Laboratory blanks, consisting of unexposed PUFs and GFFs, were extracted, cleaned and analysed along the same sample preparation scheme as the exposed samples. The blanks were used for quality assurance, to ensure that identified/ reported compounds have their origin in the collected air sample and do not appear in the blank samples above predefined levels (see sect. 2.4). This means that compounds need to exceed the area threshold of a factor 100 compared to the area in the sample blanks.

The used ISTDs, which are covering a wide area of the GC×GC chromatogram, were not used for target quantification, but for quality assurance and sample normalization. For example, the early eluting ISTDs (e.g. $^{13}C_6$-labelled hexachlorobenzene (HCB) or $^{2}H_{10}$-labelled phenanthrene) help to identify potential evaporative losses during clean-up and volume reduction, and the $^{13}C_{12}$-labelled *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT) ISTD provides information about possible matrix-effects in the injector and/ or GC-column due to its higher thermal degradation potential. Thus the *p,p'*-dichlorodiphenyldichloroethylene/ *p,p'*-dichlorodiphenyldichloroethane (*p,p'*-DDE/ *p,p'*-DDD) ratio was used for identification of injector losses. A comprehensive recovery test was done by Röhler et al. (2020) to investigate the applicability of this wide-scope sample clean-up method.

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**2.4 Data processing/ Post-acquisition data treatment**

For GC×GC-LRMS system control, data analysis and processing, LECOs® ChromaTOF® software (V 4.50.8) was used; including its advanced features, Statistical Compare and Scripts. Several in-house libraries with mass spectra of reference standards, $^{13}C$/ $^{2}H$-labelled ISTDs, National Institute of Standards and Technology (NIST) NIST 2014 mass spectral library, Scientific Working Group for the Analysis of Seized Drugs (SWGdrug (Oulton, 2019)) mass spectral library, and a customised library with selected spectra from NIST 2014 for suspect screening were used for tentative identification of detected compounds. To create the customised library with selected spectra from NIST14, all mass spectra of compounds from NIST 14, which are listed on relevant suspect lists for the Arctic (Reppas-Chrysovitsinos et al., 2017; Brown and Wania, 2008; Coscollà et al., 2011; Hoferkamp et al., 2010; Howard and Muir, 2010; NORMAN-network, 2019; Vorkamp and Rigét, 2014; Zhong et al., 2012), were copied to an own library file for more efficient suspect screening. This customised library was useful to detect and flag potential suspects during data processing. More details can be found in (Röhler et al., 2020) and a short description on how the data from suspect lists got aligned with our peak table as well as how the suspect MS libraries were built can be found in the SI.

The identification level classification concept of Schymanski et al. (2015), originally developed for liquid chromatography (LC)-HRMS data, is defining a common set of rules for harmonised communication of identification confidences of results from different SUS/ NTS studies. Due to the lack of HRMS data in the current study, this level classification concept had to be slightly to account for the limitations of LRMS data (Figure 2), c.f. Röhler et al. (2020). As LRMS analysis does not provide accurate masses, the lowest level of identification confidence, Level 5 (L5), is defined as peaks of interest, which are only characterized by retention time and a mass spectrum, and not by tentative molecular weights. The remaining levels for identification confidence with LRMS are in line with the original concept of Schymanski et al.: Level 4 (L4), defined by a possible molecular formula, e.g. a plausible molecular formula could be assigned to various compound classes, or halogen cluster detected without match to the used MS libraries. Level 3 (L3), the group of tentative candidates, which are identified as substructure/ class or a certain base structure is possible, e.g. the MS shows fragment patterns of a polycyclic aromatic hydrocarbon (PAH) with a plausible molecular formula but several alternative structures are possible. Level 2 (L2), the group of probable structures based on good library matches and additional evidence, e.g. the position or grouping on the two-dimensional GC×GC plan. Level 1 (L1) is defined by compounds confirmed by external reference standards. We introduced an additional Level 0 (L0) for compounds confirmed by ISTDs and where target quantification could be performed together with SUS and NTS. Target quantification was however not a primary aim of this study.

During SUS and NTS data processing (Figure 3), the forward match percentage to the mass spectrum (MS) library entry was used to reduce the number of peaks which require manual inspection. This is a critical step where potential compounds of interest may be lost, since the MS from the NIST14 library are not identical with the MS obtained with the GC×GC-LRMS, probably due to the unit mass resolution of the instrument, generating mass artefacts as shown in Figure 4. Compounds with higher mass defects, e.g. the brominated compounds, had non-acceptable spectra match quality (Figure 4). It is possible that

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some compounds of interest were rejected during data processing due to bad match of MS to NIST14 MS library or custom suspect libraries. To minimise such losses of compounds with higher mass defects, visual basic scripts, developed by Hilton et al.(2010), were applied for data processing. These scripts were specifically written for isotope clusters obtained from the used instrument. All compounds flagged by those scripts were checked manually. Furthermore, it was not possible to use available retention indices for further identification confidence due to the use of a medium polar GC column (BPX-50, 50 % phenyl polysilphenylene-siloxane) as first column for GC×GC separation instead of a non-polar (5 % phenyl) column, for which most of the retention indices are present in databases. In addition, there are limited concepts for the adaption of retention indices for GC×GC, e.g. (Veenaas and Haglund, 2018). This BPX-50 column, as first column for GC×GC separation, was chosen to get a better separation from compounds of interest to interfering background matrix and thus minimise negative effects on collected mass spectra.

When a compound was flagged in the result list (L1–L5 lists, Figure 3) for manually check after data processing, additional plausibility checks will be performed. These included the selectivity of the sampling and sample clean-up method as well as the complete sample analysis procedure. For instance, a compound should not degrade during sample processing (from sampling to analysis), not evaporate or sorb to the vial, injector or chromatographic column. The GC×GC retention times should also be reasonable, e.g. volatile compounds cannot elute at the end of the run and non-polar compounds cannot have a short second dimension retention time. Furthermore, the area of a candidate in a sample should exceed the area threshold of factor ≥ 100 in the corresponding sample blank to be kept in the peak table and not to be sorted out as compound occurring from the blank sample. The higher threshold is necessary since areas are not adjusted for different sample volumes.

### 2.5 Evaluation of long-range atmospheric transport potential

The detection of a substance in air at Zeppelin does not provide conclusive evidence for long-range atmospheric transport. Yet, an organic chemicals potential for LRAT into the Arctic requires that it is sufficiently persistent in air. LRATP can be estimated from theoretical calculations. The key mechanism which is believed to degrade organic chemicals in the atmosphere is reaction with OH-radicals. Because both concentrations of OH-radicals and temperatures are very low during the polar night, the atmospheric half-life due to atmospheric reaction ($t_{1/2}$) is predicted to be very long in comparison to lower latitudes (e.g. Webster et al. (1998)). For a more realistic evaluation of LRATP, reaction half-lives in air therefore need to be adjusted reflecting the actual sampling conditions. Half-lives were adjusted using an equation from Wania et al (2006) and we refer to the SI for details. To parameterise this equation, the reaction rate in air at 25 °C were retrieved for L0, L1 and L2 compounds from the EPIsuite software (U.S.EPA, 2019) and adjusted using the maximum temperature during sampling (-2.4 °C), an assumed OH-radical concentration of 6E3 mol $cm^{-3}$ and an assumed activation energy for reaction in air of 10000 J $mol^{-1}$. Estimates of OH radical concentration was based on a model developed by Bahm and Khalil (2004). However, this model does not predict OH-radicals at higher latitudes than 45° N, which crosses central Europe ([OH] at 45° N: 5E4 mol $cm^{-3}$), in December. Our samples were collected at 78° N, and our assumed OH-radical concentration of 6E3 mol $cm^{-3}$ was chosen as an initial conservative estimate, keeping in mind that our analysed air samples include air mases which may have been

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transported from lower latitudes. Results from these theoretical calculations are discussed in sect. 3.5.3 and shown in the SI (Table S3 and Excel-SI).

## 3. Results and Discussion

### 3.1 Number of detected and classified compounds in Arctic air

By applying the wide-scope clean-up based on C18 silica and Z-Sep$^+$ combined with Florisil to the air sample extracts from PUFs and GFFs, we were able to expand the chemical domain covered as compared to established target POP analysis methods, which generally are using concentrated sulfuric acid. Our method covers a broad spectrum of polarity, has sufficient matrix removal and is, for the first time, applied on Arctic air samples for the detection and identification of known and new potential CEACs. Previously, this method has been successfully applied to air samples from southern Norway (Röhler et al., 2020).

It was possible to detect and classify over 700 compounds in the particle phase (GFF samples) and over 1200 compounds in gas-phase (PUF samples) as L5 with our classification and sorting method (details on the peak reduction during data-processing for SUS and NTS, Fig. S1 in SI). The higher number of gas phase compounds was expected since particle related compounds, collected on GFFs, may have a lower LRATP compared to gas-phase related compounds, collected on PUFs. Of these L5 compounds, approximately 200 compounds in GFFs and approximately 400 compounds in PUFs could be further classified to L4, L3 or L2 (Figure 5). As the structures of the remaining L5 compounds remain unknown, these compounds are not discussed any further. In total, 65 compounds (14/51 GFF/PUF) were classified as L4. Many compounds of the L4 class could be identified as unknown halogenated compounds as a halogen pattern was observed, but no match in MS libraries were found (12/29 GFF/PUF). For the remaining L4 compounds, only a possible molecular formula could be assigned. As L3, 241 compounds (95/146 GFF/PUF) could be classified, including two major sub-groups, polycyclic aromatic compounds (PAC) and phthalates (see Figure 6). The PAC sub-group include many PAHs. Ninety compounds reached L2 (20/70 GFF/PUF) and 41 of the compounds in PUF were PCBs with 2-7 chlorine substituents. By analysing reference standards under identical conditions as the air samples, 56 compounds could be classified as L1 (14/42 GFF/PUF) (Table 1). Furthermore, six compounds could be identified and confirmed with ISTDs to L0 in the PUF sample (only traces in the GFF sample). Of the 56 confirmed L1 compounds, seven were common to GFF and PUF sample. Importantly, a compound not positively confirmed by this method does not necessarily mean that it does not occur in Arctic air.

As shown in Table 1, 39 of 56 compounds that were classified as L1 are listed in one or more suspect lists (Reppas-Chrysovitsinos et al., 2017; Brown and Wania, 2008; Coscollà et al., 2011; Hoferkamp et al., 2010; Howard and Muir, 2010; NORMAN-network, 2019; Vorkamp and Rigét, 2014; Zhong et al., 2012) or self-built suspect libraries. From L2 compounds, 17 compounds resemble compounds in one or more suspect lists. Since L2 compounds are not confirmed with reference standards, those compounds might be different isomers than those listed in the SI (Excel-SI) file and thus matches to suspect lists could be different for L2 compounds.

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For a better understanding about the importance of our findings at L0, L1 and L2, these compounds were further arranged into four groups: (i) legacy POPs and PAHs, (ii) CEACs defined in the AMAP report (2017), (iii) organic compounds that previously have been detected in Arctic media, and (iv) new potential CEACs not reported in Arctic media to date (October 2019). The new potential CEAC group was split into two subgroups, those with an estimated LRATP and those without. The default LRATP estimates are based on the EPIsuite software (U.S.EPA, 2019), reflecting standardised environmental conditions ($t_{1/2}$(air) at 25 °C, 12 h days and a hydroxyl radical concentration of 1,6E6 OH $cm^{-3}$) and results compared with the criteria in the Stockholm Convention (UNEP, 2009b) that substances with a $t_{1/2}$(air) exceeding 2 days has a LRATP. A complete table with all compounds identified, including physical-chemical properties from EPIsuite, adjusted half-life in air during sampling (Eq.S1 and Eq. S2, SI), usage and information on previous reports on occurrence in Arctic environments, toxicity and presence in HPV lists of the EU and US as well as further parameters for PBT classification (REACH and Stockholm conventions) can be found in the SI (Table S2 and Excel-SI).

### 3.2 Legacy POPs and PAHs

The currently used method revealed 59 legacy POPs and PAHs as L0, L1 and L2, specifically hexachlorocyclohexanes (α-HCH and γ-HCH), HCB, pentachlorobenzene (PeCB), DDTs (*o,p'*-DDT, *p,p'*-DDT and *p,p'*-DDD), PCB-153, dieldrin, *trans*-nonachlor, *cis*-chlordane, PBDE-28 and PBDE-47 and a metabolite of heptachlor (heptachloro *exo* epoxide) (UNEP, 2009b) as L0 or L1. Furthermore, two PAHs, benzo[*ghi]*fluoranthene (L1) and naphthalene (L2) could be identified. Other PAHs were classified as L3 (PAC). Dieldrin and benzo[*ghi]*fluoranthene were common to GFF and PUF and had GFF:PUF ratio according to Peak area of 1:8 for dieldrin and 2:1 for benzo[*ghi]*fluoranthene. It was also possible to classify 41 PCB congeners as L2. The finding of legacy POPs and PAHs, routinely measured at the same monitoring station using target methods, is an indirect validation of the method and indicates that detection of other compounds with similar physical-chemical properties are trustworthy. From the assumption that a higher concentration of a compound gives a greater peak area, the detected legacy POPs could be correlated with a good match to the average concentrations of monitored legacy POPs at the Zeppelin station (Table 2) (Nizzetto, 2016). Pearson correlation analysis indicates a strong correlation ($r = 0.978$) that is significant different from zero ($p < 0.001$). Thus, the screening approach seems to give an indication of the relative concentrations (occurrence) for semi-volatile organic compounds in Arctic air.

### 3.3 CEACs as defined by AMAP

Eleven of the detected compounds are included as CEACs in the AMAP report (2017) or in Reppas-Chrysovitsinos et al. (2017). One was classified as L0, five were classified as L1 and five were classified as L2. The CEAC, classified as L0 was the flame retardant hexabromobenzene (HBB) that also have been detected in air at Zeppelin Observatory by target analyses as a part of the Norwegian national air monitoring programme for long-range atmospheric transported contaminants. Classified as L1 were two halogenated natural products (HNPs), 2,4,6-tribromoanisole (TBA) and 2,4-dibromoanisole (2,4-DBA), the pesticide metabolite pentachloroanisole (PCA), the organophosphorus flame retardants (OPFRs) tri(2-chloroethyl) phosphate

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(TCEP) and the stimulant caffeine. The five L2 compounds were the BFR pentabromotoluene (PeBT), on isomer of TCEP, two isomers of tris(2-chloroisopropyl) phosphate (TCPP), and an isomer of dibromoanisole (DBA), likely the HNP 2,6-DBA. TBA is routinely measured in air at the Zeppelin observatory as a part of the Norwegian monitoring programme. TBA has also been reported earlier in Arctic air from the Zeppelin station by Vetter et al. (2002). Bidleman et al. detected 2,4-DBA and TBA at Pallas, Finland (Bidleman et al., 2017a) as well several locations at the Bothnian Bay region (Bidleman et al., 2017b). PCA is a pesticide metabolite, originating from biodegradation of the pentachlorophenol, which is a pesticide and wood preservative (GovCanada, 2019; Su et al., 2008). PCA has previously been found in air at other AMAP sampling sites, like Alert, Canada, but not at Zeppelin, Svalbard (Su et al., 2008; Hung et al., 2010). The stimulant and food additive caffeine, also an intermediate for pharmaceuticals as well as perfumes, fragrances, personal care products and laboratory chemicals (ECHA, 2019h), was found in effluent and seawater from Longyearbyen (Kallenborn et al., 2018) but to our knowledge not in air samples. TCPP (ECHA, 2019i; Sühring et al., 2016) is one of the main substances which have replaced TCEP in Europe (UK, 2008). TCPP and TCEP were detected in our GFF sample (i.e. particle phase), together with structurally related isomers. OPFRs have previously been detected in Arctic air from the Zeppelin Observatory (Nizzetto, 2018; Salamova et al., 2014).

### 3.4 Organic compounds, previously detected in Arctic media

Besides legacy POPs and PAHs, and CEACs listed by AMAP, it was also possible to identify eight other organic compounds as L1 and classify one compound as L2. These nine compounds have previously been reported in Arctic samples. As L1 we found tetrachloroveratrole, octachlorostyrene (OCS), 1,2,3,4-tetrachlorobenzene, 1,9-benz-10-anthrone, 9-fluorenone, 9,10-anthraquinone and 4H-cyclopenta[*def*]phenanthren-4-one. Only one isomer of tetrachloroveratrole was classified as L2. Tetrachloroveratrole, and its isomer, are both pesticide metabolites (Su et al., 2008; GovCanada, 2019), while the others were either combustion products or oxidation products of PAHs (Kirchner et al., 2016; Su et al., 2008; Hung et al., 2010; Gubala et al., 1995; Singh et al., 2017; Karavalakis et al., 2010). 4H-Cyclopenta[*def*]phenanthren-4-one was common to GFF and PUF with a GFF:PUF ratio from peak areas of 1:2. Tetrachloroveratrole and OCS have been reported from other Arctic monitoring sites like Alert, Canada, but are not included in the Norwegian monitoring programme at the Zeppelin Observatory on Svalbard (Hung et al., 2016). OCS has also been detected in air samples from the Alps (Kirchner et al., 2016), 1,2,3.4-Tetrachlorobenzene has been measured in sediments in Arctic Alaska (Gubala et al., 1995), but to our knowledge not in Arctic air before. 1,9-benz-10-anthrone, 9-fluorenone, 9,10-anthraquinone and 4H-cyclopenta[def]phenanthren-4-one have been reported in aerosols, total suspended particles, from the Alert station, Canada (Singh et al., 2017). Besides that, they were detected, among further oxy-/nitro-/ PAHs, in the emissions from a local point source in Longyearbyen, Svalbard (coal fired power plant) (Drotikova et al., 2020). Most of the known Arctic contaminants were classified as L1 as a result of available standards. Please note, most of PAHs are classified as L3 compounds due to the lack of single reference standards. We assume that several of the known PAHs, previously detected in Arctic media, could be found among the PAHs, classified as PAC in L3 (see section 3.6.).

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### 3.5 New potential chemicals of emerging arctic concern

It was possible to classify 73 new potential CEACs with a match to reference standards (L1) or probable structures (L2). These 73 compounds have, to our knowledge, previously never been reported in Arctic media. The complete list can be found in SI (Excel-SI). Almost 40 % of these new potential CEACs have a LRATP according to the Stockholm convention (UNEP, 2009b), $t_{1/2}$(air) exceeding 2 days, using the standard values from EPI suite calculation (see section 3.1.) Although those compounds were not reported in Arctic environment before, local sources cannot be excluded for some of the identified compounds. Especially compounds which might be of biogenic origin, i.e. methoxy-chloro compounds, or compounds with a widespread use, the potential for local sources need to be kept in mind. This study, however, is not designed to prove the potential influence of local sources on the overall contaminant patterns. Especially for compounds that could be HNPs, but for which we could not find any evidence that they have been detected in the Arctic before, further in-depth studies are required.

#### 3.5.1 Potential CEACs with LRATP

Out of the total of 73 identified or tentatively identified new potential CEACs, 29 were classified as compounds with LRATP according to the Stockholm convention criteria (UNEP, 2009b), $t_{1/2}$(air) exceeding 2 days, using the standard values from EPI suite calculation. Of these, six compounds were detected in the GFF sample (two as L1 and four as L2) and 23 compounds were detected in the PUF sample (13 as L1 and 10 as L2), see Table 3 and Table 4. Further information about these compounds can also be found in SI (Excel-SI). As the identities of L2 compounds was not fully confirmed, no literature search was performed for previous reports on occurrence in Arctic environments.

