# Results from the Joint Nordic and the Norwegian Non-target Screening Studies

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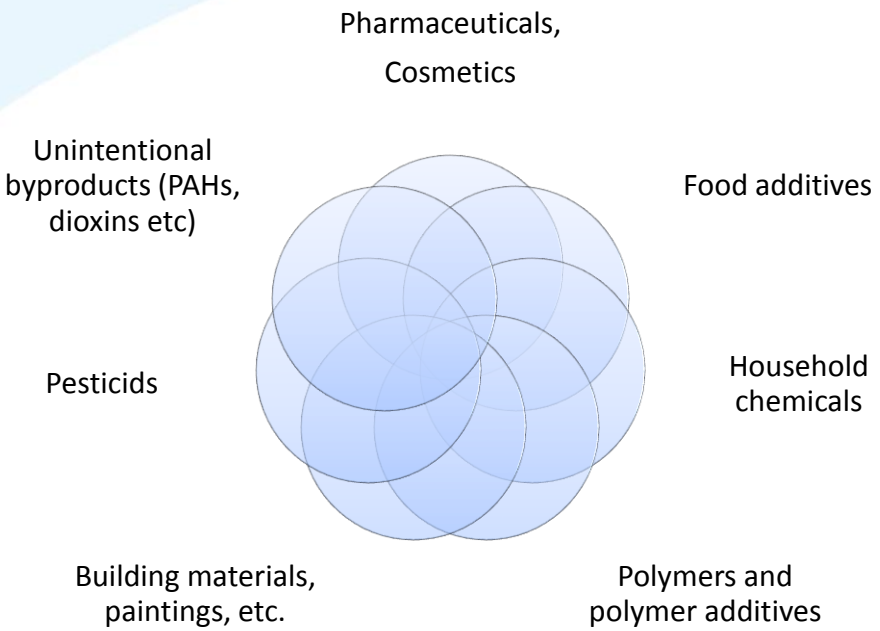
# Daily exposure to chemical cocktail

- Modern live based on chemicals
- Increasing number of chemicals
- Complex mixtures
- Most chemicals are mobile
- Find their way to environment and humans

