

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.

- 5 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.
- 10 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

- 15 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
- 20 (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
- 25 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.

25 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).

- 5 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

- 10 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

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

Equation S1

$$t_{1/2}(\text{days}) = \frac{\ln 2}{k_{RA}}$$

Equation S2

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

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

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

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

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

T_A : Sampling temperature in Kelvin [K]

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

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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

- 25 °C and a OH-radical concentration of $1.5\text{E}6 \text{ OH cm}^{-3}$ (column 3, Table S3)

As described in section 2.5 of the manuscript, we assumed a OH-radical concentration of $6.0 \times 10^3 \text{ OH cm}^{-3}$ at a maximum sampling temperature of $T = -2.4^\circ \text{C}$ 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 Khalil's (2004) model values for OH-radical concentration in December ($5 \times 10^4 \text{ OH cm}^{-3}$) (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

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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.

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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 <i>p,p'</i> -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

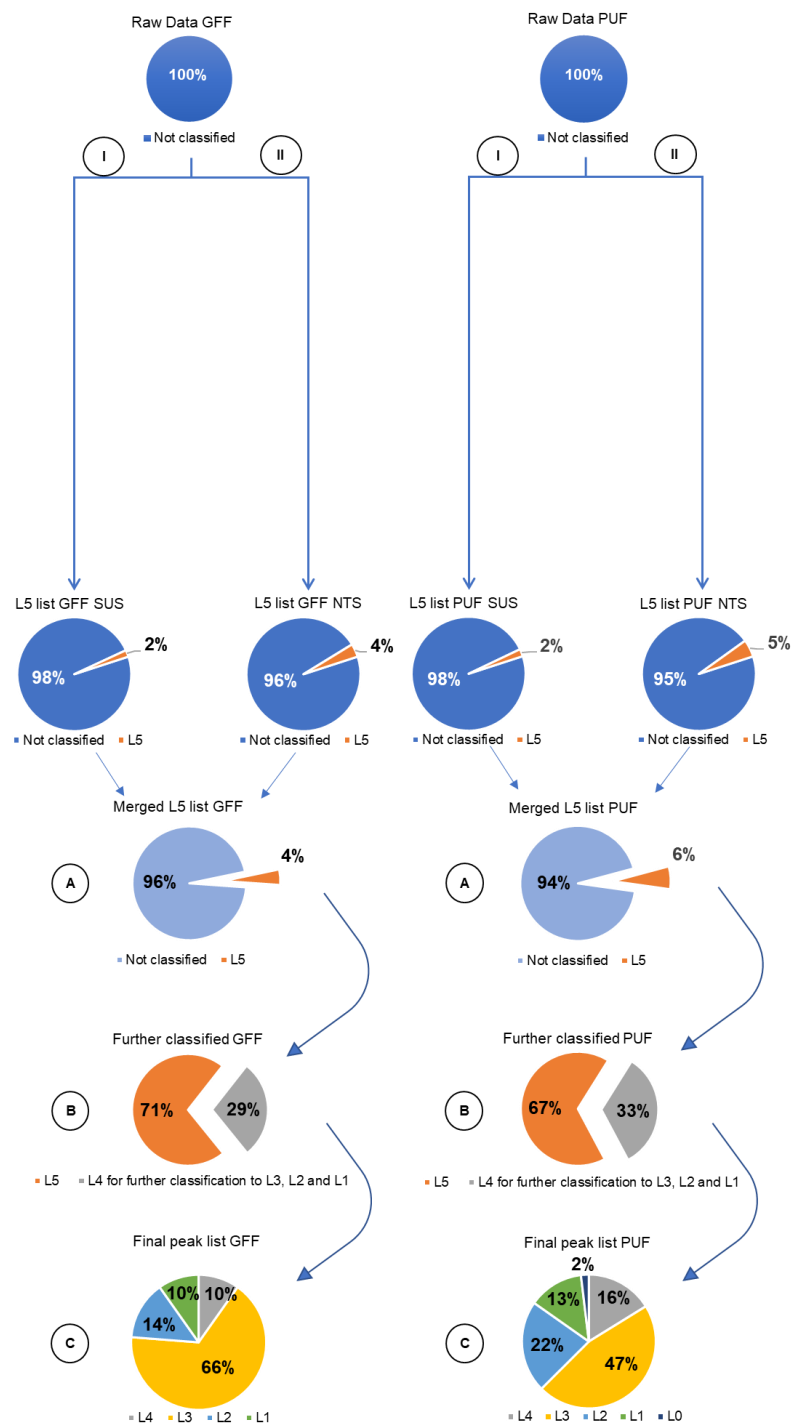


Figure S1: Peak reduction during data processing for GFF and PUF sample.