In the GFF sample, one of the two L1 compounds was benzenesulfonamide (BSA), an industrial intermediate used for the synthesis of chemicals in commerce like pesticides, photochemical products, pharmaceuticals, sweeteners or dyes (ECHA, 2019g; Naccarato et al., 2014; Herrero et al., 2014). Since BSA occurs in many products, local sources cannot be excluded and further investigations are needed to confirm a potential LRATP or local sources as major contamination source of BSA in the here investigated sample. The other L1 compound identified in the GFF is a potential combustion product, 2-methyl-9,10-anthraquinone, which can have its origin in wood combustion (Czech et al., 2018; Lui et al., 2017; Vicente et al., 2016) or can be formed by atmospheric reactions (Alam et al., 2014). 2-Methyl-9,10-anthraquinone is also an intermediate in the production of coating products, inks and toners, laboratory chemicals and explosives, or is also used for the production of plastic products (ECHA, 2019c). Beside those L1 compounds it was possible to detect one 3,4-dichloropropiophenone related compound, likely a positional isomer, three sulphur related compounds, diphenyl sulfone, dibenzothiophene sulfone and N-(2-cyanoethyl)-N-methyl-benzenesulfonamide and classified these as L2 by MS library matching.

In the PUF sample, the pesticide dichlobenil (2,6-dichlorobenzonitril) was identified, together with an isomer, 2,4-dichlorobenzonitrile (ECHA, 2019d), as L1. No information of commercial application and usage is found for 2,4-dichlorobenzonitrile. Besides dichlobenil, another pesticide, chloroneb (1,4-dichloro-2,5-dimethoxybenzene) (U.S.EPA, 2005) was identified as L1, and two chloroneb and one chlorothalonil related compounds, likely positional isomers of those, was

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assigned L2. The nitrification inhibitor, nitrapyrine (2-chloro-6-(trichloromethyl)pyridine), L1, were identified in Arctic samples for the very first time (DOW, 2012; ECHA, 2019e; Woodward et al., 2019). Furthermore, two trichloro-dimethoxybenzenes, two dichloro-methylanisols, and one dibromo-dimethoxybenzene were also assigned L2.

Biogenic origin cannot be excluded for those halogenated methoxybenzenes. Local sources also cannot be excluded for the closely related 2,4-dichloroanisole and , 2,4,6-trichloroanisole (both L1), potential metabolites of chlorophenol and chlorophenoxy pesticides, but also potential HNPs (Führer and Ballschmiter, 1998; Schenker et al., 2007; Bendig et al., 2013). 2-Naphthalenecarbonitrile, originating most probably from plastic combustion, e.g. ABS (acrylonitrile butadiene styrene) plastic or polyester fabrics (Moltó et al., 2009; Watanabe et al., 2007; Wang et al., 2007; Moltó et al., 2006) or bluing of steel (Stefanye, 1972), was identified as L1, and 1-naphthalenecarbonitrile as L2. A further group of compounds, confirmed with reference standards as L1, are intermediates, with various application areas. 2,3,5,6-Tetrachloropyridine and pentachloropyridine are intermediates occurring in the synthesis of the pesticides chlorpyrifos and triclopyr (Howard and Muir, 2010). Terephthalonitrile is identified as intermediate for the production of the pesticide dacthal (Meng, 2012). 2',3',4'-Trichloroacetophenone is an intermediate for the production of various fungicides and pharmaceuticals (WOC, 2019). Not much is known about the use of 2,4,6-tribromoaniline, but it might be used in the synthesis of pharmaceuticals, agricultural pesticides and fire-extinguish agents (Labmonk, 2019). 2-Nitroanisole can have its origin in combustion processes or can be formed by atmospheric reactions (Stiborova, 2002). In 1993, large quantities of 2-nitroanisole were emitted into air during an accident at the Hoechst plant in Germany (Weyer et al., 2014). A pentachloro-methylbenzene related compound, likely a positional isomer, were detected and assigned L2, but industrial uses are not known.

### 3.5.2 Potential CEACs without LRATP

Besides those new potential CEACs with LRATP described in the previous section, we could also identify 44 new potential CEACs which do not have a predicted LRATP, according to the Stockholm Convention criteria (UNEP, 2009b), reflecting default standardised environmental conditions. Of these 44 new potential CEACs, 19 compounds were detected in the GFF sample (six as L1 and 13 as L2) and 25 compounds were detected in the PUF sample (11 as L1 and 14 as L2). An overview of L1 compounds without a predicted LRATP reflecting default environmental conditions can be found in Table 5. None of the new L1 potential CEACs have to our knowledge been detected previously in Arctic samples, only triallate was found once before in passive air samples from Arviat, Nunavut, Canada (western shore of Hudson Bay, 61° N) (Messing et al., 2014), which is outside the Arctic circle. Triallate is an agriculture pesticide and was detected in both GFF and PUF in our sample. Four of the six L1 compounds detected in the GFF sample was also found in the PUF sample, at various GFF/PUF peak area ratios: m-Terphenyl 1:30 (GFF:PUF ratio), Triallate 1:17 (GFF:PUF ratio), Dichlofluanid 1:3 (GFF:PUF ratio) and Carbazole 1:1 (GFF:PUF ratio). The two remaining compounds, identified as L1 in the GFF sample, were 1,2-benzoanthraquinone and 6H-benzo[cd]pyren-6-one. Both are potential combustion products and can have their origin in wood or coal combustion (Czech et al., 2018; Lui et al., 2017; Vicente et al., 2016) or can be formed by atmospheric reactions (Alam et al., 2014). As

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L2, we could, besides others, classify several positional isomers of reference standards which were analysed (see SI Excel-SI file for further details).

In the PUF it was possible to identify all three isomers of terphenyl (*o*, *m*, *p*) usually applied as technical mixture, while only *m*-terphenyl was detected also in the GFF. The commercial mixture of terphenyls is used as industrial agent for heat storage and transfer as well as textile dye carriers and as intermediate of non-spreading lubricants (Netherlands, 2002). During pyrolysis and combustion of used black shorts (polyether fabric), all three terphenyl isomers were detected (Moltó et al., 2006). 4-Chloro-2-methylphenole (PCOC) is used by the industry as an intermediate for the production of phenoxy herbicides and is found as impurity in the final commercial product (B.G. Hansen et al., 2002). For dichlofluanid, carbazole, 3-iodo-2-propynyl-butylcarbamate (IPBC), and 2-(methylmercapto)benzothiazole local contamination sources cannot be excluded. Diclofluanid and IPBC are both used as wood preservatives and and carbazole is a constituent of coal tar (creosote). In addition to that, IPBC is used in cosmetics and personal care products (ECHA, 2019f, a) and carbazole is used in the production of carbazole containing polymers (PVK, poly(-N-vinylcarbazole)) used in photovoltaic devices and in semiconducting polymers (Zhao et al., 2017; Grazulevicius et al., 2003) and pharmaceuticals (Zawadzka et al., 2015). 2-(Methylmercapto)benzothiazole is a major methylation product of 2-mercaptobenzothiazole, a common used vulcanisation accelerator in rubber of car tires, shoes, cables, rubber gloves and toys (Herrero et al., 2014; Leng and Gries, 2017). Due to the widespread use of rubber products, in and around the sampling station, a potential local origin cannot be excluded. Dichlofluanid and carbazole was detected in both GFF and PUF sample, while IPBC and 2-(methylmercapto)benzothiazole only in the PUF sample. The mixed halogenated compound MHC-1 is an HNP emitted from marine natural sources. As earlier confirmed, the seaweed *Plocamium cartilagineum* is producing large amounts of MHC-1 (Vetter et al., 2008). MHC-1 was, however, not detected in Zeppelin air samples reported in an earlier study (Vetter et al., 2002). Further studies are necessary to identify the origin of MHC-1 in the Arctic. No information was found on the industrial usage of 2-bromo-3,5-dimethoxytoluene, but formation as HNP cannot be excluded, since chlorinated dimethoxytoluenes were previously identified in lichen (Elix et al., 1984).

### 3.5.3 Estimated half-life's in air reflecting Arctic environmental conditions

Our $t_{1/2}$(air) is based on default values retrieved from EPIsuite (U.S.EPA, 2019). Standardised estimates are commonly used for the estimation of LRATP (Muir and Howard, 2006; Howard and Muir, 2010; Brown and Wania, 2008; Reppas-Chrysovitsinos et al., 2017). These default half-lives are likely underestimated when adjusted to Arctic environmental conditions. When adjusting the estimates of $t_{1/2}$(air) for the sampling temperature and assumed OH radical concentrations in December (see sect. 2.5), all compounds, classified as L1 and L2 have an estimated $t_{1/2}$(air), exceeding 2 days. Results for selected compounds can be found in Table 6 and further results in SI Table S3 and Excel-SI. This supports our assumption that those new potential CEACs could be subject to LRAT as a result of enhanced persistence in air during Arctic winter. While influences from nearby sources cannot be excluded, those properties are relevant for 2 out of 4 hazard criteria defining a POP, according to the Stockholm convention (UNEP, 2009b), suggesting they deserve further focus from the research and policy communities. While the selected numerical values used to predict adjusted reaction half-lives may be questioned, these

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data in combination with their findings in Arctic air samples suggest that LRATP cannot be excluded. While half-lives are prolonged under relevant Arctic conditions, we caution that our estimates do not account for differences in net atmospheric deposition among the substances studied which may limit LRATP (e.g. (Beyer et al., 2003)).

#### 3.5.4 Comparison of findings in Arctic air to air samples from southern Norway

For some compounds it was possible to compare findings from this study of Arctic air samples to findings of similar high-volume air samples from Birkenes in southern Norway (Röhler et al., 2020). The Birkenes observatory is a part of EMEPs monitoring stations for background air, and the air samples were collected during April–May 2015. For a complete overview of compounds that were identified both studies, see Excel file SI. Among the new potential CEACs detected in Arctic air, it was possible to find five of 15 L1 compounds with LRAT and 10 of 13 L1 compounds without LRAT also in the Birkenes air. The identification of new potential CEACs in air samples from both southern Norway (Birkenes) and the Arctic (Zeppelin, Svalbard), combined with predictions of $t_{1/2}$(air) which are adjusted to reflect actual environmental conditions, supports our assumption that these compounds may undergo LRAT.

### 3.6 Summary for Level 3 compounds

A large number of L3 compounds, tentative candidates, were detected in the Arctic air samples. The bulk of them are PACs, primarily PAHs, substituted PAHs (e.g. alkane side chains), halogenated PAHs and sulphur- nitrogen- and oxygen-containing PAHs (Figure 6). The tentatively identified compounds also include several phthalates, carbonic acid esters, and miscellaneous halogenated compounds. The list of L3 compounds can be found in SI (Excel-SI).

### 3.7 Level 4 compounds

The group of L4 compounds includes compounds with an assigned molecular formula and several unknown halogenated compounds, which did not match any of the MS in the used MS libraries. The approximate molecular weight (nominal mass), the degree of halogenation, and some major fragments could be extracted from the LRMS spectra (see SI Excel-SI). Additional structural information was obtained using GC×GC-HRMS for some of the unknown halogenated compounds.
The acquired accurate mass spectra from HRMS (see SI for HRMS spectra) were processed using MetFrag software (MetFrag, 2019; Ruttkies et al., 2016) and possible molecular formula/s were generated (Table 7).
After searching SciFinder® with possible molecular formulas and identified substructures from the mass spectra, it was possible to find possible structures suggestions for several of the unknown halogenated compounds analysed with HRMS. The number of citations of a compound in SciFinder could give a further limitation of possible structures. Since the mass spectra do not occur in the NIST14 MS library, the found compound might be a less cited compound or might not have registered/ assigned with a CAS number and is not yet listed in the CAS registry in SciFinder. Using HRMS and SciFinder data, additional structural information could be extracted for four unknown halogenated compounds (Table 7 and SI Fig. S2-S7), originally classified as L4. Two of the compounds were tentatively identified as methoxylated halogenated benzenes, one dibromo-monochloro-

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anisole and one dichloro-methyl-dimethoxy-benzene. Several structurally related compounds were found among the potential CEACs with a default LRATP (see sect. 3.5.1 and Table 4) of which one, chloroneb, was assigned L1 confidence, which supports the tentative structure assignments and qualify the two for L3.

## 4. Conclusions

By applying a dedicated non-target and suspect screening method based on a non-destructive sample clean-up method (excluding acid treatment) combined with GC×GC-LRMS on high-volume air samples from Arctic Svalbard, a large number of known and new potential CEACs could be identified at prioritised. During this study, 73 new potential CEACs (compounds previously not reported in Arctic environments) were classified at confidence level L1 or L2, which indicate that comprehensive suspect and non-target screening can reveal new potential CEACs that might be needed to be monitored or risk assessed. All these compounds are predicted to have atmospheric reaction half-lives exceeding two days, if these are adjusted to reflect actual environmental conditions during sampling. Reaction half-lives reflecting standardised environmental conditions (e.g. 25 °C) are, thus, poor predictors for persistence in the Arctic environment. The here reported study underpins the importance of combining model estimates with empirical measurements for environmental assessment of chemicals. The newly identified organic CEACs from this study are recommended for inclusion in regulatory monitoring strategies and for target specific analytical methods. Although the applied identification method is a promising tool for identification of new priority pollutants, but we do not consider the current study as exhaustive. Further in-depth studies, carried out using GC×GC-HRMS are expected to provide additional information about CEACs not yet included in MS libraries. Those should preferably use a column set featuring a non-polar first dimension column, which allow comparisons to retention time databases or retention index prediction data (Veenaas and Haglund, 2018) in order to accept or reject the candidate structures of hitherto unknown CEACs.

## Competing interests

The authors declare that they have no conflict of interest.

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Compound structures were created using ChemOffice19 (PerkinElmerInformatics, 2019).
LogP and logD values were created using JChem for Excel (ChemAxon, 2019).

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**Author contribution**

LR, MS, PBN and RK developed the idea behind this study.

LR performed chemical work, analysis, created the figures and wrote the paper.

MS and PBN provided guidance and contributed to the paper preparation

PH provide guidance, HRMS measurements and contributed to the paper preparation

KB provided guidance on theoretical calculations and contributed to the paper preparation

RK provided financial support, academic guidance and contributed to the paper preparation

All authors read and approved the submitted manuscript.

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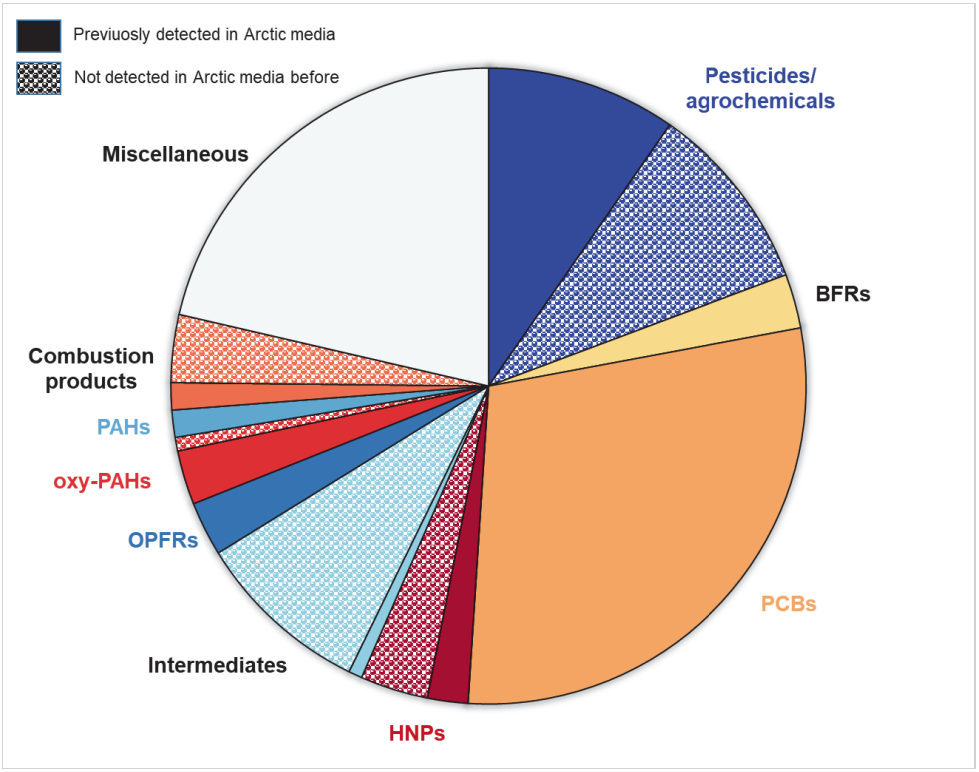


**Figure 1: Graphical abstract, summary of compounds confirmed with reference standards and compounds with tentative structure.**

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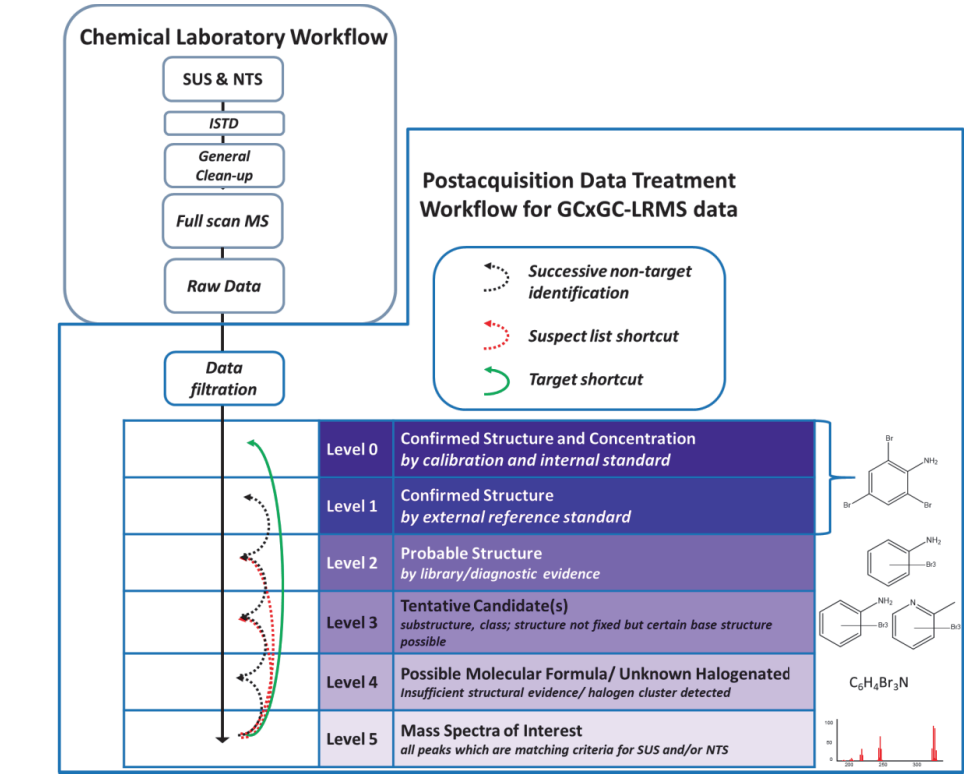


**Figure 2: General strategy and identification confidence for GC×GC-LRMS. Adapted from Schymanski et al. (2015) and Röhler et al. (2020).**

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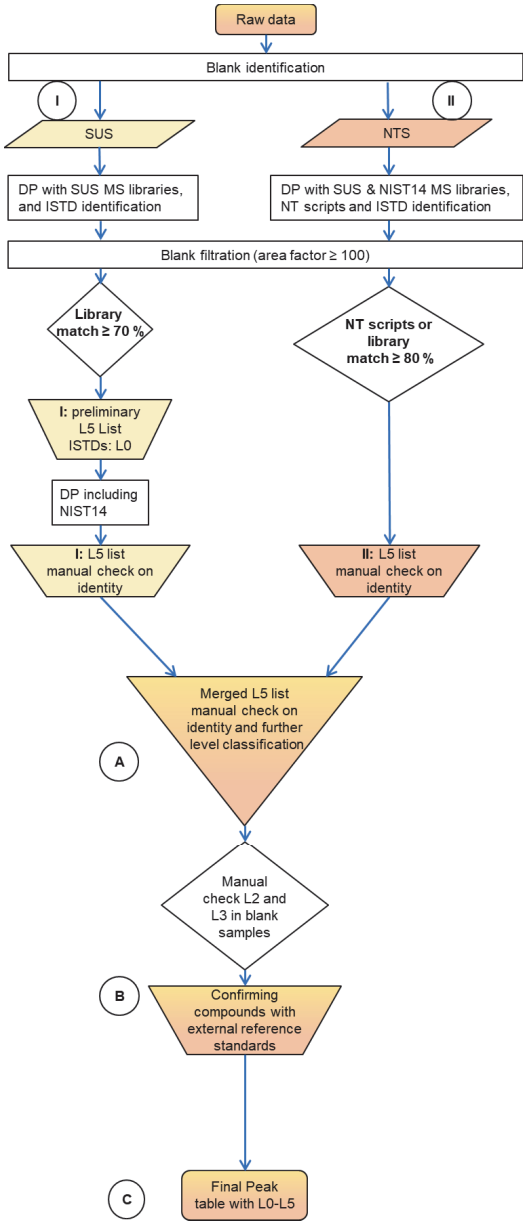