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# Analytical approaches

- Traditional – *targeted* screening approach

- *Non-targeted (non-specific)* screening approach

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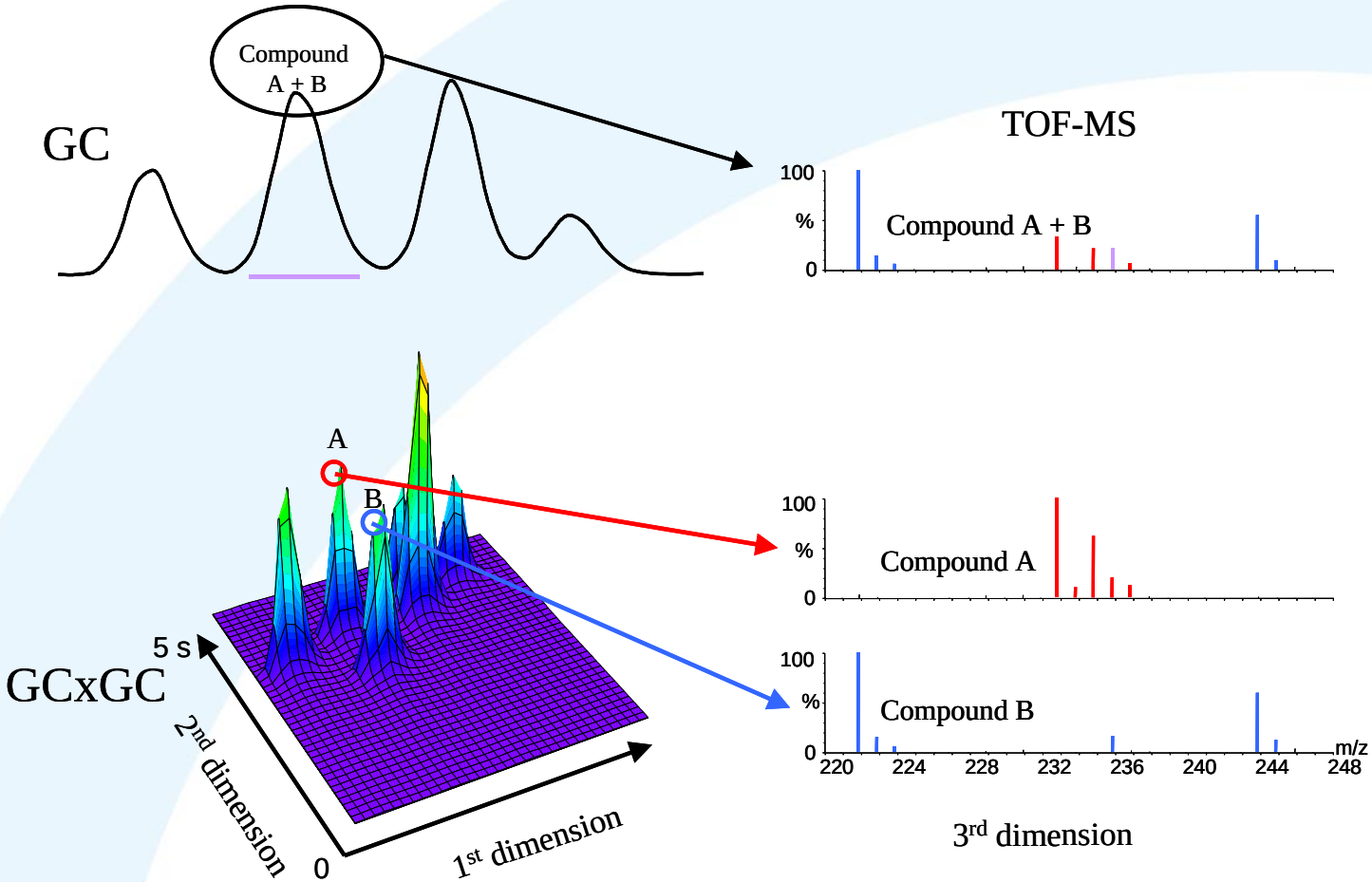
# Improve resolution

Ultimate separation power (long columns, UPLC, high res MS)

Two dimensional/hyphenated techniques (GCxGC or LCxLC)

Advanced data treatment (deconvolution)