Table S2: Summary of PBT criteria.

	REACH (European Parliament, 2018)	Stockholm convention (UNEP, 2009)
Persistent (P)	$t_{1/2}$ water fresh/marine $\geq 960/1440$ h (40/60 days) (vP ¹ ≥ 1440 h (60 days)) $t_{1/2}$ soil ≥ 2880 h (120 days) (vP ¹ ≥ 4320 h (180 days)) $t_{1/2}$ sediment fresh/marine $\geq 2880/4320$ h (120/180 days) (vP ¹ ≥ 4320 h (180 days))	$t_{1/2}$ water ≥ 2 months (1440 h) $t_{1/2}$ soil ≥ 6 months (2880 h) $t_{1/2}$ sediment ≥ 6 months (2880 h)
Bioaccumulative (B)	$BCF^2 \geq 2000$ (vB ³ ≥ 5000)	BCF^2 or $BAF^4 \geq 5000$ Or $\log K_{ow} \geq 5$
Toxic (T)	NOEL or EC10 ≤ 0.01 mg/ L Or Carcinogen cat. 1A, 1B or 2 Or mutagenic cat. 1A or 1B Or reproduction toxic cat. 1A, 1B or 2 Or evidence for chron. tox. STOT RE cat. 1 or 2	Evidence of adverse effects to human health, or toxicity or ecotoxicity indicate potential for damage to human health or the environment
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: $t_{1/2air} \geq 2$ days

¹ vP: very persistent; ² BCF: bioconcentration factor; ³ vB: very bioaccumulative; ⁴ BAF: bioaccumulation factor;

⁵ not applicable

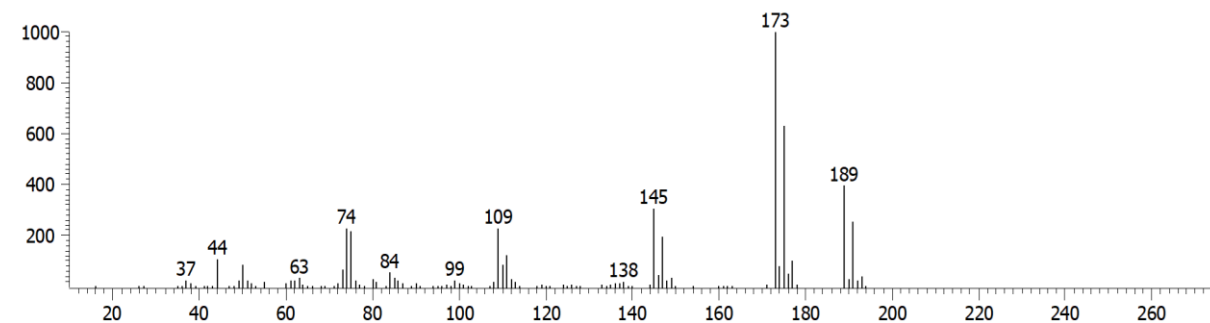
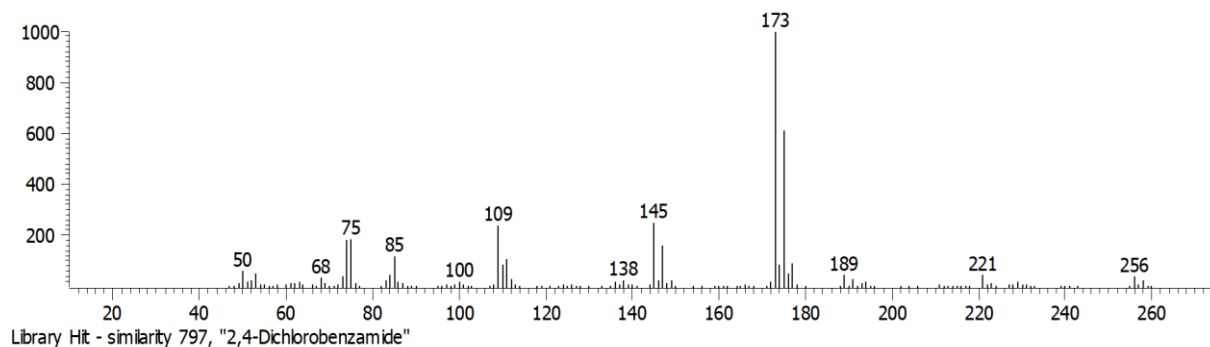
Table S3: Half-life in air: non-adjusted values from EPIsuite and adjusted for Arctic conditions (Eq.S1-S2), for selected compounds.