**Figure 3: Data Processing workflow for suspect and non-target screening.**

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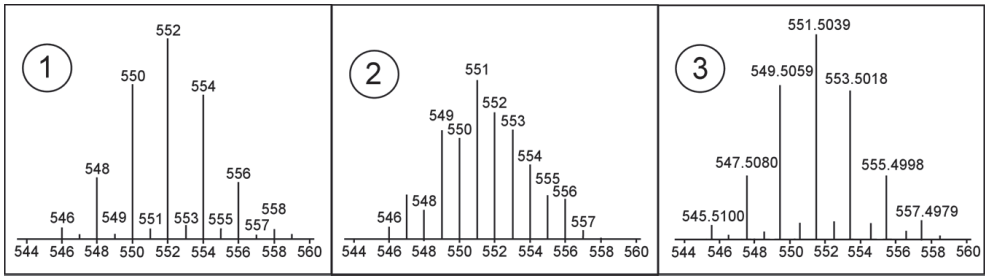


**Figure 4: 1: Isotope cluster of hexabromobenzene (HBB) in NIST14, 2: own measured HBB on GC×GC-LRMS and 3: HRMS isotope cluster HBB (Röhler et al., 2020)**

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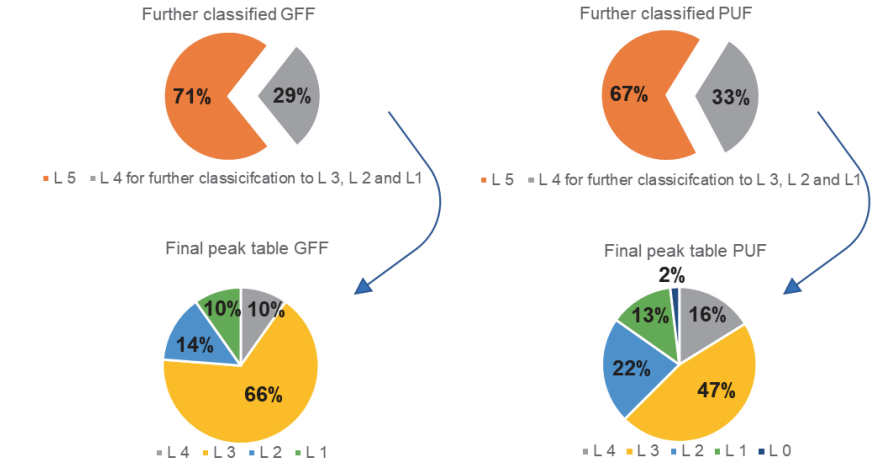


**Figure 5: Distribution of L0-L5 compounds in the GFF and PUF sample.**

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**Table 1: Overview of the L0–L4 compounds, classified in Arctic air samples.**

| Level | Compounds classified | PUF sample | GFF sample | Common to PUF and GFF | Found in suspect lists |
|---|---|---|---|---|---|
| **L0** | 6 | 6 | Only traces detected | 0 | 1 |
| **L1** | 56 | 42 | 14 | 7 | 39 |
| **L2** | 90 | 70 (41 PCBs) | 20 | 0 | 17[a] |
| **L3** | 241 | 146 | 95 | 0 | -[b] |
| **L4** | 65 | 51 (29 unknown halogenated) | 14 (12 unknown halogenated) | 0 | -[b] |

[a] showing similarity to suspect lists, isomer not confirmed; [b] not applicable

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**Table 2: : Ranking of most abundant POPs in this study (based on peak area) in comparison to concentrations from target analysis (pg m-3) in the Norwegian national monitoring programme of long-range transported environmental contaminants (Nizzetto, 2016).**

| Compound | Area from this study | Average concentration in December 2015 at Zeppelin [pg $m^{-3}$](Nizzetto, 2016) |
|---|---|---|
| HCB | 8032400 | 80.8 |
| PeCB | 890100 | 25.1[a] |
| α-HCH | 652200 | 3.25 |
| *p,p'*-DDE | 297500 | 0.89 |
| γ-HCH | 177700 | 0.6 |
| *o,p'*-DDT | 46700 | 0.16 |
| Dieldrin | 37700 | -[b] |
| *trans*-Nonachlor | 36900 | 0.37 |
| *cis*-Chlordane | 36100 | 0.35 |
| Heptachloro *exo* epoxide | 25800 | -[b] |
| *p,p'*-DDT | 18800 | 0.11 |
| PCB-153 | 15100 | 0.15 |
| PBDE-47 | 9800 | 0.07 |
| PBDE-28 | 600 | 0.006 |

***[a]: Not shown in report; [b]: Non-acid stable compound and not included in the Norwegian national air monitoring***

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**Table 3: Structure overview of L1 compounds, classified as new potential CEACs with LRATP**

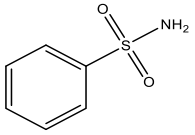
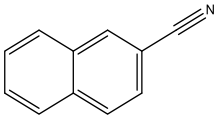
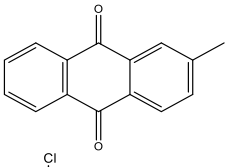
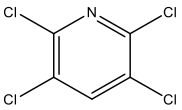
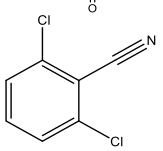
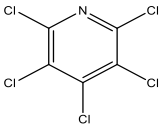
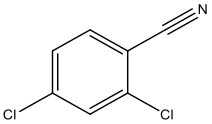
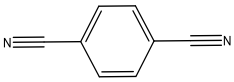
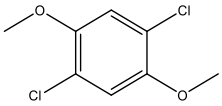
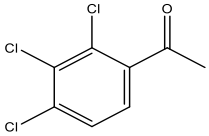
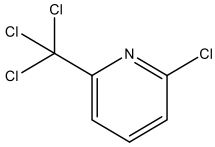
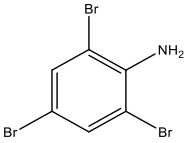
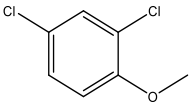
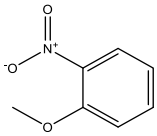
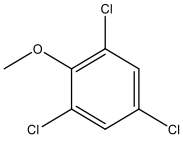
| Name/ CAS/ Sample | Structure | Name/ CAS/ Sample | Structure |
|---|---|---|---|
| Benzenesulfonamide (BSA)/ 98-10-2 GFF (particle phase) |  | 2-Naphthalenecarbonitrile/ 613-46-7 PUF (gas phase) |  |
| 2-Methyl-9,10-Anthraquinone/ 84-54-8 GFF (particle phase) |  | 2,3,5,6-Tetrachloropyridine/ 2402-79-1 PUF (gas phase) |  |
| 2,6-Dichlorobenzonitrile (dichlorobenil)/ 1194-65-6 PUF (gas phase) |  | Pentachloropyridine/ 2176-62-7 PUF (gas phase) |  |
| 2,4-Dichlorobenzonitrile/ 6574-98-7 PUF (gas phase) |  | 1,4-Benzenedicarbonitrile (Terephthalonitrile)/ 623-26-7 PUF (gas phase) |  |
| 1,4-Dichloro-2,5-dimethoxybenzene (chloroneb)/ 2675-77-6 PUF (gas phase) |  | 2',3',4'-Trichloroacetophenone / 13608-87-2 PUF (gas phase) |  |
| 2-Chloro-6-(trichloromethyl)pyridine (Nitrapyrin)/ 1929-82-4 PUF (gas phase) |  | 2,4,6-Tribromoaniline / 147-82-0 PUF (gas phase) |  |
| 2,4-Dichloroanisole/ 553-82-2 PUF (gas phase) |  | 2-Nitroanisole/ 91-23-6 PUF (gas phase) |  |
| 2,4,6-Trichloroanisole/ 87-40-1 PUF (gas phase) |  | | |

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**Table 4: Overview of L2 compounds, classified as new potential CEACs with LRATP.**

| Name | Sample | Molecular formula |
|---|---|---|
| 3,4-Dichloropropiophenone related positional isomer[a] | GFF (particle phase) | $C_9H_8Cl_2O$ |
| Diphenyl sulfone | GFF (particle phase) | $C_{12}H_{10}O_2S$ |
| Dibenzothiophene sulfone | GFF (particle phase) | $C_{12}H_8O_2S$ |
| N-(2-Cyanoethyl)-N-methyl-benzenesulfonamide | GFF (particle phase) | $C_{10}H_{12}N_2O_2S$ |
| Two chloroneb related positional isomers[b] | PUF (gas phase) | $C_8H_8Cl_2O_2$ |
| One chlorothalonil related positional isomer[c] | PUF (gas phase) | $C_8Cl_4N_2$ |
| Two trichloro-dimethoxybenzen isomers | PUF (gas phase) | $C_8H_7Cl_3O_2$ |
| Two dichloro-methylanisole isomers | PUF (gas phase) | $C_8H_8Cl_2O$ |
| One dibromo-dimethoxybenzene isomer | PUF (gas phase) | $C_8H_8Br_2O_2$ |
| 1-naphthalenecarbonitrile | PUF (gas phase) | $C_{11}H_7N$ |
| One pentachloro-methylbenzene positional isomer[d] | PUF (gas phase) | $C_7H_3Cl_5$ |

[a] Retention times close to, but not identical to, that of a 3,4-dichloropropiophenone standard

[b] Retention times close to, but not identical to, that of a chloroneb standard

[c] Retention times close to, but not identical to, that of a chlorothalonil standard

[d] Retention times close to, but not identical to, that of a pentachlorotoluene standard

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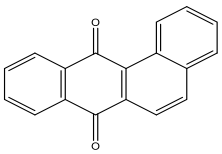
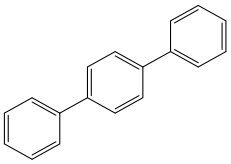
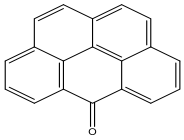
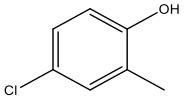
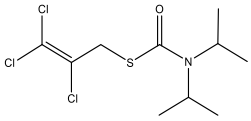
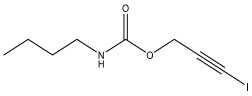
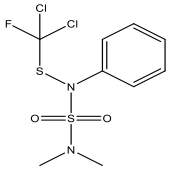
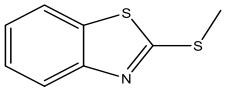
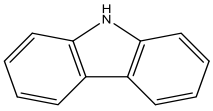
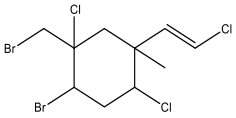
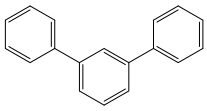
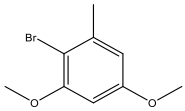
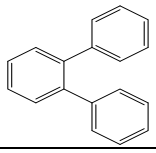
**Table 5: Structure overview of L1 compounds, classified as new potential CEACs without a predicted LRATP under standardised environmental conditions.**

| Name/ CAS/ Sample | Structure | Name/ CAS/ Sample | Structure |
|---|---|---|---|
| 1,2-Benzanthraquinone/<br>2498-66-0<br>GFF (particle phase) |  | *p*-Terphenyl/<br>l92-94-4<br>PUF (gas phase) |  |
| 6H-Benzo[*cd*]pyren-6-one/<br>3074-00-08<br>GFF (particle phase) |  | 4-Chloro-2-methylphenole<br>(PCOC)/<br>1570-64-5<br>PUF (gas phase) |  |
| Triallate/<br>2303-17-5<br>GFF and PUF |  | 3-Iodo-2-propynyl-butylcarbamate<br>(Iodocarb, IPBC)/<br>55406-53-6<br>PUF (gas phase) |  |
| Dichlofluanid/<br>1085-98-9<br>GFF and PUF |  | 2-(Methylmercapto)-benzothiazole/<br>615-22-5<br>PUF (gas phase) |  |
| Carbazole/<br>86-74-8<br>GFF and PUF |  | MHC-1<br>(2-bromo-1-bromomethyl-1,4-<br>dichloro-5-(2′-chloroethenyl)-5-<br>methylcyclohexane)/<br>66321-24-2<br>PUF (gas phase) |  |
| *m*-Terphenyl/<br>l92-06-8<br>GFF and PUF |  | 2-bromo-3,5-dimethoxytoluene/<br>13321-73-8<br>PUF (gas phase) |  |
| *o*-Terphenyl/<br>84-15-1<br>PUF (gas phase) |  | | |

https://doi.org/10.5194/acp-2020-105
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Atmospheric Chemistry and Physics Discussions

**Table 6: Half-life in air: Standard values from EPIsuite and adjusted for Arctic conditions (Eq.S1-S2), for selected compounds.**

| Name | CAS | Standard half-life [days] (25 °C; 1.5E6 mol $cm^{-3}$) | Adjusted half-life [days] (-2.4 °C; 6.0E3 mol $cm^{-3}$) |
|---|---|---|---|
| 9-Fluorenone | 486-25-9 | 1.7 | 651 |
| *p,p'*-DDE | 72-55-9 | 1.4 | 541 |
| Dieldrin | 60-57-1 | 1.2 | 437 |
| 1,9-Benz-10-anthrone | 82-05-3 | 0.6 | 223 |
| Caffeine | 58-08-2 | 0.6 | 207 |
| TCIPP | 13674-84-5 | 0.2 | 90 |
| TCEP | 115-96-8 | 0.5 | 183 |
| Benzo[*ghi*]fluoranthene | 203-12-3 | 0.2 | 65 |
| Naphthalene | 91-20-3 | 0.5 | 186 |
| Tris(3-chloropropyl) phosphate | 1067-98-7 | 0.1 | 55 |
| *m*-Terphenyl | 92-06-8 | 0.8 | 159 |
| Dichlofluanid | 1085-98-9 | 0.7 | 135 |
| IPBC | 55406-53-6 | 0.4 | 79 |

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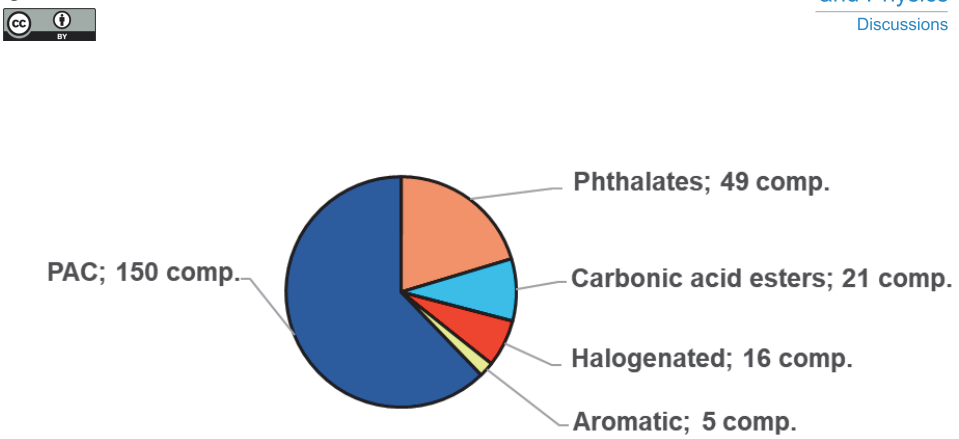


**Figure 6: L3 compound groups.**

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Preprint. Discussion started: 13 February 2020
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Atmospheric Chemistry and Physics Discussions

**Table 7: Unknown halogenated compounds with HRMS data.**

| Compound | Accurate mass | Possible molecular formula from MetFrag | Formula supported by manual fragment interpretation |
|---|---|---|---|
| A#9842 GFF | 256.0169 | $C_{11}H_{10}Cl_2N_2O$ | $C_{11}H_{10}Cl_2N_2O$ |
| B#11108 GFF | 230.0134 | $C_8H_8Cl_2N_4$ | m/z 230, dichloro- fragment $C_{10}H_{10}Cl_2NO$ |
| C#4444 PUF | 299.8372 | $C_7H_5Br_2ClO$<br>$C_6H_5Br_2O_2P$ | $C_7H_5Br_2ClO$ |
| D#5672 PUF | 220.0053 | $C_9H_{10}Cl_2O_2$<br>$C_8H_{10}ClO_3P$ | $C_9H_{10}Cl_2O_2$ |

# Supplementary Material ACP-2020-105

The Excel-SI document for ACP-2020-105 can be found on ACPs webpage:
https://www.atmos-chem-phys-discuss.net/acp-2020-105/

**Used Chemicals**

Internal standards were used for method quality control (Table S1).
All solvents and consumables were purchased by VWR, Oslo, Norway or Merck, Darmstadt, Germany and were of trace analytical quality.
Aceton (VWR Pestinorm® for Pesticide residue analysis), n-hexane (VWR Pestinorm® for Pesticide residue analysis), acetonitrile (LiChrosolv, isocratic grade for LC, Merck), toluene and Isooctane (EMSURE® for analysis, Merck), Extran® (Merck) and sodium sulphate (anhydrous, EMSURE® for analysis, Merck). Cotton was purchased from Mediq Norge, Norway. Supelco Discovery DSC-18 and Supel™QuE Z-Sep+ (Supelco, Belfonte, PA, USA), Florisil® 60-100 Mesh (Sigma Aldrich) and citric acid (anhydrous, puriss., Sigma Aldrich) were purchased from Sigma Aldrich Chemie GmbH, Germany.
All used glassware was washed with Extran®, heated to 450 °C for 8 h and rinsed with Acetone prior use.
Florisil and sodium sulphate were heated to 450°C for 8 h prior use and cotton was Soxhlet extracted with n-Hexane/ 24h, rinsed with acetone and dried prior use.
PUF plugs (11 cm in diameter and 5 cm in height) were purchased from Sunde Søm & Skumplast A/S, Gan, Norway.

**Air sample clean-up**

For sample clean-up, a glass column, 250 mm length and 20 mm inner diameter, were packed with cotton, a mixture of Z-Sep+ and DSC-18 (2 g each), Florisil (10 g) and a top layer of sodium sulphate (1 cm), for each sample. After conditioning the column with acetone (1,5x volume of the column), the column was dried by using of a KNF vacuum pump (Laboport, N86KT.18, Village-Neuf, France). The extract was added to the dry column in isooctane and eluted with Acetonitrile/ 0.5 % Citric acid (w/w, 80 mL). The extract was reduced to 0.5 mL, rinsed with Acetonitrile and transferred to a conical vial (Chromacol 1.1-STVG), for further concentrated to 200 µL under a gentle stream of nitrogen gas (5.0 quality, Nippon gases Norge AS, Oslo, Norway). Prior to analysis, recovery standard was added.

**GC×GC- LRMS analysis**

PTV solvent vent mode with 30 sec solvent vent time, 50 mL min-1 solvent vent flow at 0 psi, with a Gerstel PTV injector. Initial inlet temperature was 50 °C with a duration of 0.55 min, ramped with 200 °C min-1 to 280 °C with a duration of 6 min and ramped with 100 °C min-1 to 320 °C with a duration of 2 min.