# GCxGC-TOF-MS

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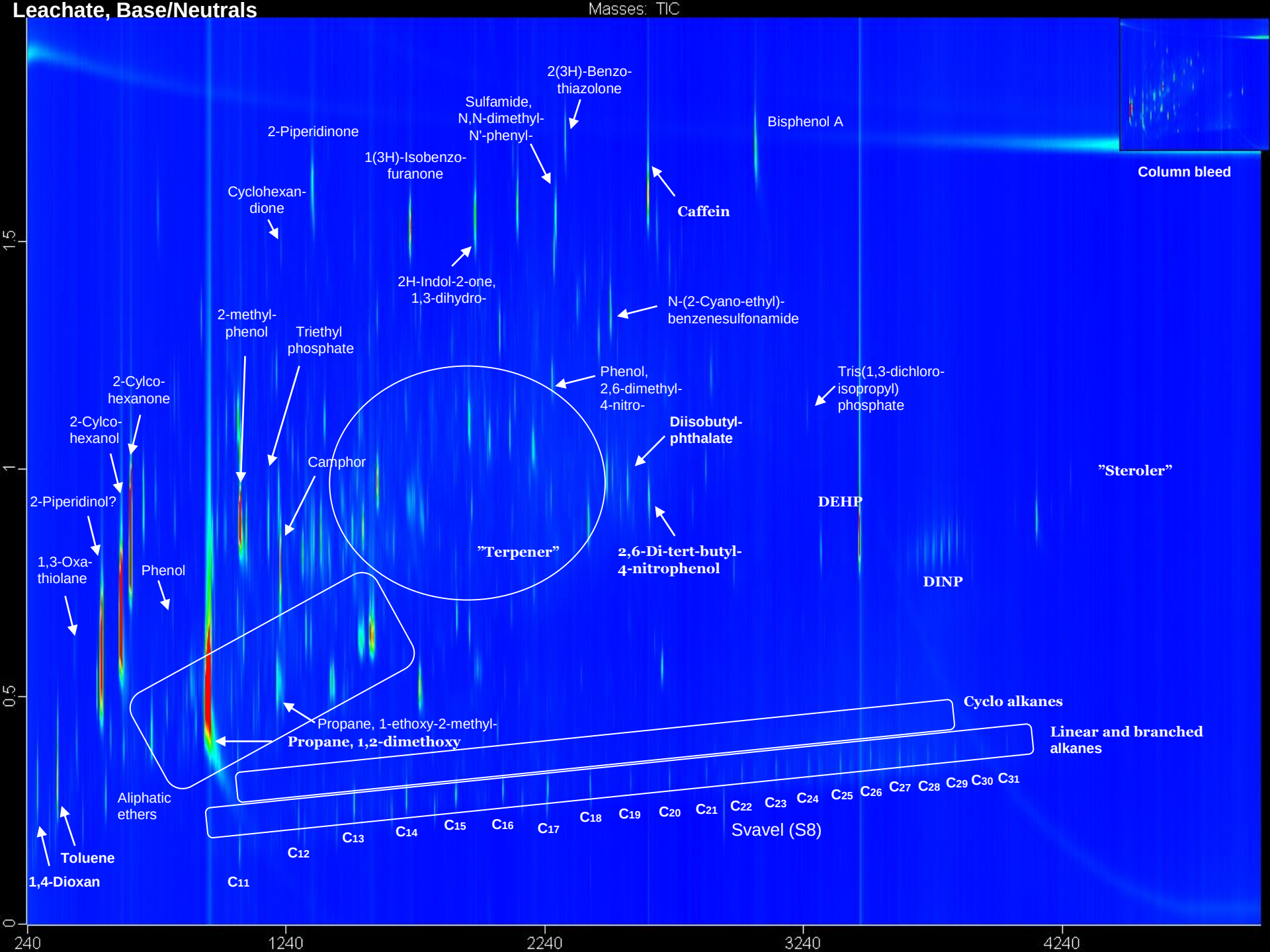
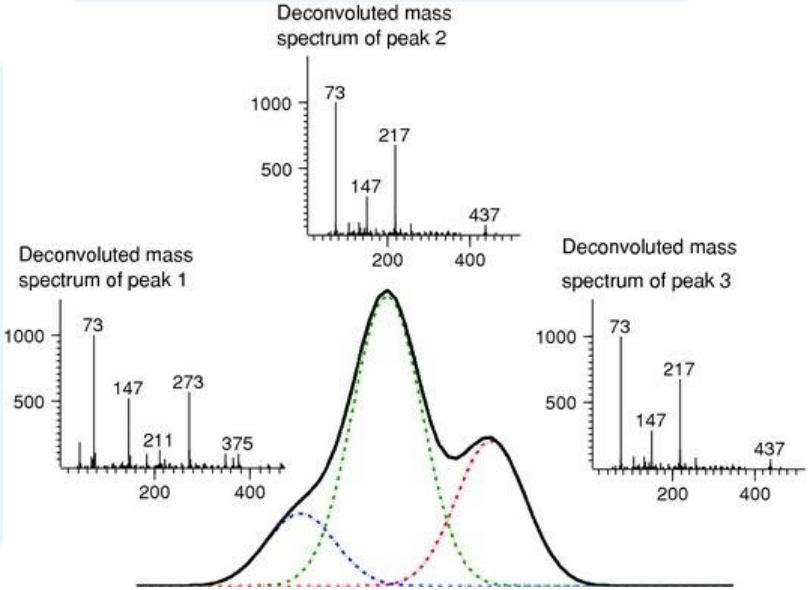