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
<i>p,p'</i> -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[<i>ghi</i>]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
<i>m</i> -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 GFF	256.0169	C ₁₁ H ₁₀ Cl ₂ N ₂ O	C ₁₁ H ₁₀ Cl ₂ N ₂ O
B#11108 GFF	230.0134	C ₈ H ₈ Cl ₂ N ₄	m/z 230, dichloro-fragment C ₁₀ H ₁₀ Cl ₂ NO
C#4444 PUF	299.8372	C ₇ H ₅ Br ₂ ClO C ₆ H ₅ Br ₂ O ₂ P	C ₇ H ₅ Br ₂ ClO
D#5672 PUF	220.0053	C ₉ H ₁₀ Cl ₂ O ₂ C ₈ H ₁₀ ClO ₃ P	C ₉ H ₁₀ Cl ₂ O ₂

Peak True - sample "16_733 GFF ArticAir 2xGFF 16_192+195 3uL_1", peak 9842, at 2482.5 , 1.640 sec , sec



Peak True - sample "Arctic GFF 16_0733-G_2", #9842 unknown LRMS NOT Isomer to 3,4-Dichloropropiophenone, at 2417.07 s, 1.806 s, Area (Abundance)

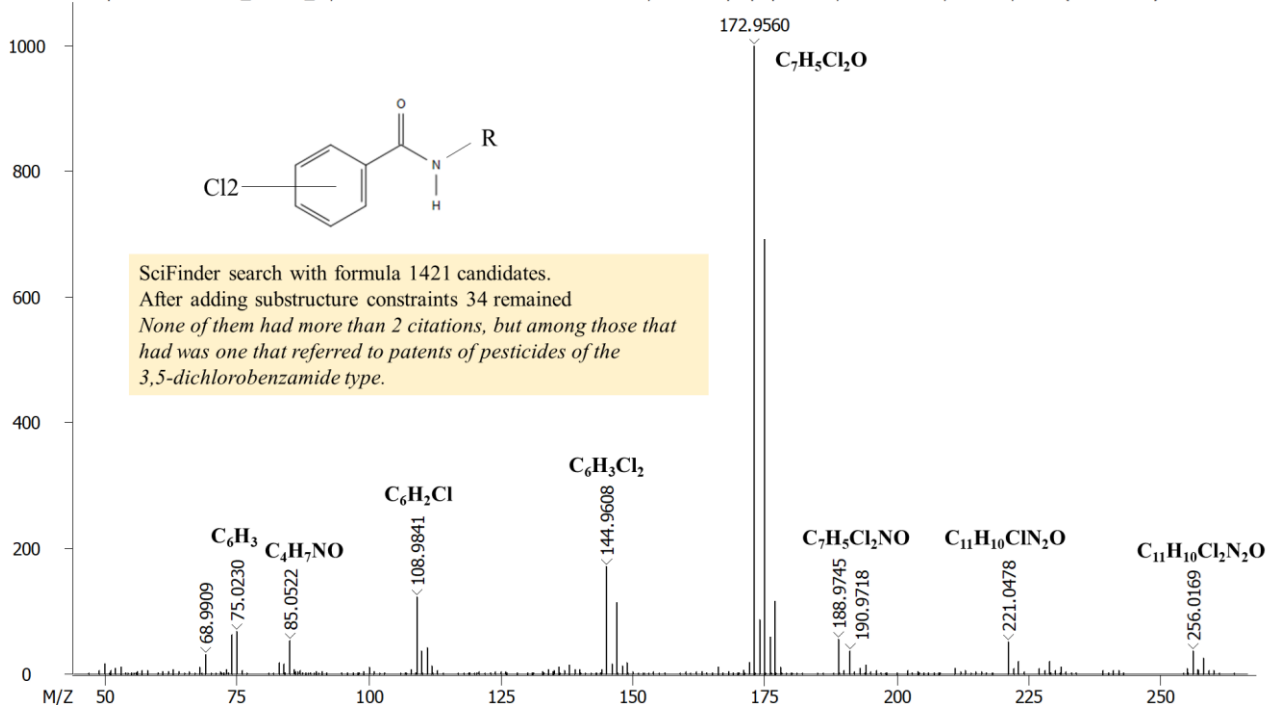
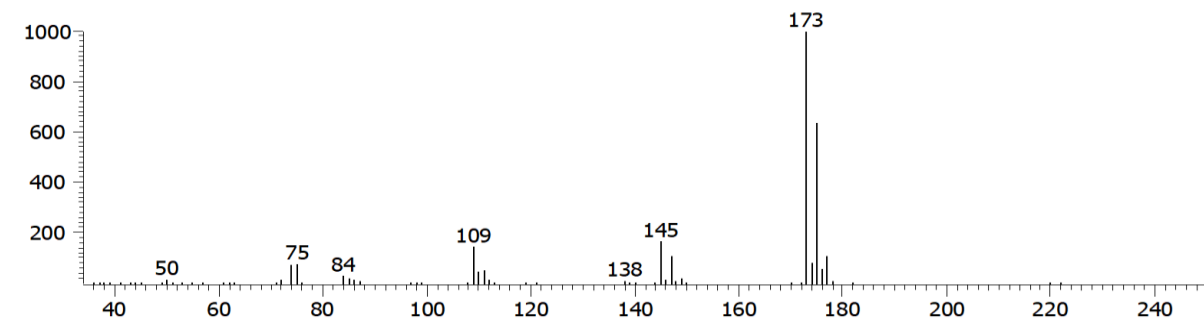
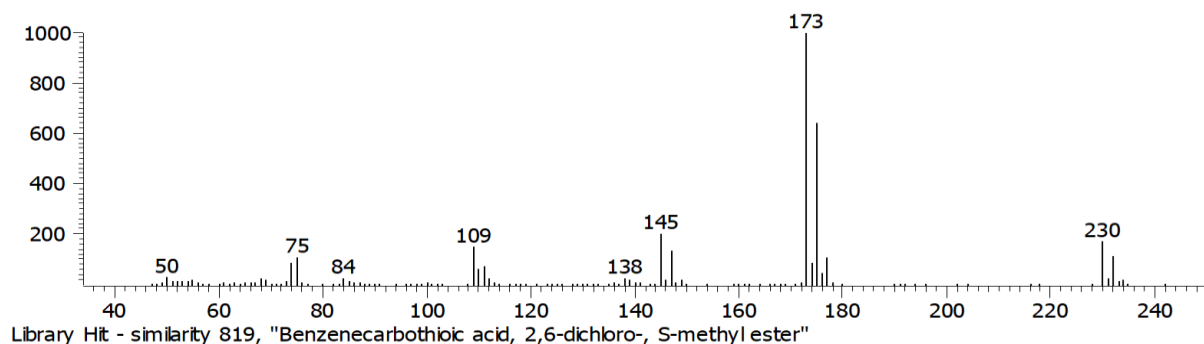


Figure S2: LRMS and HRMS spectra of unknown halogenated compound A in GFF.

Peak True - sample "16_733 GFF ArticAir 2xGFF 16_192+195 3uL_1", peak 11108, at 2734.5 , 1.720 sec , sec



Peak True - sample "Arctic GFF 16_0733-G_2", #11108 unknown LRMS, at 2664.88 s, 1.882 s (Spec # 149747), Area (Abundance)