The temperature program of the primary GC column was set as follows: 45 °C (hold time 0.55 min), ramped with 50 °C min-1 to 80 °C (hold time 1.5 min) and ramped with 4 °C min-1 to 300 °C (hold time 8 min). The secondary oven temperature was programmed 105 °C (hold time 2.25 min) and ramped at 4 °C min-1 to 315 °C (hold time 10.5 min). Modulation period was set to 4.5 s with 0.54 s hot pulse time and 19 °C modulator temperature offset relative to the primary oven temperature. Liquid N2 (Nippon gases Norge AS, Oslo, Norway) was used as coolant for the GC×GC modulator. The ion source and the transfer line temperatures were set to 200 °C and 300 °C, respectively and the MS was operated in electron ionisation (EI) mode with an electron energy of 70 eV. A data acquisition rate of 100 spectra s-1 was used in combination with an acquired mass range of m/z (mass to charge ratio) 45 – 1000. Autotuning was performed by using the m/z 219 perfluorotributylamine (PFTBA) ion instead of the default m/z 69 ion. In order to avoid system contamination and memory effects, clean solvent (Toluene followed by Acetonitrile) was injected after each sample run.

**GC×GC-HRMS Analysis**

The GC×GC/ToF-HRMS system consisted of a Pegasus® GC×GC-HRT+ (LECO, St. Joseph, MI, USA) system equipped with a Restek (Bellefonte, PA, USA) Siltek Guard column (4 m, 0.25mm) and a SGE (Trajan Scientific and Medical, Ringwood, VIC, Australia) BPX-50 (25 m, 0.25 mm, 0.25 µm) as the first dimension column and an Agilent J&W (Folsom, CA, USA) VF-1ms (1.5 m, 0.15 mm, 0.15 µm) as the second dimension column. Helium (5.0 quality) was used as carrier gas with a constant flow of 1 mL min-1. Aliquots (2 µL) of each extract were injected in PTV solvent vent mode with 30 sec solvent vent time, 50 mL min-1 solvent vent flow at 0 psi, with a Gerstel PTV injector. Initial inlet temperature was 50 °C with a duration of 0.55 min, ramped with 200 °C min-1 to 280 °C with a duration of 6 min and ramped with 100 °C min-1 to 320 °C with a duration of 2 min.

The primary GC column was programmed as follows: 45 °C (hold time 0.55 min), ramped with 50 °C min-1 to 80 °C (hold time 1.5 min) and ramped with 4 °C min-1 to 300 °C (hold time 8 min). The secondary oven temperature was programmed 105 °C (hold time 2.25 min) and ramped at 4 °C min-1 to 315 °C (hold time 10.5 min). The modulation period was set to 4.5 s with 0.54 s hot pulse time and 19 °C modulator temperature offset relative to the primary oven temperature. Liquid N2 was used as coolant for the GC×GC modulator. The ion source and the transfer line temperatures were set to 210 °C and 300 °C, respectively, and the MS was operated in electron ionisation (EI) mode with an electron energy of 70 eV. A data acquisition rate of 80 spectra s-1 with high-resolution (>25 000) was used in combination with an acquired mass range of m/z 45–1000.

**Data alignment for suspect lists, which mass spectra are to find in NIST 14/ self-build libraries and how to highlight findings of suspects in peak tables**

To account for different CAS numbers and/ or different names of compounds in the used suspect lists and MS libraries, compound names from the suspect lists were transformed to CAS numbers and compared to the original CAS number in the suspect list. If the transformed CAS from compound name was not identical with the original CAS number in the publication a manual search was performed in SciFinder to identify the correct CAS number for a compound. After all compounds were assigned with corrected CAS numbers, SMILES stings were created of each compound, using JChem for Excel (ChemAxon, 2019).

Conditional formatting in Excel was used to create a merged suspect list, including the information from which list a suspect is originating (e.g. AMAP list or NORMAN list etc.).

To identify which of those suspects might be listed in the used MS libraries, all entries of the used MS libraries were exported to Excel (Name, CAS and molecular formula).

With conditional formatting in Excel, all suspects, of which a MS is available in the used MS libraries, were highlighted and copied to a separate column.

The mass spectra of these suspects were manually copied from the used MS libraries to a separate, own build library.

This MS library, containing the selected mass spectra, was used beside other own build MS libraries for suspect screening. During suspect screening, the first library search was only performed with own build libraries. Here all peak markers in ChromaTOF were highlighted as suspects before further data processing and classification. The final peak list, L0–L2 compounds, was cross checked with the initial suspect list and the origin list of a suspect was included.

**Evaluation of long-range atmospheric transport potential**

$$k_{RA} = k_{RA,ref}[OH]e^{\frac{AE_A}{R}\left(\frac{1}{298.15K}-\frac{1}{T_A}\right)} \qquad \textbf{Equation S1}$$

$$t_{\frac{1}{2}}(days) = \frac{ln2}{k_{RA}} \qquad \textbf{Equation S2}$$

$k_{RA}$: Estimated OH reaction rate for a specific temperature [$cm^3$ $mol^{-1}$ $sec^{-1}$]

$k_{RA,ref}$: Estimated reference OH reaction rate (25 °C) from EPIsuite [$cm^3$ $mol^{-1}$ $sec^{-1}$]

[OH]: Assumed OH conc. at Zeppelin station in December [mol $cm^{-3}$]

$AE_A$: Assumed activation energy [J $mol^{-1}$]

R: Gas constant [J $mol^{-1}$ $K^{-1}$]

$T_A$: Sampling temperature in Kelvin [K]

$t_{1/2}$: half-life [days]

Excel-SI file provides a column with results of this calculation, as well as Table S3.

**Adjusted half-life's in air for detected compounds**

Calculations of adjusted half-life's in comparison to non-adjusted half-life from EPIsuite:

We calculated different scenarios in comparison to the non-adjusted standard values for half-life from EPIsuite, based on 25 °C and a OH-radical concentration of 1.5E6 OH $cm^{-3}$ (column 3, Table S3)

As described in section 2.5 of the manuscript, we assumed a OH-radical concentration of 6.0E3 OH $cm^{-3}$ at a maximum sampling temperature of T= -2.4 °C during sampling (column 5, Table S3). In addition to those two scenarios, we adjusted the half-life of EPIsuite only for temperature (column 4, Table S3). Furthermore, we used Bahm and Khalils (2004) model values for OH-radical concentration in December (5E4 OH $cm^{-3}$) (column 6, Table S3). As already mentioned in section 2.5 of the manuscript, this OH-radical concentration is from 45 °N latitude, which crosses central Europe. Further north, the model of Bahm and Khalil does not predict OH-radical concentration in December.

The results of our adjusted half-life support our assumption, that also with a higher OH-radical concentration from central Europe in December, our findings could be persistent in air during December and might be content of LRATP

**References**

Bahm, K., and Khalil, M. A. K.: A new model of tropospheric hydroxyl radical concentrations, Chemosphere, 54, 143-166, https://doi.org/10.1016/j.chemosphere.2003.08.006, 2004.

ChemAxon: JChem for Excel Add-In V 19.25.0.559. 2019.

**Table S1: Spiking amounts of ISTDs**

| Internal standard | Spiking amount [ng] | Purchased |
|---|---|---|
| $^{2}H_{10}$ phenanthrene | 2.08 | Chiron |
| $^{13}C_{6}$ HCB | 4.78 | Wellington Laboratories |
| $^{13}C_{12}$ *p,p'*-DDT | 16.12 | Wellington Laboratories |
| $^{13}C_{12}$ PCB-153 | 12,20 | Wellington Laboratories |
| $^{13}C_{6}$ HBB | 21.14 | Wellington Laboratories |
| $^{13}C_{12}$ PBDE-28 | 5.28 | Wellington Laboratories |
| $^{13}C_{12}$ PBDE-47 | 5.22 | Wellington Laboratories |
| $^{13}C_{12}$ PBDE-99 | 5.30 | Wellington Laboratories |
| | | |
| Recovery standard | | |
| 1,2,3,4-Tetrachloronaphthalene (TCN) | 7.96 | Ultra-Scientific |

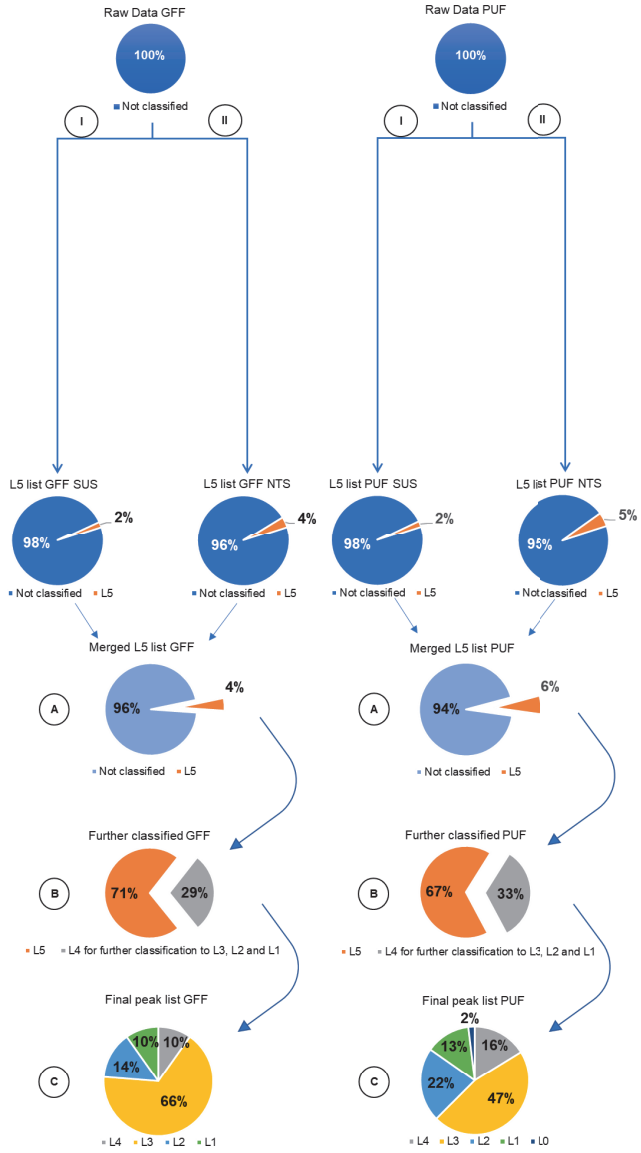


**Figure S1: Peak reduction during data processing for GFF and PUF sample.**

**Table S2: Summary of PBT criteria.**

| | REACH (European Parliament, 2018) | Stockholm convention (UNEP, 2009) |
|---|---|---|
| **Persistent (P)** | $t_{1/2}$water fresh/marine ≥ 960/1440 h (40/60 days) | $t_{1/2}$water ≥ 2 months (1440 h) |
| | (vP[1] ≥ 1440 h (60 days)) | |
| | $t_{1/2}$soil ≥ 2880 h (120 days) | $t_{1/2}$soil ≥ 6 months (2880 h) |
| | (vP[1] ≥ 4320 h (180 days)) | |
| | $t_{1/2}$sediment fresh/marine ≥ 2880/4320 h (120/180 days) | $t_{1/2}$sediment ≥ 6 months (2880 h) |
| | (vP[1] ≥ 4320 h (180 days)) | |
| **Bioaccumulative (B)** | BCF[2] ≥ 2000 | BCF[2] or BAF[4] ≥ 5000 |
| | (vB[3] ≥ 5000) | Or log $K_{OW}$ ≥ 5 |
| **Toxic (T)** | NOEL or EC10 ≤ 0.01 mg/L | Evidence of adverse effects to human health, or |
| | Or Carcinogen cat. 1A, 1B or 2 | toxicity or ecotoxicity indicate potential for |
| | Or mutagenic cat. 1A or 1B | damage to human health or the environment |
| | Or reproduction toxic cat. 1A, 1B or 2 | |
| | Or evidence for chron. tox. STOT RE cat. 1 or 2 | |
| **Long-range transport potential (LRTP)** | -[5] | Measured levels in distant of source of relevance |
| | | Or monitoring data showing LRT with potential |
| | | to transfer to a receiving environment |
| | | Or environment fate properties/model results that |
| | | show LRTP: $t_{1/2}$air ≥ 2 days |

[1] vP: very persistent; [2] BCF: bioconcentration factor; [3] vB: very bioaccumulative; [4] BAF: bioaccumulation factor;
[5] not applicable

**Table S3: Half-life in air: non-adjusted values from EPIsuite and adjusted for Arctic conditions (Eq.S1-S2), for selected compounds.**

| Name | CAS | Non-adjusted half-life [days] (25 °C; **1.5E6 mol cm$^{-3}$**) | Adjusted half-life [days] (-2.4 °C; **1.5E6 mol cm$^{-3}$**) | Adjusted half-life [days] (-2.4 °C; **6.0E3 mol cm$^{-3}$**) | Adjusted half-life [days] (-2.4 °C; **5E4 mol cm$^{-3}$**) |
|---|---|---|---|---|---|
| 9-Fluorenone | 486-25-9 | 1.7 | 2.6 | 651 | 78 |
| *p,p'*-DDE | 72-55-9 | 1.4 | 2.2 | 541 | 65 |
| Dieldrin | 60-57-1 | 1.2 | 1.7 | 437 | 52 |
| 1,9-Benz-10-anthrone | 82-05-3 | 0.6 | 0.9 | 223 | 27 |
| Caffeine | 58-08-2 | 0.6 | 0.8 | 207 | 25 |
| TCIPP | 13674-84-5 | 0.2 | 0.4 | 90 | 11 |
| TCEP | 115-96-8 | 0.5 | 0.7 | 183 | 22 |
| Benzo[*ghi*]fluoranthene | 203-12-3 | 0.2 | 0.3 | 65 | 8 |
| Naphthalene | 91-20-3 | 0.5 | 0.7 | 186 | 22 |
| Tris(3-chloropropyl) phosphate | 1067-98-7 | 0.1 | 0.2 | 55 | 7 |
| *m*-Terphenyl | 92-06-8 | 0.8 | 1.3 | 159 | 38 |
| Dichlofluanid | 1085-98-9 | 0.7 | 1.1 | 135 | 32 |
| IPBC | 55406-53-6 | 0.4 | 0.6 | 79 | 19 |

**Table S4: Unknown halogenated compounds with HRMS data**

| Compound | Accurate mass | Possible molecular formula from MetFrag | Formula supported by manual fragment interpretation |
|---|---|---|---|
| A#9842 | 256.0169 | $C_{11}H_{10}Cl_2N_2O$ | $C_{11}H_{10}Cl_2N_2O$ |
| GFF | | | |
| B#11108 | 230.0134 | $C_8H_8Cl_2N_4$ | m/z 230, dichloro-fragment |
| GFF | | | $C_{10}H_{10}Cl_2NO$ |
| C#4444 | 299.8372 | $C_7H_5Br_2ClO$ | $C_7H_5Br_2ClO$ |
| PUF | | $C_6H_5Br_2O_2P$ | |
| D#5672 | 220.0053 | $C_9H_{10}Cl_2O_2$ | $C_9H_{10}Cl_2O_2$ |
| PUF | | $C_8H_{10}ClO_3P$ | |