Leachate, Base/Neutrals
Masses: TIC
2(3H)-Benzo-thiazolone
Sulfamide, N,N-dimethyl-N'-phenyl-
Bisphenol A
2-Piperidinone
1(3H)-Isobenzo-furanone
Column bleed
Cyclohexan-dione
Caffein
2H-Indol-2-one, 1,3-dihydro-
N-(2-Cyano-ethyl)-benzenesulfonamide
2-methyl-phenol
Triethyl phosphate
Phenol, 2,6-dimethyl-4-nitro-
Tris(1,3-dichloro-isopropyl) phosphate
2-Cylco-hexanone
2-Cylco-hexanol
Diisobutyl-phthalate
Camphor
"Steroler"
2-Piperidinol?
DEHP
"Terpener"
2,6-Di-tert-butyl-4-nitrophenol
1,3-Oxa-thiolane
Phenol
DINP
Cyclo alkanes
Propane, 1-ethoxy-2-methyl-
Propane, 1,2-dimethoxy
Linear and branched alkanes
Aliphatic ethers
C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31
Svavel (S8)
Toluene
1,4-Dioxan
0
0.5
1
1.5
240
1240
2240
3240
4240

# Deconvolution

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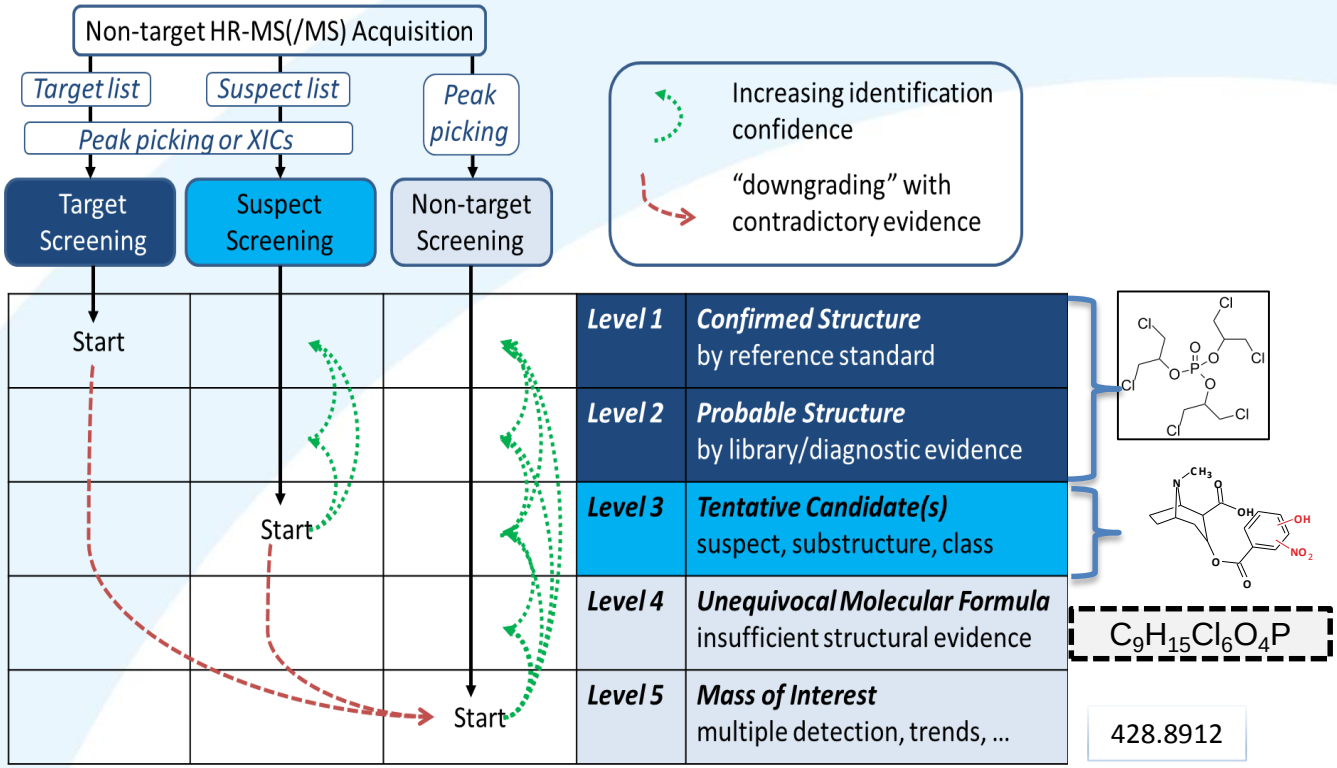
# Identification of emerging compounds