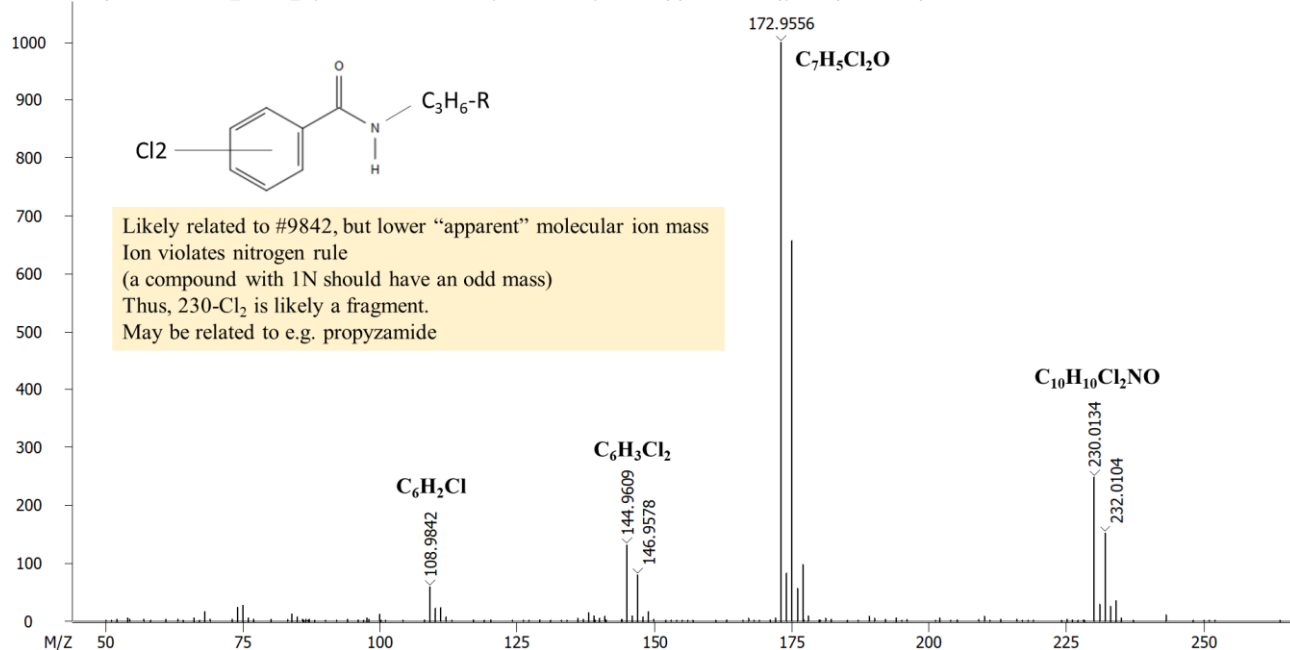
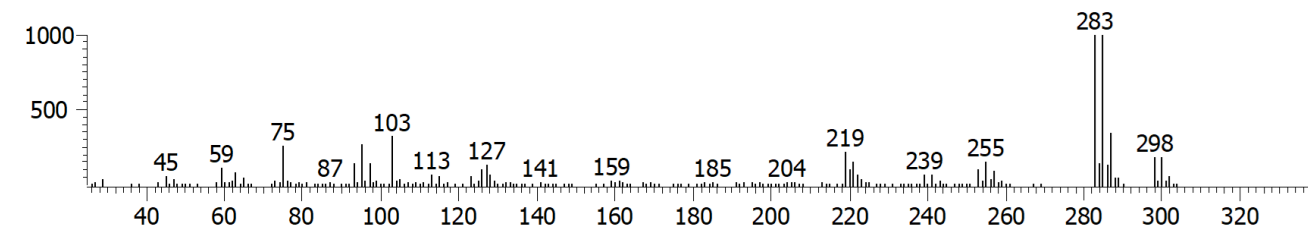
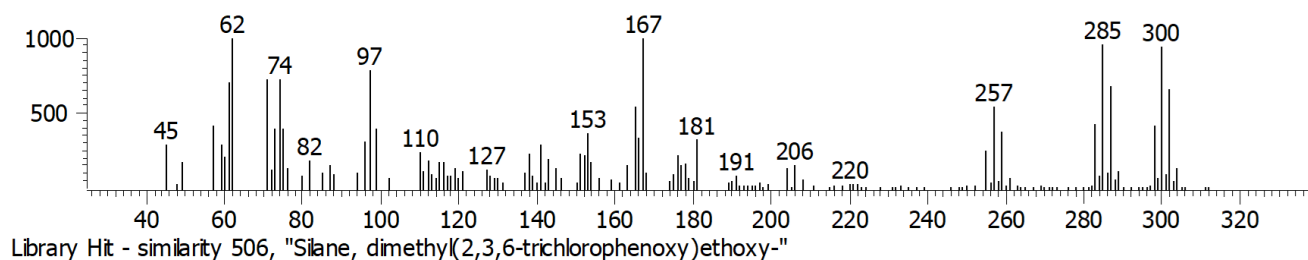


Figure S3: LRMS and HRMS spectra of unknown halogenated compound B in GFF.