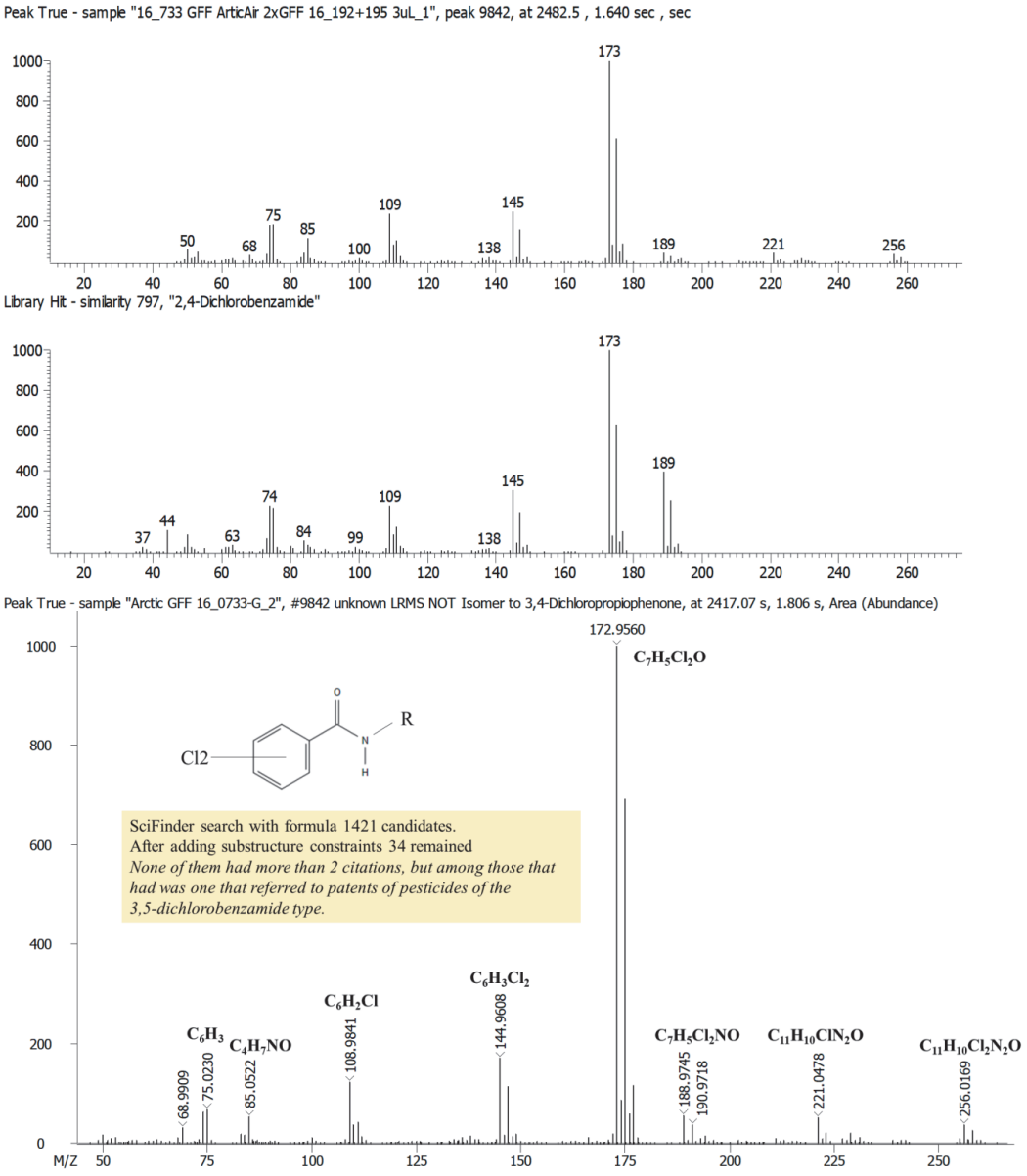


**Figure S2: LRMS and HRMS spectra of unknown halogenated compound A in GFF.**

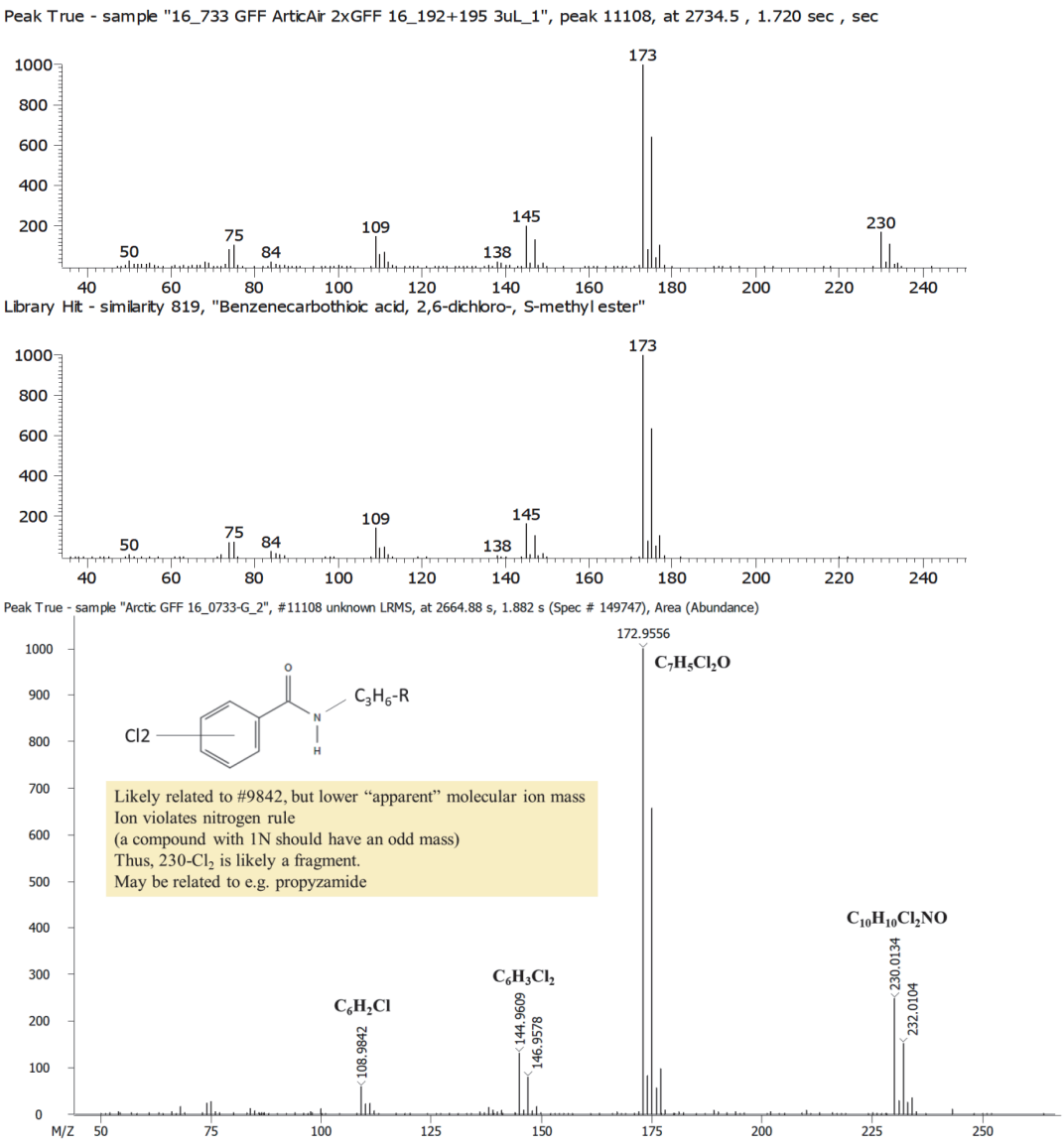


**Figure S3: LRMS and HRMS spectra of unknown halogenated compound B in GFF.**

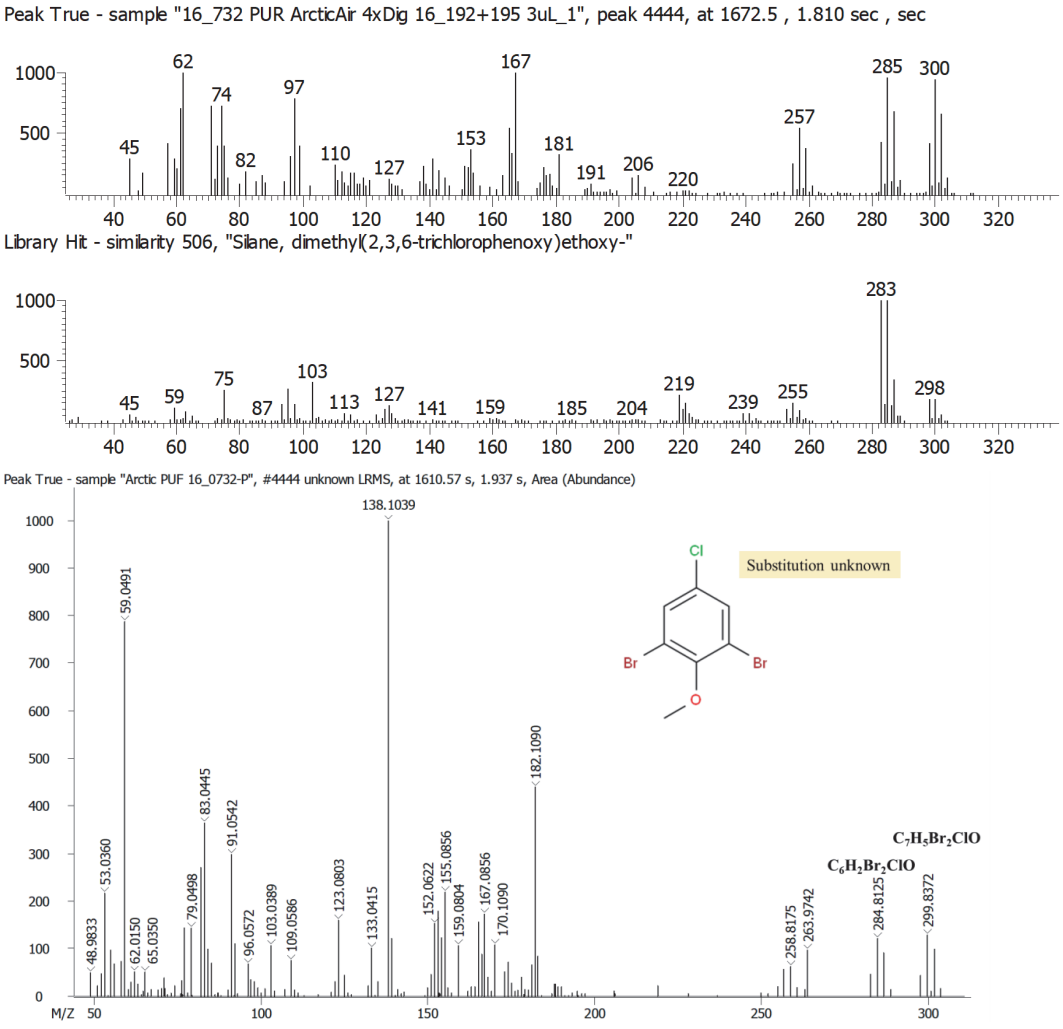


**Figure S4: LRMS and HRMS spectra of unknown halogenated compound C in PUF.**

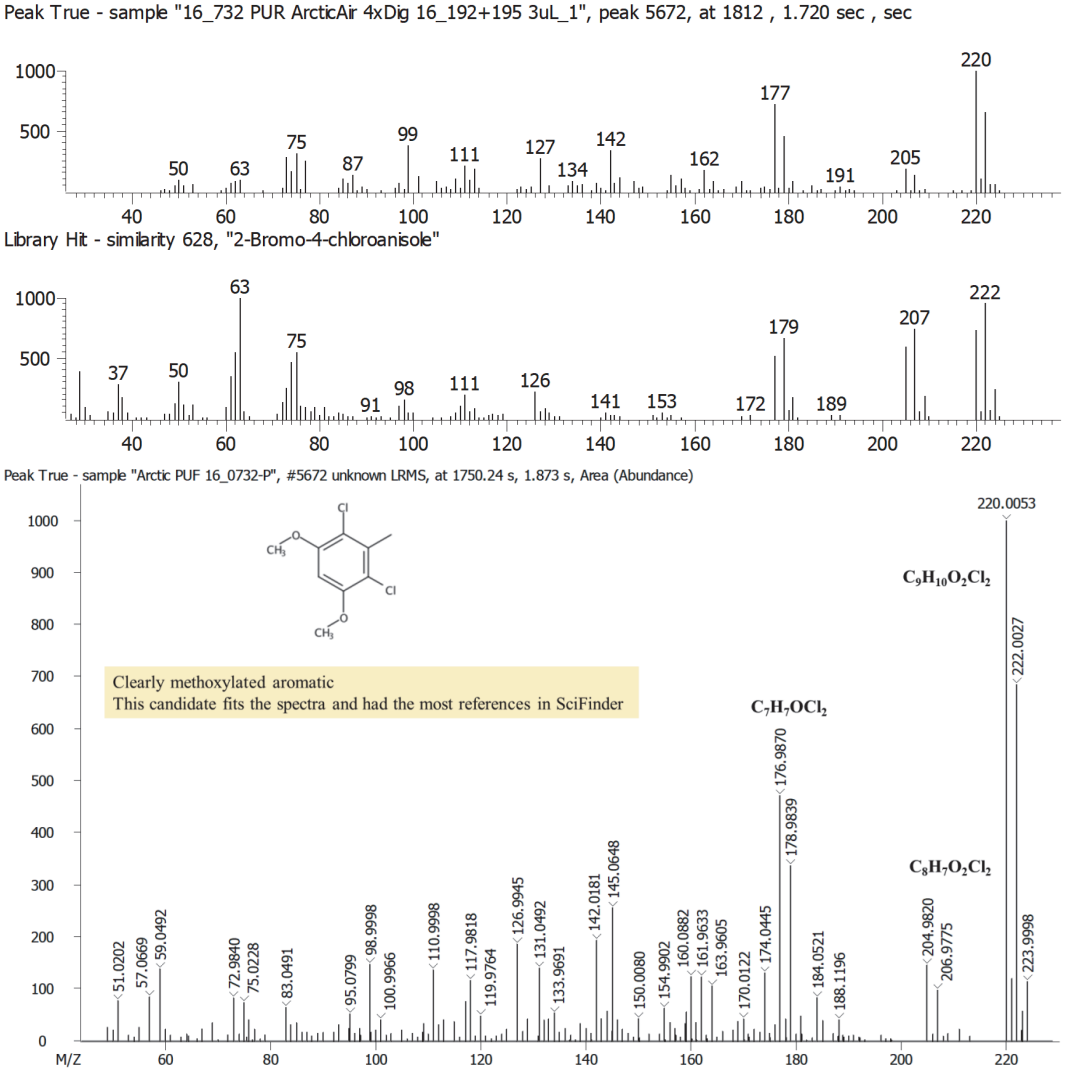


**Figure S5: LRMS and HRMS spectra of unknown halogenated compound D in PUF.**

# Paper III

Non-target and suspect characterisation of organic contaminants in biota, Part III: Selected levels of a marine and freshwater food chains in Norway.

Röhler, L., Bohlin-Nizzetto, P., Rostkowski, P., Kallenborn, R., and Schlabach, M. *In preparation.*

The Excel-SI document for paper III can be found on NILUs server:

https://nilu365.sharepoint.com/:f:/s/Project-MILK-NMBU/EiiNOoQ3B9lIu1EawVdzpq4BWQZdVuZSoLWQKHvO_wBcag?e=JBimHD

**Non-target and suspect characterisation of organic contaminants in biota, Part III: Selected levels of a marine and freshwater food chains in Norway**

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**Abstract**

tbc

## 1 Introduction

Every year, the Norwegian Environmental Agency initiate several screening studies to investigate the occurrence of chemicals of emerging concern (CECs) and keep track of known/priority chemicals as well as monitoring chemicals, which are nationally/internationally regulated, e.g. Norwegian priority list (Norwegian Environmental Agency, 1997), European Union (EU) Water Framework Directive, REACH (European Parliament, 2018), etc. These screening studies included various organic and inorganic chemicals, e.g. chemical additives and chemicals with PBT (persistent, bioaccumulative, toxic) characteristics, UV-filters, various pharmaceuticals, siloxanes, per- and polyfluoroalkyl substances (PFASs), in addition to trace metals and trace rare earth elements (Norwegian Environmental Agency, 2020). The presented study is a part of a screening study, using samples of selected levels of one marine and one freshwater food chain: the inner Oslofjord and lake Mjøsa, Norway. The majority of the Norwegian population lives in and around Oslo, which is localised at the end of the Oslofjord. The water exchange from inner Oslofjord, the part of the Oslofjord from Drøbak towards Oslo and ending in Bunnefjord (distance Drøbak-Akershus fortress in Oslo is approx. 30 km, total distance from Drøbak-end of Bunnefjord is approx. 45 km), is naturally hampered at Drøbak (water depth approx. 19 m). Thus, local pollution of the inner Oslofjord, mainly wastewater from industry and housing, is not diluted very quickly. Therefore, the inner Oslofjord is included in many screening studies and is particularly suitable for the early stage detection of potential CECs in the environment. The other sampling site, lake Mjøsa, is Norway's largest fresh water lake (approx. 100 km long), localised approx. 60 km north-east of Oslo. Lake Mjøsa

is rich in fish and used for drinking water in the surrounding districts. Since the fertile plains around lake Mjøsa are used for agriculture, pollution of lake Mjøsa originates from agriculture, in addition to industry and housing. The investigation of environmental effects of human activity, preserve a major drinking water and fishing source from contamination with CECs, and the easy accessibility, makes lake Mjøsa an ideal site for screening studies on potential new CECs.

The presented study provides additional details on the non-target screening part on organic CECs from the Norwegian Environmental Agency in 2014, covering biota samples from inner Oslofjord and lake Mjøsa. The goal of this study was the detection of new potential CECs in biota and to evaluate their hazardous potential along the PBT criteria, defined by REACH (European Parliament, 2018) and the Stockholm Convention on persistent organic pollutants (POPs) (UNEP, 2009), by using comprehensive two-dimensional gas chromatography coupled to low-resolution time of flight mass spectrometry (GC×GC-LRMS).

## 2 Experimental Section

### 2.1 Sampling and sample types

Biological samples were collected at two different sites, inner Oslofjord for marine samples and lake Mjøsa for freshwater samples (Table 1). The samples from the inner Oslofjord were collected between Askerlandet and Steilene in the inner Oslofjord by trawling and consisted of four sample types: Atlantic cod (*Gadus morhua*), herring (*Clupea harengus*), northern shrimp (*Pandalus borealis*) and krill (*Meganyctiphanes norvegica*). The samples from lake Mjøsa were collected at three different sites between Gjøvik and Hamar with gillnets for smelt (*Osmerus eperlanus*; larger, cannibalistic and smaller, planktivorous ones), vendace (*Coregonus albula*) and brown trout (*Salmo trutta*), and horizontal net hauls for mysis (*Mysia relicta*) and zooplankton (epipelagic: mainly cladoceran *Daphnia galeata* and *Bosmina longispina;* hypopelagic: mainly codepods *Limnocalanus macrururs, Cyylops lacustris* and *Eudiaptomus gracilis*).

*Table 1: Sample types and sample sites of used samples.*

| Sampling site | Sample type | Date | Depth (m) | °E | °N |
|---|---|---|---|---|---|
| Inner Oslofjord | Atlantic cod | 23.06.2014 | trawling | 10.510-10.603 | 59.810-59.817 |
| | Herring | 23.06.2014 | trawling | 10.510-10.603 | 59.810-59.817 |
| | Northern shrimp | 23.06.2014 | trawling | 10.510-10.603 | 59.810-59.817 |
| | Krill | 23.06.2014 | trawling | 10.510-10.603 | 59.810-59.817 |
| Lake Mjøsa | Smelt and vendace | 15-30.08.14 | 20-35 | 11.059 | 60.766 |
| | Brown trout | 15-30.08.14 | 10-20 | 10.680 | 60.816 |
| | Mysis | 15-30.08.14 | 3-5 | 11.04 | 60.69 |
| | Zooplankton | 15-30.08.14 | epipelagic: 3-5<br>hypopelagic: 70-110 | 11.04 | 60.69 |

For cod, the liver was used and for herring, smelt, vendace and brow trout, the whole fish (except head, spine and tail) were used for analysis.

Pooled samples of shrimps (one catch for all shrimps) were packed (10 samples, each sample was comprised about 30 peeled individuals). For krill, the catch was split into 10 samples.

The smelt belonged to two size groups: small bodied planktivorous individuals and somewhat larger cannibalistic individuals. 10 samples were prepared of each species and size group. For the small bodied planktivorous smelt, pooled samples from about 3-5 individuals per sample were necessary to obtain sufficient material for chemical analysis.

Mysis were separated from epipelagic zooplankton by filtering the samples through a sieve (mesh of stainless-steel strands) while flushing gently with water from the lake and handpicking with tweezers. Further details about sampling, sampling sites etc. can be found in the SI (Table S2 and S3) and Norwegian Environmental Agencies Screening program report 2014 (Thomas et al., 2015).

## 2.2 Extraction and sample clean-up

**Extraction.** Approx. 0.25 g lipid aliquots/ sample were homogenised separately with sodium sulphate, depending on available sample amount (Table S1 in SI). From each sample type (Atlantic cod, herring, northern shrimp, krill, smelt, vendace, brown trout, mysis and zooplankton), 5 different samples were prepared, in total 45 samples. Prior to extraction, the homogenates were mixed with additional sodium sulphate and packed into a glass column (L= 400 mm, i.d. 30 mm) with cotton in the bottom. Internal standards (see SI Table S5) were added and two extraction solvents were used, acetone/*n*-hexane (1:3 v/v, 115 mL) followed by acetone/*n*-hexane (1:1 v/v, 50 mL). After extraction, the extracts were reduced to 0.5 mL with

a Zymark TurboVap evaporator, solvent was changed to isooctane and the sample extracts were transferred to conical vials.

The same steps were carried out with sample blanks (sodium sulphate processed the same way than samples) for quality assurance (see sect. 2.4).

Samples were stored at -80 °C for at least 12 h to freeze lipids and storage until clean-up.

**Sample clean-up.** For each sample, a precleaned glass column (L= 250 mm, i.d. 20 mm) was packed with cotton, Florisil (10 g) and a top layer of sodium sulphate (1 cm). After conditioning the column with acetone (1,5x volume of the column), the column was dried, using a vacuum pump. The samples were centrifuged with 2000 rpm at -9 °C for 20 min to separate lipids from the extract. The extract was transferred to the dry column and eluted with 80 mL acetonitrile/ 0.5 % citric acid (w/w). The individual extracts were reduced to 0.5 mL with a TurboVap, solvent was changed to cyclohexane/ ethyl acetate (1:1, v/v) and injected to a GPC (gel permeation chromatography) system (mobile phase: cyclohexane/ ethyl acetate (1:1, v/v) equipped with Waters Envirogel columns, details in SI sect. 3). After GPC, each sample was reduced to 0.5 mL by TurboVap and solvent was changed to isooctane for further clean-up. A glass column (L= 250 mm, i.d. 20 mm) was packed with cotton, a mixture of Z-Sep$^{+}$ and DSC-18 (2 g each), Florisil (10 g) and a top layer of sodium sulphate (1 cm). After conditioning the column with acetone (1.5x volume of the column), the column was dried, using a vacuum pump. The individual extracts were applied to the dry column and eluted with 80 mL acetonitrile/0.5 % citric acid (w/w). After clean-up, each extract was reduced to 0.5 mL with a TurboVap and further concentrated to approximately 200 uL under a gentle steam of nitrogen gas. Prior analysis, the recovery standard was added. Details about used chemicals and equipment can be found in the SI Table S4.

## 2.3 GC×GC-LRMS Analysis

The GC×GC-LRMS system consisted of a Pegasus® 4D (LECO, St. Joseph, MI) system with a low-resolution time of flight mass spectrometer, with unit mass resolution operating in EI mode. The GC was equipped with a Restek (Bellefonte, PA, USA) Siltek Guard column (2.5 m, 0.25 mm), a SGE (Trajan Scientific and Medical, Ringwood, VIC, Australia) BPX-50 (28 m, 0.25 mm x 0.25 µm) first dimension column and an Agilent J&W (Folsom, CA, USA) VF-1ms (1.5 m, 0.15 mm x 0.15 µm) second dimension column. Helium (5.0 quality, Nippon gases Norge AS, Oslo, Norway) was used as carrier gas with a constant flow of 1 mL/min. 1 µL of each extract were injected in a Gerstel PTV (programmed temperature vaporiser) inlet, operating in solvent vent mode.