- Very difficult task, over 98 million of substances registered in CAS database, approx. 15 000 new added daily
- Around 1 million of mass spectra available in commercial libraries (for GC and LC-MS)
- Library search and accurate mass spectral information, fragmentation, *in silico* models and multivariate statistics utilized in identification of the compounds

# Work flow Norman approach




*Adapted from Schymanski et al., 2015*

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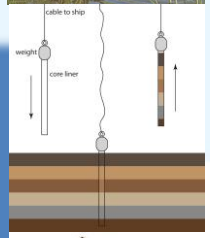
# Joint Nordic NTScreening





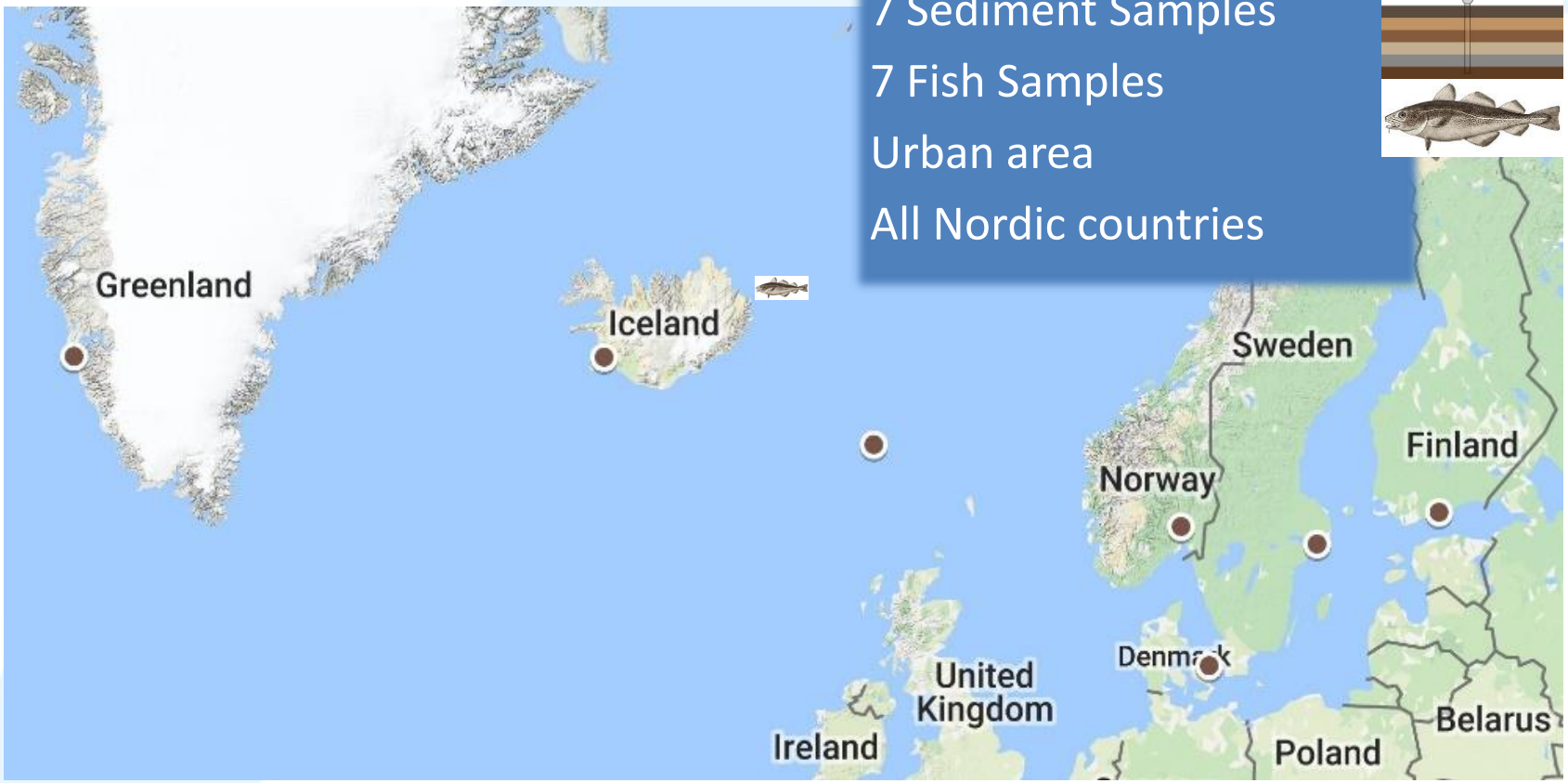
7 Effluent Samples

7 Sediment Samples

7 Fish Samples

Urban area

All Nordic countries

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# Norwegian NTScreening Studies