Peak True - sample "16_732 PUR ArcticAir 4xDig 16_192+195 3uL_1", peak 4444, at 1672.5 , 1.810 sec , sec



Peak True - sample "Arctic PUF 16_0732-P", #4444 unknown LRMS, at 1610.57 s, 1.937 s, Area (Abundance)

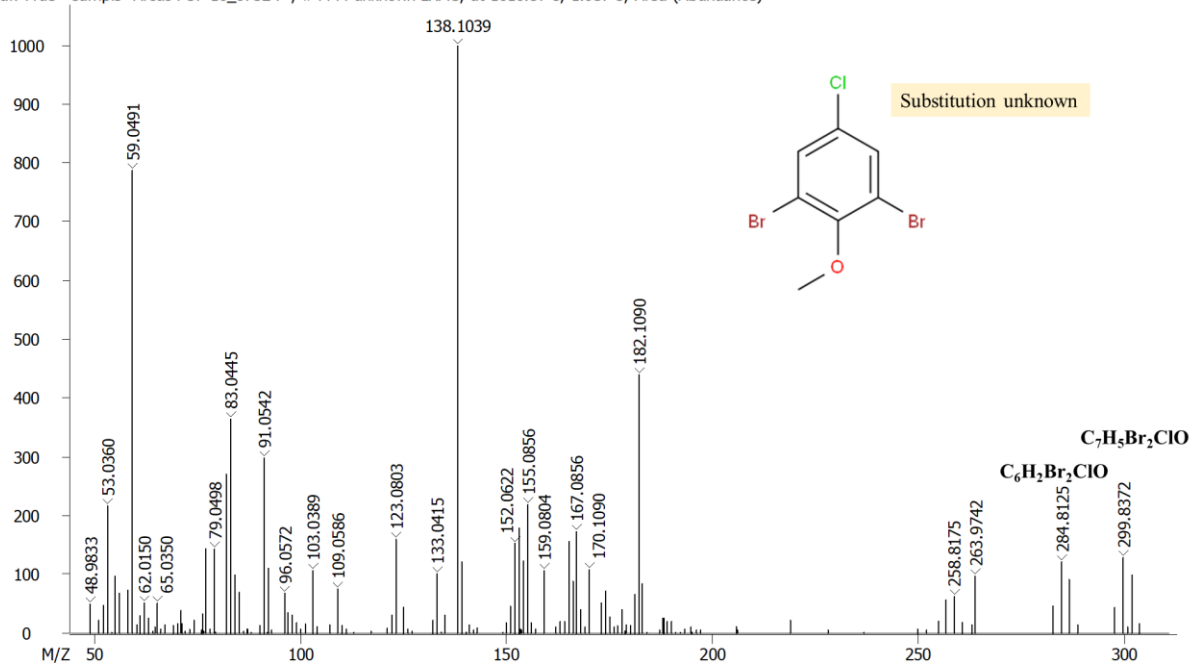
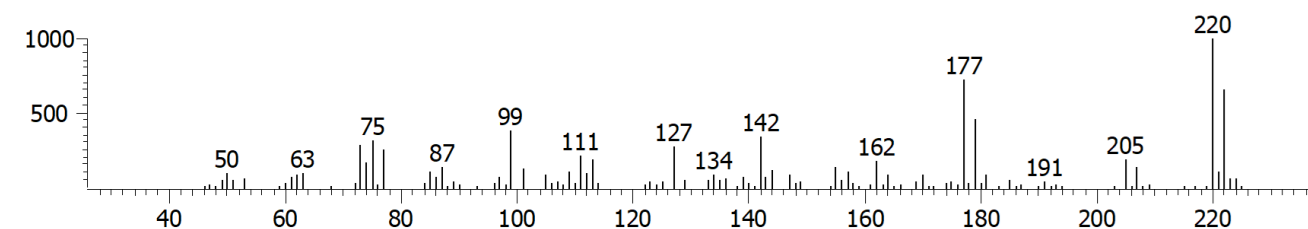
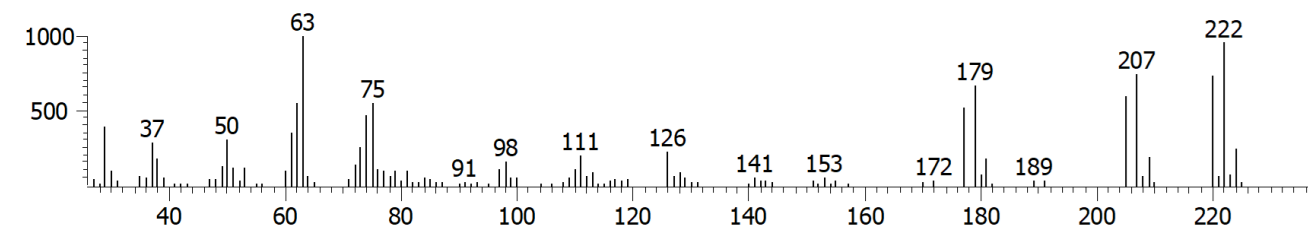