**Gerstel PTV injector**. 30 sec solvent vent time, 50 mL/min solvent vent flow at 0 psi. Initial inlet temperature was 50 °C with a duration of 0.55 min, ramped with 200 °C/min to 280 °C with a duration of 6 min and ramped with 100 °C/min to 320 °C with a duration of 2 min.

**Primary oven temperature program**. 45 °C (hold time 0.55 min), ramped with 50 °C/min to 80 °C (hold time 1.5 min) and ramped with 4 °C/min to 300 °C (hold time 8 min).

**Secondary oven temperature program.** 105 °C (hold time 2.25 min) and ramped at 4 °C/min to 315 °C (hold time 10.5 min).

**Modulator.** Modulation period was set to 3.8 s with 0.46 s hot pulse time and 19 °C modulator temperature offset relative to the primary oven temperature. Liquid $N_2$ was used as the coolant of the GC×GC modulator.

The ion source and the transfer line temperatures were set to 200 °C and 300 °C, respectively. The electron energy was 70 eV and the detector voltage was 1600 V. A data acquisition rate of 100 spectra/s was used in combination with an acquired mass range of 33 – 1000 u. Autotuning was performed by using the *m/z* 219 perfluorotributylamine (PFTBA) ion instead of the default *m/z* 69 ion. In order to avoid system contamination, solvent (toluene followed by acetonitrile) was injected after each sample run.

## 2.4 Quality control

Laboratory blanks (minimum one) for each sample type, consisting of sodium sulphate, were processed, extracted, cleaned and analysed along the same sample preparation scheme as the biota samples. These sample blanks are essential for the identification of compounds which have their origin in the sample processing and thus can be highlighted and removed during the respective data filtration step. Since this study is using a qualitative suspect, non-target and bioaccumulation screening (SUS, NTS and BAS) approach, results are not corrected for sample amounts (only visual normalisation of approximately 200 µL of the final extract volume and visual comparison of the peak hight of the recovery standard during analysis). In order to account for variations in response between sample blanks and biota samples, as well as variations in sample volumes, a compound need to exceed an area factor ≥ 100 compared to a sample blank to be accepted as an identified compound. All compounds which do not pass this threshold will be filtrated and removed from the dataset during data processing. Furthermore, internal standards (ISTDs) were used for sample normalisation, comparison and quality assurance, and not for target quantification (Röhler et al., 2020a, Röhler et al., 2020b).

## 2.5 Data processing/ post-acquisition data treatment

As described in previous studies, LECOs® ChromaTOF® (V 4.50.8) software with Scripts and Statistical Compare, which also controls the system, was used for data analysing and processing. SUS/NTS strategies from earlier studies were adjusted to match requirements of the here discussed study, and the adopted level classification for GC×GC-LRMS (Figure 1) was used to characterise detected compounds (Röhler et al., 2020a, Röhler et al., 2020b). In addition to the SUS/NTS strategies for the previous studies, we included a bioaccumulation screening (BAS) (Figure 2) for samples from inner Oslofjord and lake Mjøsa separately. In-house custom libraries, with mass spectra (MS) of reference standards, $^{13}C/^{2}H$-labeled ISTDs, a customised library with selected spectra from NIST 14, as well as the Scientific Working Group for the Analysis of Seized Drugs (SWGdrug, (Oulton, 2019) MS library were used as MS libraries for SUS (Röhler et al., 2020a). The entire NIST 2014 MS library was used for a more comprehensive and reliable library identification in all three DP strategies, SUS, NTS and BAS. Details about the level classification concept and data processing/ post-acquisition data treatment were described previously (Röhler et al., 2020a, Röhler et al., 2020b), new/different steps during data processing (DP) and prioritisation from this study were included, see sect. 3.1 for more details and Figure 2 for a complete DP workflow.

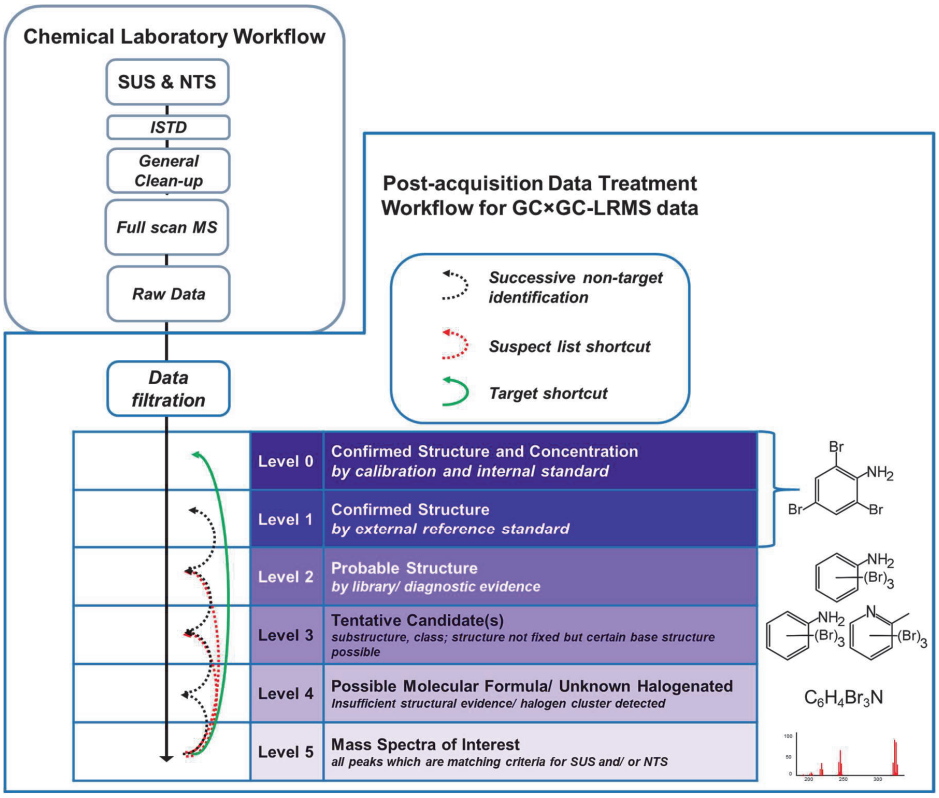


*Figure 1: General strategy and levels for identification confidence for GC×GC-LRMS (Röhler et al., 2020a), adapted from Schymanski et al. (2015).*

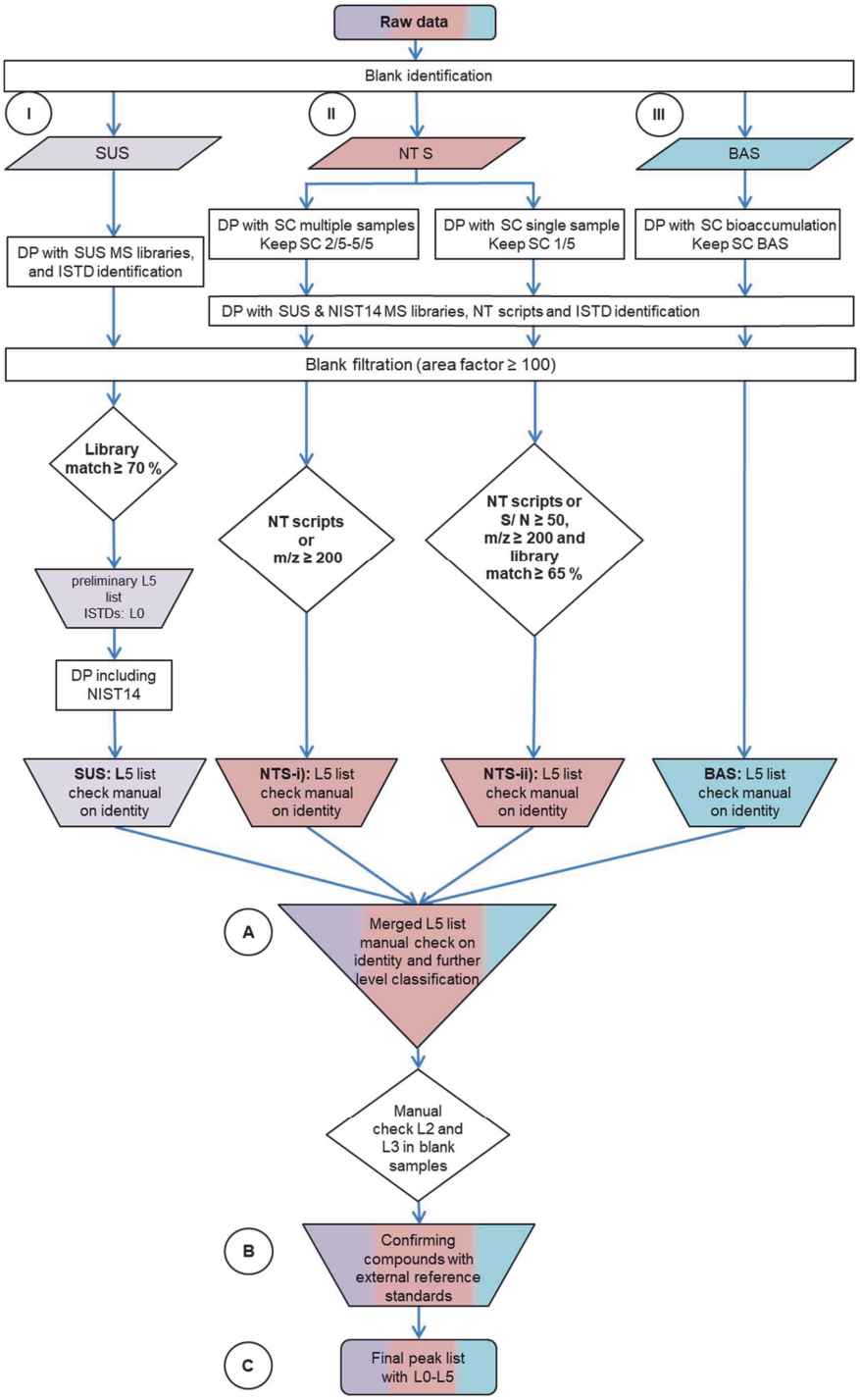


*Figure 2: Data processing workflow.*

# 3 Results and Discussion

A successful SUS/NTS study depends on the right selection of samples and sample preparation methods for a sound interpretation of the collected data. There are not yet existing standardised workflows for SUS/NTS studies of biota, but the cross-working group activity NTS of the NORMAN network (NORMAN-NTS, 2015) did discuss and agreed in 2018 on how SUS/NTS studies for biota should be designed in addition to how to design a possible sample preparation procedure for NTS study which is using liquid chromatography (LC) and gas chromatography (GC) (NORMAN NTS WS, 2018). The presented study is a GC-MS based study only, and the chosen extraction and clean-up method for biota samples was designed to cover samples with different lipid content and compounds with a wide range of polarity. The non-destructive sample preparation method was based on commonly used lipid removal by GPC and further clean-up with a custom made three-layer liquid chromatography column (see sect. 2.2) which was previously evaluated with compounds, covering a wide range of polarity (Röhler et al., 2020a).

Sample extracts were analysed by GC×GC-LRMS which revealed 11000-25000 features per sample for prioritisation and identification. The data processing workflow for SUS/NTS, previously applied on air samples (Röhler et al., 2020a, Röhler et al., 2020b) was adjusted for biota samples and an additional step, BAS, was included to the SUS/NTS workflow (see sect. 3.1 and Figure 2). This adjustment was not optimal, due to the design of the study. It included 10 samples of the same sample type, but those samples were from the same sampling spot. Ideally, these samples could be from a non-contaminated sampling site and from a more affected/contaminated site. With this kind of sampling design, it would be possible to distinguish between endogenous/biogenic compounds and those which are anthropogenic. Since this was not possible in the presented study, the prioritisation of detected features was carried out as described in the following section.

## 3.1 SUS, NTS and BAS data processing workflow

To prioritise compounds for identification out of 11000-25000 features per sample, different data processing strategies were applied to identify compounds of interest in this study. One out of five samples from each sample type (e.g. Atlantic cod, herring, northern shrimp, krill, smelt, vendace, brown trout, mysis and zooplankton) was used for SUS (see Figure 2, I).

For NTS and BAS (Figure 2, II and III), LECOs Statistical Compare (SC) tool was used to identify compounds that occur in different samples, instead to process each sample separately. This was necessary since matrix blanks for each sample were not available and sodium sulphate

blanks, processed the same way than the samples, used in their place. Thus, matrix related compounds could not be eliminated. As such, the blank filtration was reducing approximately 20-45 % of the total peak number of a sample, where the total peak number of a raw dataset is variating between 11000-25000 peaks per sample (depending on sample type).

The NTS strategy with SC (Figure 2, II) was divided in two separate approaches: i) SC multiple sample and ii) SC single sample. For i) SC multiple samples, all compounds which occur in more than one sample of one sample type (e.g. 2/5-5/5 samples of krill) were identified and kept for further processing. For ii) SC single sample, all compounds which only occur in the first of 5 samples of one sample type (1/5), were kept for further processing. This division in approach i) and ii) was necessary to prioritise compounds which occur in several samples and due to the fact that compounds that only occur in ii) SC 1/5 sample approach, contain 7000-19000 compounds per sample type after library search and blank filtration. Thus, making identification more complex. In comparison to approach i) SC multiple samples approach, contain only 300-1100 compounds per sample type. Thus, it is necessary to apply a more extensive data filtration technique for approach ii) to reduce the number of compounds to manually check identity, compared to approach i). To reduce the number of compounds for manual inspection (reaching A in Figure 2) all peaks from approach i) which were highlighted by NT scripts (Röhler et al., 2020a) or have a molecular weight ≥ 200 (m/z ≥ 200) will be listed on the NTS-i) L5 list. All peaks from approach ii) which were highlighted by NT scripts or have a molecular weight ≥ 200, in addition to a library match ≥ 65% and a S/N ≥ 50 will be listed on the NTS-ii) level 5 (L5) list.

The BAS (Figure 2, III) strategy is using the first sample (the same sample which was used for SUS) of each sample type of one sampling site, this means one BAS for inner Oslofjord (4 samples) and one BAS for lake Mjøsa (6 samples). With SC bioaccumulation, all compounds which occur in the used samples from one sampling site will be listed on the BAS L5 list.

For a more effective processing, the L5 lists from SUS, NTS-i), NTS-ii) and BAS were merged to one L5 list for manual inspection on right library identification and further level classification (Figure 2, A). Depending on the sample type, each merged L5 list contained 400-950 compounds. See SI Figure S1-S2 for more details on reducing peak lists from raw data sets to final peak lists, containing compounds classified as L0-L4 for each sample type.

## 3.2 Number of classified compounds

Compounds, listed on the merged L5 lists, were checked manually on their right library identification, revised for multiple peak markers for identical compounds and classified to L2-

L4. These multiple peak marker occurring during automatically performed peak detection and deconvolution, where ChromaTOF can mark a single compound with multiple peak markers (Lu et al., 2008). After manual inspection, all compounds classified as L2 or L3 were, in addition to the initial automatic blank identification and filtration during DP, also manually checked against the blank samples. This is a necessary step to ensure that these compounds have not been overlooked by the automatic blank filtration and thus, not occur in sample blanks, or exceed an area factor of ≥ 100 compared to the sample blanks (Figure 2, A to reach B) (Röhler et al., 2020a). After comparison to new and in-house reference standards, the identity of several compounds could be confirmed and reached L1, which is the highest level of identification confidence with external standards (Figure 1). The distribution of L0-L4 compounds for samples from inner Oslofjord can be found in Table 2 and for lake Mjøsa in Table 3 respectively.

*Table 2: Overview of L0-L4 compounds, classified in samples from inner Oslofjord.*

| Sample type | L0 | L1 | L2 | L3 | L4 |
|---|---|---|---|---|---|
| Krill | 3 | 9 | 32 (30 PCBs) | 18 | 7 (3 unknown halogenated) |
| Northern shrimp | 2 | 8 | 39 (27 PCBs) | 11 | 17 (10 unknown halogenated) |
| Herring | 3 | 17 | 101 (94 PCBs) | 16 | 9 (6 unknown halogenated) |
| Atlantic cod liver | 1 | 10 | 55 (53 PCBs) | 6 | 18 (14 unknown halogenated) |
| Compounds classified | 9 | 44 | 227 | 49 | 51 |

PCB: Polychlorinated biphenyl

*Table 3: Overview of L0-L4 compounds, classified in samples from lake Mjøsa.*

| Sample type | L0 | L1 | L2 | L3 | L4 |
|---|---|---|---|---|---|
| Mysis | 2 | 3 | 7 (1 PCB) | 27 | 7 (3 unknown halogenated) |
| Zooplankton | 4 | 4 | 10 (1 PCB) | 31 | 14 (7 unknown halogenated) |
| Smelt small | 2 | 4 | 3 (1 PCB) | 4 | 7 (7 unknown halogenated) |
| Smelt large | 3 | 12 | 36 (30 PCBs) | 14 | 12 (8 unknown halogenated) |
| Vendace | 4 | 6 | 30 (25 PCBs) | 13 | 9 (4 unknown halogenated) |
| Brown trout | 4 | 9 | 46 (39 PCBs) | 20 | 9 (6 unknown halogenated) |
| Compounds classified | 19 | 38 | 132 | 109 | 58 |

In total, there are less compounds classified per sample than in previous SUS/NTS studies, which were carried out with air samples and the same GC×GC-LRMS system (Röhler et al., 2020a, Röhler et al., 2020b). The presented study used biota samples where compounds of interest could undergo biotransformation during metabolism and thus, the MS and/or SUS MS libraries utilised may be insufficient to identify these biotransformation products. This is why international co-operations and open-access databases are of great importance to improve SUS/NTS in biota. Additionally, biota sample data include a large amount of biogenic or endogenous compounds, which required filtrating during data prioritisation of findings in SUS/NTS. Due to the design of this study, which was missing a spatial trend possibility, a large number of compounds required sorting out during manual check of L2 and L3 compounds, especially a large number of non-polar compounds and/or hydrocarbons (Figure 2: A, to reach B). However, not everything detected in air samples has the potential to accumulate in biota.

Although many non-polar were sorted out, it was possible to identify compounds which were occurring in different sample types from their respective sampling site. This was visualised with Venn diagrams (VIB/UGent, 2020) for compounds classified as L0-L4 (Figure 3 and Figure 4) and discussed in the following sections.

## 3.3 Compounds identified in the Oslofjord food chain

The Venn diagram for samples from Oslofjord (Figure 3) visualises how many compounds are common in the four different sample types. In Table 4, common findings for samples from the inner Oslofjord food chain are summarised. Due to the large variety of different polychlorinated biphenyl (PCB) congeners for each degree of chlorination and possible coelution of several isomers, it was not possible to correct the detected PCBs for retention time (RT) shifts between the different sample types, and, thus, there might be missing or wrong common findings for PCBs. This includes all PCBs classified as L2 in Table 4 and Table 5. Compounds, L0-L4, detected only in one sample type, are presented in Table 5, and all compounds classified as L3 or L4 are presented in Table 8 or Table 9 respectively. A list with all detected and classified compounds can be found in the SI Excel-SI spreadsheet.