Figure S4: LRMS and HRMS spectra of unknown halogenated compound C in PUF.

Peak True - sample "16_732 PUR ArcticAir 4xDig 16_192+195 3uL_1", peak 5672, at 1812 , 1.720 sec , sec



Library Hit - similarity 628, "2-Bromo-4-chloroanisole"



Peak True - sample "Arctic PUF 16_0732-P", #5672 unknown LRMS, at 1750.24 s, 1.873 s, Area (Abundance)

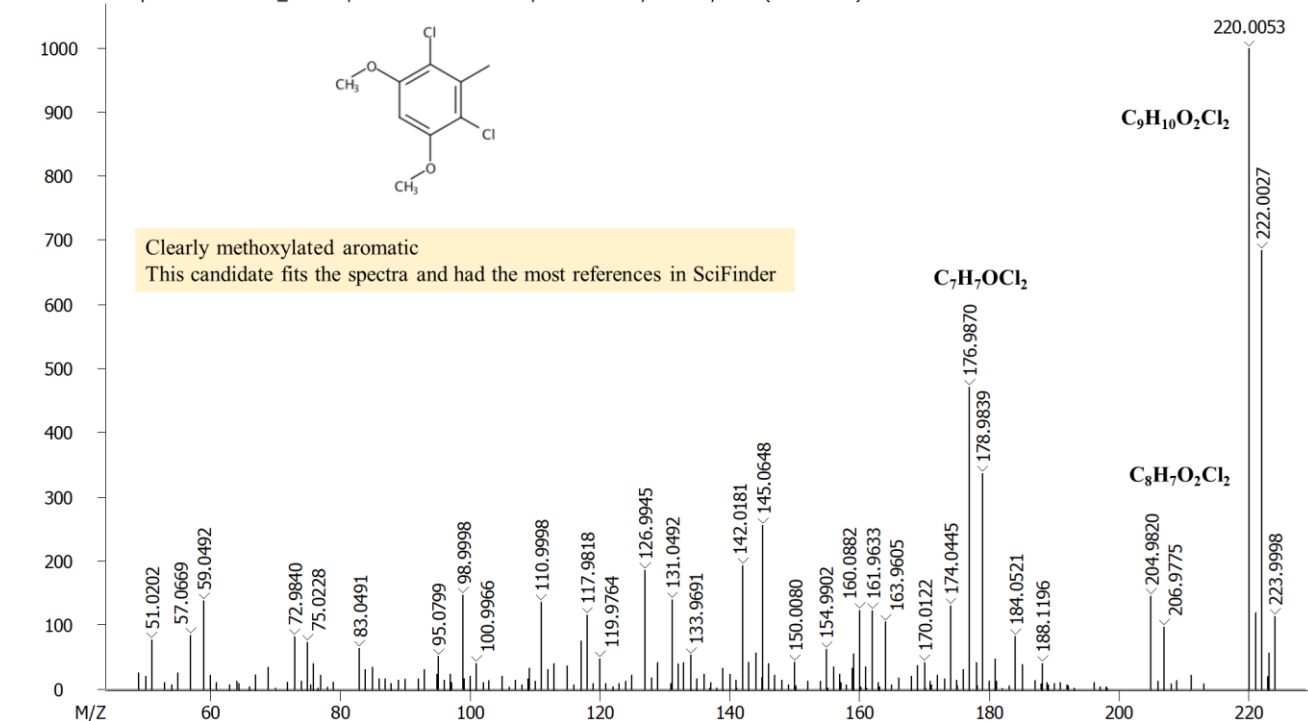


Figure S5: LRMS and HRMS spectra of unknown halogenated compound D in PUF.