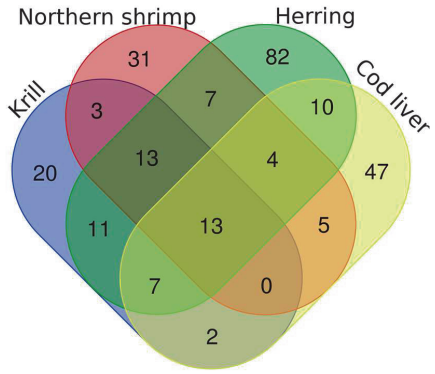


*Figure 3: Venn diagram for compounds classified as L0-L4 in samples from inner Oslofjord.*

As expected, it was possible to detect several legacy POPs in the samples from inner Oslofjord. Different sample types from the inner Oslofjord are used for different annual screening and monitoring studies, e.g. Screening program, Environmental Contaminants in an Urban Fjord or Contaminants in coastal waters of Norway (Norwegian Environmental Agency, 2020) The most dominant POP compound group in all samples types from inner Oslofjord were PCBs (see Table 2), eight of these PCBs were identified in all four sample types. Thus, the occurrence in the studied food chain is likely (see Table 4). The biomagnification of PCBs in the inner Oslofjord food chain is known and confirmed through the annual Urban Fjord monitoring (Ruus

et al., 2014). Even though the individual PCB congeners were not identified (classified as L2), except PCB-153 which was included as ISTD and the native compound confirmed (L0), the degree of chlorination could be determined. HexaPCBs were the largest sub-group of PCBs detected, supporting the fact that they are the congeners with the greatest bioconcentration potential. Chlorinated pesticides were also frequently identified and included compounds such as hexachlorobenzene (HCB), *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE), *o,p'/p,p'*-dichlorodiphenyldichloroethane (*o,p'/p,p'*-DDD), *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT), *cis/trans*-nonachlor, *cis/trans*-chlordane, dieldrin, hepatchloro *exo*-epoxide and mirex, of which all were identified as L1. In addition to these POPs, *o,p'/p,p'*-methoxychlor (L1), which are under revision to be included to the Stockholm convention on POPs, was detected together with its degradation product *p,p'*-methoxychlor-olefin (L2) (Johnson and Finley, 1980). Also a degradation product of DDE, 2-Chloro-1,1-bis(4-chlorophenyl)ethylene (*p,p'*-DDMU) could be identified. Furthermore, 14 halogenated compounds, five organo phosphorus flame retardants (PFRs), two halogenated natural products (HNPs) and seven other compounds not belonging to those groups could be identified as L1 or classified as L2. PCBs, polybrominated diphenyl ethers (PBDEs), DDE, polycyclic aromatic hydrocarbons (PAHs) and PFRs are content in the annual monitoring programme, which included the inner Oslofjord (Ruus et al., 2014, Green et al., 2014). Not all sample types of the current study were included in the monitoring reports, but biomagnification of PCBs from the inner Oslofjord is confirmed through monitoring programme (Ruus et al., 2014). Several PFRs were reported in biota samples from inner Oslofjord, 2-ethylhexyl-di-phenylphosphate (EHDPP) was detected in cod liver (Green et al., 2014), and tri(2-chloroethyl)phosphate (TCEP), tri(2-chloroisopropyl)phosphate (TCPP), tri(1,3-dichloro-2-propyl)phosphate (TDCP), tri(2-butoxyethyl)phosphate (TBEP) and EHDPP in blue mussel (Ruus et al., 2014). In this study, no PFRs were detected in cod liver. This is most likely due to higher detection limits in the used SUS/NTS method and analytical system, which was not optimised for the detection of PFRs. However, it was possible to identify TCEP (L1) and triphenyl phosphate (TPP, L1) in the herring and shrimp sample, as well as TCPP (L1) and two isomers of isopropylphenyl diphenyl phosphate (L2) in the herring sample. But herring and shrimp are not included in the monitoring reports. During the 2014 screening study, butylated hydroxytoluene (BHT) could be detected in all samples from the inner Oslofjord by gas chromatography with high-resolution mass spectrometry detection (GC-HRMS) (Thomas et al., 2015), but could not be identified with the SUS/NTS method and analytical system. Most likely due to higher detection limits for SUS/NTS, since this is a wide scope NT method and not an optimised method for the targeted

detection of BHT in these samples. The detection of PBDE-47 in all sample types from the inner Oslofjord was expected, since higher brominated PBDE, especially PBDE-99, undergo biotransformation to the more stable PBDE-47 (Benedict et al., 2007). Besides PBDE-47, one further TetraBDE could be identified in herring, and one PentaBDE in cod liver. Tonalide and galaxolide, two synthetic musk compounds, were compounds of interest and detected in cod liver from the inner Oslofjord during the Screening 2016 and 2017 programme. In this study from 2014, galaxolide was detected by GC-HRMS in northern shrimp, herring and cod liver, but only detected in krill by GC×GC-LRMS. Tonalide was detected in cod liver by GC-HRMS in the study from 2014, 2016 and 2017. However, by GC×GC-LRMS it was possible to identify tonalide in herring (L1), but not in cod liver. Diuron, a pesticide that inhibits photosynthesis, was identified most likely for the very first time in northern shrimp samples from the inner Oslofjord (L1). Diuron was included in the annual monitoring of coastal waters in 2014, but the monitoring included only cod liver and blue mussels, were diuron was below limit of detection in all samples (Green et al., 2014). Two isomers of 2-bromo-6-(3-bromo-prop-1-ynyl)-pyridine could be detected in northern shrimp (L2). This compound was previously detected in sediment from Oslofjord as L3 (Schlabach et al., 2017). All of the other L1 and L2 findings have to our knowledge not previously been detected in biota samples from the inner Oslofjord. The presented study is reporting qualitative data, which means if a compound is identified in a sample; no assumptions about a potential biomagnification can be drawn. However, as shown in Table 4, several compounds were present in the lower and higher levels of the food chain.

*Table 4: Overview of detected L0-L4 compounds, common in different sample types from inner Oslofjord.*

| Sample types | Common compounds | Compounds (classification level) |
|---|---|---|
| Krill, northern shrimp, herring, cod liver | 13 | PCB-153 (L0)<br>*p,p'*-DDE (L1)<br>TetraBDE-47 (L1)<br>Indole-5-aldehyde (L2)<br>1 TetraPCB (L2)<br>3 PentaPCB (L2)<br>2 HexaPCB (L2)<br>1 HeptaPCB (L2)<br>1 OctaPCB (L2)<br>1 Possible molecular formula (L4) |
| Krill, northern shrimp, herring | 13 | HCB (LO)<br>*p,p'*-Methoxychlor-olefin (L2)<br>2 TetraPCB (L2)<br>2 PentaPCB (L2)<br>1 HexaPCB (L2)<br>4 PAC (L3)<br>1 Aromatic (L3)<br>1 Possible molecular formula (L4) |
| Krill, herring, cod liver | 7 | *p,p'*-DDD (L1)<br>*cis*-Nonachlor (L1)<br>*trans*-Nonachlor (L1)<br>2 PentaPCB (L2)<br>1 HexaPCB (L2)<br>1 PAC (L3) |
| Northern shrimp, herring, cod liver | 4 | 2 HexaPCB (L2)<br>2 HeptaPCB (L2) |
| Krill, herring | 11 | *p,p'*-DDT (L0)<br>*cis*-Chlordane (L1)<br>Q1 (L1)<br>2 PentaPCB (L2)<br>2 HexaPCB (L2)<br>1 HeptaPCB (L2)<br>1 PAC (L3)<br>1 Phthalate (L3)<br>1 Polycyclic musk (L3) |
| Northern shrimp, herring | 7 | Triphenyl phosphate (TPP) (L1)<br>Tri(2-chloroethyl)phosphate (TCEP) (L1)<br>1 TetraPCB (L2)<br>2 HeptaPCB (L2)<br>1 PAC (L3)<br>1 Unknown halogenated (L4) |
| Krill, northern shrimp | 3 | 1 Aromatic (L3)<br>1 Possible molecular formula (L4)<br>1 Unknown halogenated (L4) |

| | | |
|---|---|---|
| Herring, cod liver | 10 | Dieldrin (L1)<br>1 TetraPCB (L2)<br>2 PentaPCB (L2)<br>3 HexaPCB (L2)<br>1 HeptaPCB (L2)<br>2 OctaPCB (L2) |
| Northern shrimp, cod liver | 5 | 3 HexaPCB (L2)<br>1 HeptaPCB (L2)<br>1 Unknown halogenated (L4) |
| Krill, cod liver | 2 | 1 HeptaPCB (L2)<br>1 PAC (L3) |

*Table 5: Summary of detected L0-L4 compounds, only detected in one sample type from inner Oslofjord.*

| Sample type | Number of compounds | Compounds (classification level) |
|---|---|---|
| Krill | 20 | *o,p*'-DDD (L1)<br>Galaxolide (L1)<br>1 TetraPCB (L2)<br>6 HexaPCB (L2)<br>1 HeptaPCB (L2)<br>1 Aromatic (L3)<br>6 PAC (L3)<br>1 Possible molecular formula (L4)<br>2 Unknown halogenated (L4) |
| Northern shrimp | 31 | 3,5-Dichlorobenzenamine (L1)<br>*p*-Toluenesulfonamide (L1)<br>Diuron (L1)<br>Isomer of dichlorobenzenamine (L2)<br>2 Isomers of 2-bromo-6-(3-bromo-prop-1-ynyl)-pyridine (L2)<br>2-Bromophenylacetonitrile (L2)<br>Isomer of Phenol, 4-chloro-5-methyl-2-nitro- (L2)<br>Isomer of 2-bromo-6-chloro-4-fluoroaniline (L2)<br>Isomer of 3-chloro-2,6-dibromo-4-fluoroaniline (L2)<br>3,5-di-tert-butyl-4-hydroxybenzaldehyde (L2)<br>Octocrylene (L2)<br>3-Methyl-2,4,6-tribromoaniline (L2)<br>2 PentaPCB (L2)<br>1 HexaPCB (L2)<br>2 Aromatic (L3)<br>1 PAC (L3)<br>1 Phthalate (L3)<br>4 Possible molecular formula (L4)<br>7 Unknown halogenated (L4) |
| Herring | 82 | DDMU (L1)<br>Tris(2-chloroisopropyl)phosphate (TCPP) (L1)<br>MHC-1 (L1) |

| | | |
|---|---|---|
| | | Heptachlor *exo* epoxide (L1)<br>2,5-Dichlorobenzenamine (L1)<br>*trans*-Chlordane (L1)<br>Tonalide (L1)<br>3 isomers of dichlorophenyl-isocyanate (L2)<br>2 isomers of isopropylphenyl diphenyl phosphate (L2)<br>2-chloro-4-hydroxybenzonitrile (L2)<br>1 Isomer of *p*-quaterphenyl (L2)<br>1 TriPCB (L2)<br>9 TetraPCB (L2)<br>12 PentaPCB (L2)<br>17 HexaPCB (L2)<br>13 HeptaPCB (L2)<br>3 OctaPCB (L2)<br>1 TetraBDE (L2)<br>1 Polycyclic musk (L3)<br>2 Aromatic (L3)<br>1 Halogenated (L3)<br>2 PAC (L3)<br>1 Possible molecular formula (L4)<br>5 Unknown halogenated (L4) |
| Cod liver | 47 | *p,p'*-Methoxychlor (L1)<br>*o,p'*-Methoxychlor (L1)<br>Mirex (L1)<br>PCB-209 (L1)<br>2 TetraPCB (L2)<br>5 PentaPCB (L2)<br>3 HexaPCB (L2)<br>7 HeptaPCB (L2)<br>5 OctaPCB (L2)<br>1 NonaPCB (L2)<br>1 PentaBDE (L2)<br>3 Halogenated (L3)<br>1 PAC (L3)<br>3 Possible molecular formula (L4)<br>12 Unknown halogenated (L4) |

## 3.4 Compounds identified in the lake Mjøsa food chain

As was constructed for the Oslofjord samples, a Venn diagram (Figure 4) was constructed to illustrate common compounds detected in the samples from lake Mjøsa and were summarised in Table 6.. In order to create the Venn diagram, findings from smelt small and smelt large were combined to form one sample type. As with the results from inner Oslofjord, the findings for PCBs could be affected by missing or wrong common finding due to RT shifts between the different sample types. All remaining compounds, which were detected in only one sample type, are presented in Table 7 for L0-L4, and all compounds classified as L3 are presented in

Table 8 and Table 9 for L4 compounds respectively. The complete list of all compounds classified as L0-L4 can be found in Excel-SI.

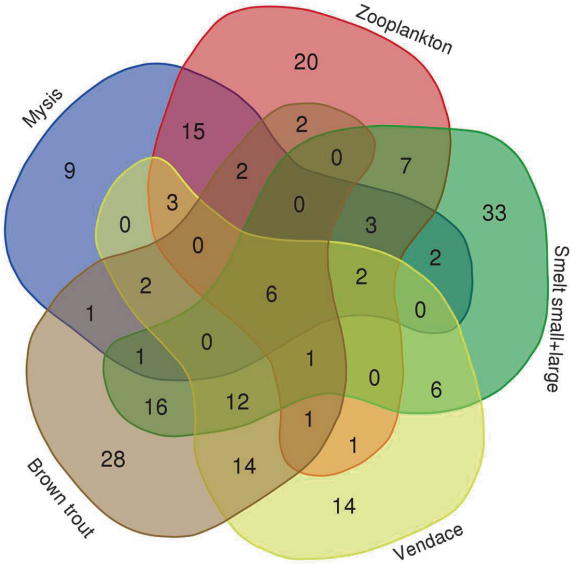


*Figure 4: Venn diagram for compounds classified as L0-L4 in samples from lake Mjøsa.*

Similar to inner Oslofjord, it was expected to detect several legacy POPs in the food chain from lake Mjøsa. The largest group of POPs are PCBs, with various degree of chlorination (tetra- octa chlorinated PCBs), and are found in all samples from the food chain. During annual screening and monitoring studies (Fjeld et al., 2014, Thomas et al., 2015), the biomagnification of PCBs through the food chain from lake Mjøsa is likely, since higher concentrations are found in higher trophic levels compared to lower trophic levels. Other detected POPs, like *o,p'/p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, HCB, *cis/trans*-nonachlor and *cis*-chlordane, could also be detected as L1, but were not included in the annual monitoring. PBDEs, which are part of the annual monitoring, could also be detected in the current study. PBDE-47 (L1) could be detected in smelt, vendace and trout together with further tetra, penta and/or hexa brominated PBDEs (L2) (see Table 6, Table 7 or Excel-SI). Besides legacy POPs and PBDEs, four other halogenated compounds (L1), four PFRs (L1 and L2), three PAHs (L1), 12 aromatic compounds (L1 and L2) as well as galaxolide (L1), tonalide (L1) and caffeine (L1) could be detected and identified as L1 or L2 compounds (see Table 6, Table 7 or Excel-SI for details). Galaxolide and tonalide are compounds of interest in the screening study of 2017 (Konieczny et al., 2018), but only galaxolide and was detected in roach. The samples in the current study were not included in the screening study in 2017. However, in the screening study from 2014 (Thomas et al., 2015),

galaxolide could be identified in mysis, vendace and smelt by GC-HRMS, but no occurrence of tonalide is reported. The GC×GC analysis of the study from 2014 detected galaxolide in smelt and zooplankton, and, in addition, tonalide could be detected in smelt. In contrast to studies from Oslofjord were PFRs and diuron not yet a part of a study from lake Mjøsa. It is not known if the detected PFRS TCEP (L1), TPP (L1), two isomers of isopropylphenyl diphenyl phosphate (L2) or diuron (L1) were detected previously in samples from lake Mjøsa. As for samples from Oslofjord, it is not known if the remaining L1 and L2 compounds were detected previously in biota samples from lake Mjøsa.

*Table 6: Overview of detected L0-L4 compounds, common in different sample types from lake Mjøsa.*

| Sample types | Common compounds | Compounds (classification level) |
|---|---|---|
| Mysis, zooplankton, smelt small and large, vendace, brown trout | 6 | *p,p'*-DDE (L0 and L1)<br>PCB 153 (L0)<br>*p,p'*-DDT (L0)<br>2 Isomers of cyanoquinoline (L2)<br>1 Unknown halogenated (L4) |
| Mysis, zooplankton, smelt small and large, vendace | 2 | Biphenyl (L1)<br>1 Possible molecular formula (L4) |
| Zooplankton, smelt small and large, vendace, brown trout | 1 | HCB (L0) |
| Mysis, zooplankton, smelt small and large | 3 | 1 PAC (L3)<br>1 Phthalate (L3)<br>1 Possible molecular formula (L4) |
| Mysis, zooplankton, vendace | 3 | Isomer of *p*-quaterphenyl (L2)<br>2 PAC (L3) |
| Mysis, zooplankton, brown trout | 2 | 2 PAC (L3) |
| Mysis, smelt small and large, brown trout | 1 | 1 HexaPCB (L2) |
| Mysis, vendace, brown trout | 2 | 1 PAC (L3)<br>1 Butylphosphonic acid ester (L3) |
| Zooplankton, vendace, brown trout | 1 | 1 PAC (L3) |
| Smelt small and large, vendace, brown trout | 12 | *o,p'*-DDT (L1)<br>*p,p'*-DDD (L0 and L1)<br>Tri(2-chloroethyl) phosphate (L1)<br>*trans*-Nonachlor (L1)<br>TetraBDE-47 (L1)<br>3 PentaPCB (L2)<br>3 HexaPCB (L2)<br>1 HeptaPCB (L2) |

| | | |
|---|---|---|
| Mysis, zooplankton | 15 | Isomer of *p*-quaterphenyl (L2)<br>2-Hydroxy-9-fluorenone (L2)<br>2,4,6-tris(1,1-dimethylethyl)phenol (L2)<br>9 PAC (L3)<br>2 Phthalate (L3)<br>1 Polycyclic musk (L3) |
| Mysis, smelt small and large | 2 | 1 PAC (L3)<br>1 Unknown halogenated (L4) |
| Mysis, brown trout | 1 | 1 Aromatic (L3) |
| Zooplankton, smelt small and large | 7 | Galaxolide (L1)<br>4,6-di-tert-Butyl-m-cresol (L2)<br>4 PAC (L3)<br>1 Unknown halogenated (L4) |
| Zooplankton, vendace | 1 | 1 Unknown halogenated (L4) |
| Zooplankton, brown trout2 | 2 | 1 PAC (L3)<br>1 Unknown halogenated (L4) |
| Smelt small and large, vendace | 6 | 1 PentaPCB (L2)<br>1 HexaPCB (L2)<br>3 HeptaPCB (L2)<br>1 Unknown halogenated (L4) |
| Smelt small and large, brown trout | 16 | *cis*-Nonachlor (L1)<br>Triphenyl phosphate (L1)<br>1 TetraPCB (L2)<br>1 PentaPCB (L2)<br>4 HexaPCB (L2)<br>3 HeptaPCB (L2)<br>1 TetraBDE (L2)<br>1 PentaBDE (L2)<br>1 Phthalate (L3)<br>1 Possible molecular formula (L4)<br>1 Unknown halogenated (L4) |
| Vendace, brown trout | 14 | 1 Isomer of heptachlor (L2)<br>1 PentaPCB (L2)<br>1 HexaPCB (L2)<br>1 OctaPCB (L2)<br>1 PentaBDE (L2)<br>1 Halogenated (L3)<br>3 PAC (L3)<br>1 Phthalate (L3)<br>1 Butylphosphonic acid ester (L3)<br>2 Possible molecular formula (L4)<br>1 Unknown halogenated (L4) |

*Table 7: Summary of detected L0-L4 compounds, only detected in one sample type from lake Mjøsa.*

| Sample type | Number of compounds | Compounds (classification level) |
|---|---|---|
| Mysis | 9 | 2,4,6-trimethylbenzophenone (L1)<br>4 PAC (L3)<br>1 Butylphosphonic acid ester (L3)<br>2 Possible molecular formula (L4)<br>1 Unknown halogenated (L4) |
| Zooplankton | 20 | Azobenzene (L1)<br>Benzenamine, 2,5-dichloro (L1)<br>Isomer of isopropylphenyl diphenyl phosphate (L2)<br>N-(Phenethyl)phenylacetamide (L2)<br>1 HexaPCB (L2)<br>4 PAC (L3)<br>1 Phthalate (L3)<br>2 Polycyclic musk (L3)<br>5 Possible molecular formula (L4)<br>3 Unknown halogenated (L4) |
| Smelt small and large | 33 | Caffeine (L1)<br>Fluorene (L1)<br>Tonalide (L1)<br>Diuron (L1)<br>5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine (L2)<br>3,5-di-tert-Butyl-4-hydroxybenzaldehyde (L2)<br>1 TetraPCB (L2)<br>1 PentaPCB (L2)<br>3 HexaPCB (L2)<br>2 HeptaPCB (L2)<br>1 OctaPCB (L2)<br>1 Aromatic (L3)<br>1 Halogenated (L3)<br>3 PAC (L3)<br>1 Phthalate (L3)<br>3 Polycyclic musk (L3)<br>1 Possible molecular formula (L4)<br>9 Unknown halogenated (L4) |
| Vendace | 14 | 3 PentaPCB (L2)<br>4 HexaPCB (L2)<br>3 HeptaPCB (L2)<br>1 PAC (L3)<br>1 Phthalate (L3)<br>2 Possible molecular formula (L4) |

| | | |
|---|---|---|
| Brown trout | 28 | *cis*-Chlordane (L1)<br>Octachlorostyrene (L1)<br>2 TetraPCB (L2)<br>7 PentaPCB (L2)<br>2 HexaPCB (L2)<br>4 HeptaPCB (L2)<br>2 OctaPCB (L2)<br>1 HexaBDE (L2)<br>1 Halogenated (L3)<br>2 PAC (L3)<br>3 Phthalate (L3)<br>2 Unknown halogenated (L4) |

## 3.5 Summary for Level 3 compounds

Tentative candidates, L3 compounds, were grouped into compound classes. The largest class group of compounds are PAC (polyaromatic compounds) and a few other compounds per compound class as shown in Table 8.

*Table 8:Nnumbers of L3 compounds per compound class.*

| | Krill | Northern shrimp | Herring | Cod liver | Mysis | Zooplankton | Smelt small and large | Vendace | Brown trout |
|---|---|---|---|---|---|---|---|---|---|
| PAC | 13 | 6 | 9 | 3 | 20 | 24 | 10 | 8 | 10 |
| Aromatic | 3 | 4 | 3 | - | 1 | - | 1 | - | 1 |
| Polycylic musks | 1 | - | 2 | - | 1 | 3 | 3 | - | - |
| Phthalates | 1 | 1 | 1 | | 3 | 4 | 3 | 2 | 5 |
| Halogenated | - | - | 1 | 3 | - | - | 1 | 1 | 2 |
| Buthylphosphonic acid esters | - | - | - | - | 2 | - | | 2 | 2 |
| Isomer of dichlorophenyl-isocyanate | - | - | 3 | - | - | - | - | - | - |

## 3.6 Summary for Level 4 compounds

There are two groups of compounds, which were classified as L4. One group are compounds which were identified with a potential molecular formula, the other group are halogenated compounds without match in the used MS libraries (unknown halogenated) (Table 9). For these compounds, a tentative content of chlorine and/or bromine and an approximate molecular weight could be extracted from the given LRMS spectra (see Excel-SI).

*Table 9: Numbers of L4 compounds per compound group.*

| | Krill | Northern shrimp | Herring | Cod liver | Mysis | Zooplankton | Smelt small and large | Vendace | Brown trout |
|---|---|---|---|---|---|---|---|---|---|
| Possible molecular formula | 4 | 7 | 3 | 4 | 4 | 7 | 4 | 5 | 3 |
| Unknown halogenated | 3 | 10 | 6 | 14 | 3 | 7 | 15 | 4 | 6 |

# 4 Conclusions

The GC×GC-LRMS SUS/NTS part of the Norwegian Environmental Agency Screening program of 2014 revealed several new contaminants in the biota food chain from the inner Oslofjord and lake Mjøsa, Norway. These, and previous NTS studies, shows the importance of SUS/NTS studies for the early detection of potential new CECs in these food chains. Since this study is reporting qualitative data, the findings should be followed up by quantitative targeted methods to evaluate their fate or potential hazard to the respective environment of lake Mjøsa or Oslofjord. The sample preparation workflow was combining the freezing protein/lipid procedure and GPC, as suggested by NORMAN NTS WS (2018) for low fat and high fat/large samples for SUS/NTS in biota. In order to avoid to exceed the chromatographic capacity of the used GC×GC-LRMS analytical system, the freezing and GPC procedure was combination with column chromatography for further clean-up.

Furthermore, for more successful SUS/NTS studies, the design of these studies should be optimised. To enable the filtration of endogenous/biogenic compounds, samples should be taken with the possibility for spatial trend analysis. This means, samples should be taken from a less or ideally non-contaminated site and compared to samples from a more affected/contaminated sampling site. It should be kept in mind that these samples should be of same matrix type for filtration of endogenous/biogenic compounds. In addition, a larger suspect list for biota, including endogenous/biogenic compounds should be created for a more comprehensive and successive SUS in biota.

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# Supplementary Material biota GC×GC

The Excel-SI document for the biota GC×GC manuscript can be found on NILUs server:
https://nilu365.sharepoint.com/:f:/s/Project-MILK-NMBU/EiiNOoQ3B9lIu1EawVdzpg4BWQZdVuZSoLWQKHvO_wBcag?e=JBimHD

## 1. Sample amounts used for extraction

*Table S1: Sample amounts used for extraction.*

| Sample type | Lipid contend [%] | Sample amount [g] | extracted lipid/ sample [g] |
|---|---|---|---|
| Cod liver | 32.34 | 0.62 | 0.201 |
| Cod liver | 54.8 | 0.34 | 0.186 |
| Cod liver | 47.3 | 0.42 | 0.199 |
| Cod liver | 55.6 | 0.36 | 0.200 |
| Cod liver | 32.5 | 0.64 | 0.208 |
| Krill | 0.74 | 5.58 | 0.041 |
| Krill | 0.59 | 5.41 | 0.032 |
| Krill | 0.44 | 0.99 | 0.004 |
| Krill | 0.77 | 4.43 | 0.034 |
| Krill | 0.58 | 4.95 | 0.029 |
| Zooplankton EPI | 0.1 | 1.87 | 0.002 |
| Zooplankton EPI | 0.2 | 2.37 | 0.005 |
| Zooplankton EPI | 2.3 | 1.36 | 0.031 |
| Zooplankton Hypo | 2.47 | 1.26 | 0.031 |
| Zooplankton Hypo | 4.96 | 2.08 | 0.103 |
| Vendace | 2.92 | 7.11 | 0.208 |
| Vendace | 2.63 | 3.13 | 0.082 |
| Vendace | 2.45 | 3.71 | 0.091 |
| Vendace | 2.22 | 6.88 | 0.153 |
| Vendace | 2.63 | 3.09 | 0.081 |
| Mysis | 2.34 | 1.88 | 0.044 |
| Mysis | 2.31 | 1.96 | 0.045 |
| Mysis | 2.57 | 2.66 | 0.068 |
| Mysis | 2.29 | 2.58 | 0.059 |
| Mysis | 2.68 | 2.48 | 0.066 |
| Northern shrimp | 1 | 9.20 | 0.092 |
| Northern shrimp | 0.83 | 11.39 | 0.095 |
| Northern shrimp | 0.88 | 8.88 | 0.078 |
| Northern shrimp | 0.91 | 9.69 | 0.088 |
| Northern shrimp | 0.92 | 5.26 | 0.048 |
| Herring | 5.76 | 4.34 | 0.250 |
| Herring | 1.32 | 16.35 | 0.216 |
| Herring | 4.68 | 5.61 | 0.263 |
| Herring | 8.33 | 2.92 | 0.243 |

| | | | |
|---|---|---|---|
| Herring | 5.17 | 9.66 | 0.499 |
| Smelt large | 2.37 | 13.89 | 0.329 |
| Smelt large | 1.32 | 1.89 | 0.025 |
| Smelt large | 2 | 7.44 | 0.149 |
| Smelt large | 0.64 | 6.74 | 0.043 |
| Smelt large | 0.66 | 3.25 | 0.021 |
| Smelt small | 0.54 | 2.37 | 0.013 |
| Smelt small | 0.57 | 2.60 | 0.015 |
| Smelt small | 0.69 | 3.07 | 0.021 |
| Smelt small | 0.25 | 2.9 | 0.007 |
| Smelt small | 0.32 | 2.55 | 0.008 |
| Brown trout | 1.18 | 7.93 | 0.094 |
| Brown trout | 2.18 | 3.03 | 0.066 |
| Brown trout | 0.82 | 12.34 | 0.101 |
| Brown trout | 4.6 | 5.45 | 0.251 |
| Brown trout | 2.09 | 6.84 | 0.143 |

*Table S2: Size, sex and liver weight of cod caught in the Inner Oslofjord.*

| Fish No. | Length (cm) | Weight (kg) | Sex (M/F) | liver weight (g) |
|---|---|---|---|---|
| 1 | 54 | 1.414 | F | 34 |
| 2 | 47 | 1.232 | F | 43 |
| 3 | 42 | 0.759 | M | 26.4 |
| 4 | 41 | 0.753 | F | 22.5 |
| 5 | 49 | 0.976 | F | 21.5 |

*Table S3: Size of herring caught in the Inner Oslofjord.*

| Fish no | length (cm) | weight (g) | sex |
|---|---|---|---|
| 1 | 29,5 | 160 | female |
| 2 | 29,0 | 154 | male |
| 3 | 28,2 | 163 | male |
| 4 | 29,3 | 131 | female |
| 5 | 29,0 | 181 | female |

## 2. Chemicals, standards and equipment

*Table S4: Used chemicals and equipment.*

| Chemical/ Equipment | Purchased |
|---|---|
| Acetone | VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway |
| *n*-Hexane | VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway |
| Cyclohexane | VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway |
| Ethyl acetate | SupraSolv, for GC ECD and FID, Merck, Darmstadt, Germany |
| Acetonitrile | LiChrosolv, isocratic grade for LC, Merck, Darmstadt, Germany |
| Toluene | EMSURE® for analysis, Merck, Darmstadt, Germany |
| Isooctane | EMSURE® for analysis, Merck, Darmstadt, Germany |
| Extran® | Merck, Darmstadt, Germany |
| Sodium sulphate | anhydrous, EMSURE® for analysis, Merck, Darmstadt, Germany |
| Discovery DSC-18 | Supelco, Bellefonte, PA, USA |
| Supel™QuE Z-Sep$^{+}$ | Supelco, Bellefonte, PA, USA |
| Florisil® 60-100 Mesh | Sigma Aldrich Chemie GmbH, Germany |
| Citric acid | anhydrous, puriss., Sigma Aldrich Chemie GmbH, Germany |
| Cotton | Mediq Norge, Norway |
| KNF vacuum pump | Laboport, N86KT.18, Village-Neuf, France |
| Nitrogen gas | 5.0 quality, Nippon gases Norge AS, Oslo, Norway |

All used glassware was washed with Extran®, heated to 450 °C for 8 h and rinsed with acetone prior use.
Florisil and sodium sulphate were heated to 450 °C for 8 h prior use.
Cotton was Soxhlet extracted with n-hexane for 24 h, rinsed with acetone and dried prior use.

Internal standards were used for method quality control.
$^{13}$C-labeled standards were purchased from Wellington Laboratories, Guelph, ON, Canada.
$^{2}H_{10}$-labeled phenanthrene was purchased from Chiron AS, Trondheim, Norway.
1,2,3,4-Tetrachloronaphthalene was purchased from Ultra-Scientific, North Kingstown, RI, USA

*Table S5: Spiking amounts ISTDs.*

| Internal standard | Spiking amount [ng] |
|---|---|
| $^{2}H_{10}$ phenanthrene | 2.08 |
| $^{13}C_{6}$ HCB | 4.78 |
| $^{13}C_{12}$ *p,p'*-DDT | 16.12 |
| $^{13}C_{12}$ PCB-153 | 12.20 |
| $^{13}C_{6}$ HBB | 21.14 |
| $^{13}C_{12}$ PBDE-28 | 5.28 |
| $^{13}C_{12}$ PBDE-47 | 5.22 |
| $^{13}C_{12}$ PBDE-99 | 5.30 |
| Recovery standard | |
| 1,2,3,4-Tetrachloronaphthalene (TCN) | 7.96 |

## 3. GPC clean-up

Extracts were diluted to 3 mL in GPC mobile phase solvent (cyclohexane/ ethyl acetate (1:1, v/v) and injected in a Waters Envirogel GPC system (2 µm particle filter, 4.6 x 30 mm guard column and 19 x 150 mm + 19x300 mm main column) with a flow of 5 mL/ min. The typical fraction for POP analysis (approx. 14-30 min) was adjusted to 12-35 min. Potential lipids in the collected fraction will be removed by the following clean-up step.

# Reducing peak lists from raw data to final L0-L4 list

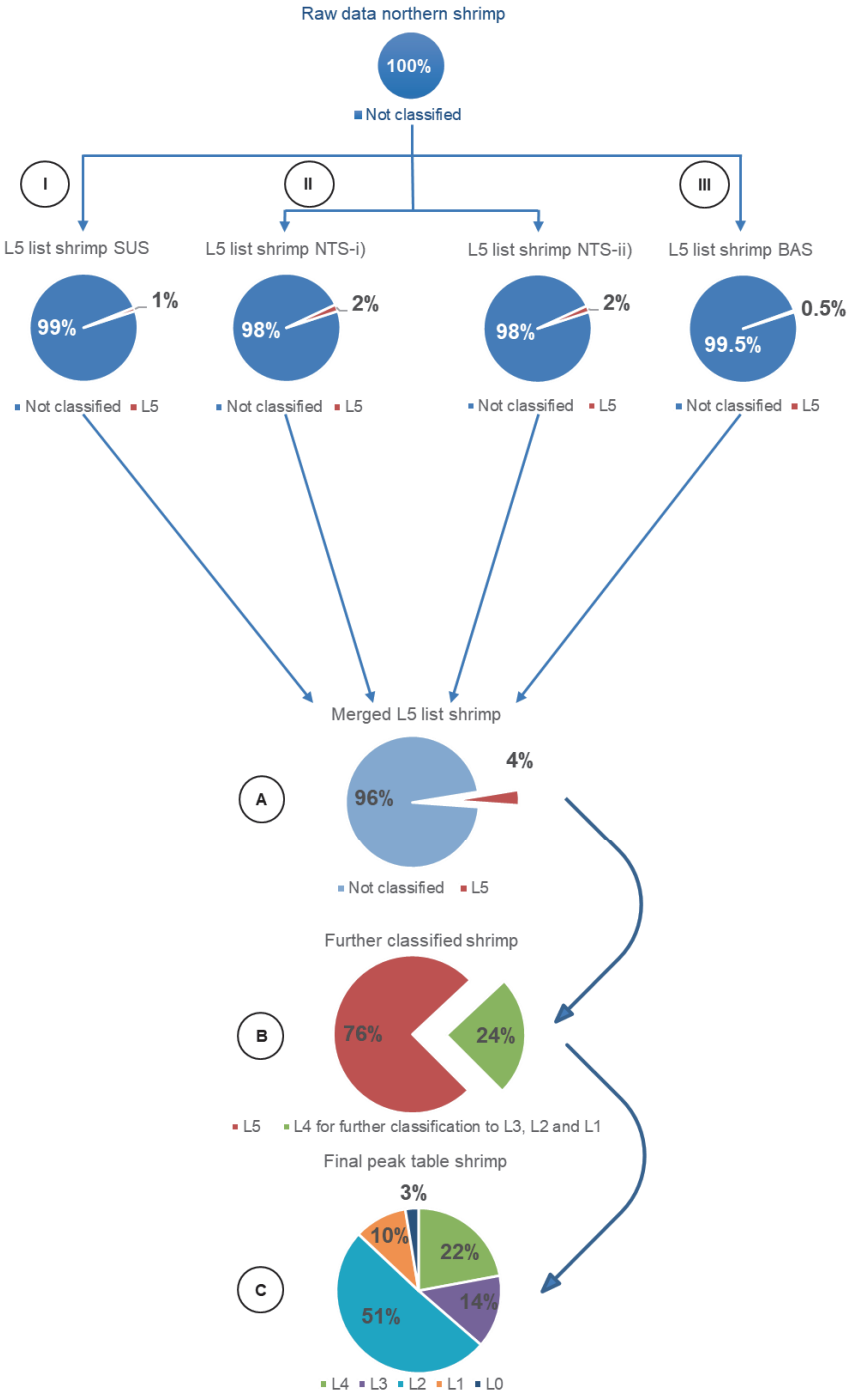


*Figure S1: Peak reduction during SUS/NTS/BAS for northern shrimp.*

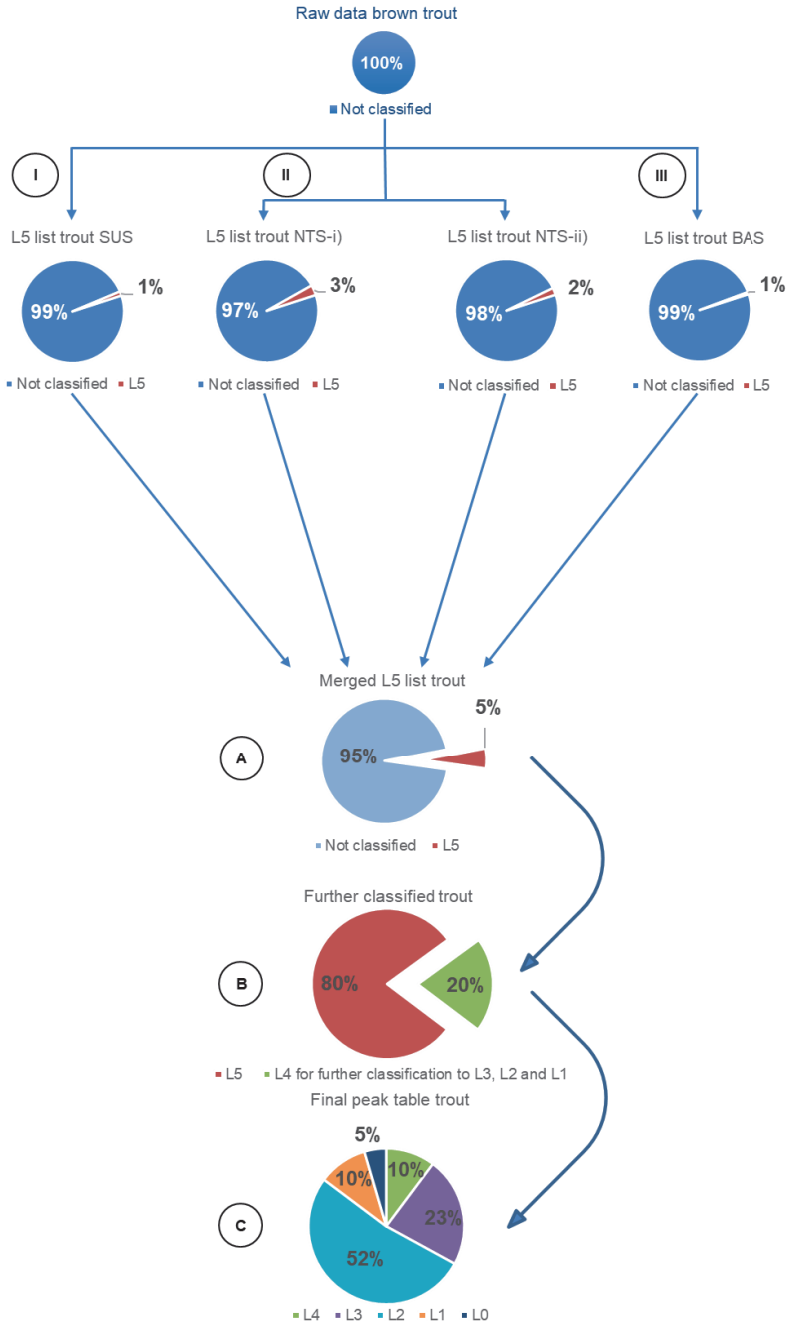


*Figure S2: Peak reduction during SUS/NTS/BAS for brown trout.*

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