2013: Test study using random samples

(Air, WWTP, Sediment, and Biota)

2014: 2 aquatic food-chains (Oslofjord&Mjøsa)

1. Krill, Shrimp, Herring, and Cod
2. Zooplankton, Mysis, Vendace, Smelt, and Trout

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# Compounds detected

| Groups | Compounds |
|---|---|
| Petroleum derivatives | Different hydrocarbons<br>Oxidation products |
| Combustion products | PAHs and Alkyl-PAHs<br>N-, S-, O-heterocyclic aromatics<br>Oxidation products |
| Pharmaceuticals and Personal Care Products (PPCP) | Medicines<br>UV-screens<br>Fragrances<br>Antioxidants |
| Plasticizers and flame retardants | Phthalates and adipates<br>OPFRs<br>BFRs |
| Polymer additives | Benzothiazoles<br>Benzenesulfonamides and -amines<br>UV stabilizers<br>Antioxidants |
| POPs | PCBs<br>Chlorinated pesticides |

Long result lists

In best case semiquantitative

How do we prioritize?

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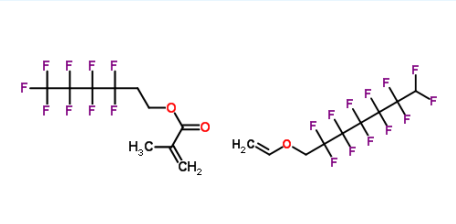
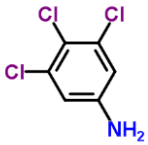
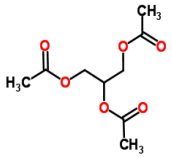
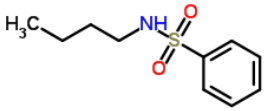
# Interesting compounds – Joint Nordic NTS

| Compound/Compound group | CAS | Matrix | Frequency |
|---|---|---|---|
| **PFC:** | | | |
| 4:2 Fluorotelomer methacrylate | 1799-84-4 | Effluent | 5 |
| Perfluoroheptyl vinyl ether | 78971-81-0 | Fish | 2 |
| Perfluoroctylsulfonamide | 754-91-6 | Sediment | 1 |
| C13H8F21O5P | 94158-70-0 | Sediment | 1 |
| **Halogenated:** | | | |
| 2,3-dichloro aniline | 608-27-5 | Sediment | 1 |
| 3,4,5-dichloro aniline | 634-91-3 | Sediment | 1 |
| Natural Cl3Br3-monoterpene | | Fish | 2 |
| **Biocides:** | | | |
| 1-[(1-Butoxy-2-propanyl)oxy]-2-propanol | 29911-28-2 | Effluent | 5 |
| 1-[(1-Butoxy-2-propanyl)oxy]-2-propanol | 29911-28-2 | Fish | 1 |
| Triacetin | 102-76-1 | Effluent | 4 |
| Triacetin | | Sediment | 3 |
| **Different bisphenols** | | All | 1-7 |
| **Industrial additives:** | | | |
| 2-(Methylthio)benzothiazole | 615-22-5 | Effluent | 5 |
| N-Butylbenzenesulfonamide | 3622-84-2 | Effluent | 3 |
| **PPCPs:** | | | |
| Oxypurinol | 2465-59-0 | Fish | 5 |
| Lamotrigine | 84057-84-1 | | |
| Cetirizine | 83881-51-0 | | |
| Paroxypropione | 70-70-2 | Fish | 5 |
| Carvone | 99-49-0 | Effluent | 5 |

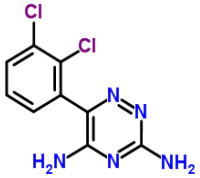












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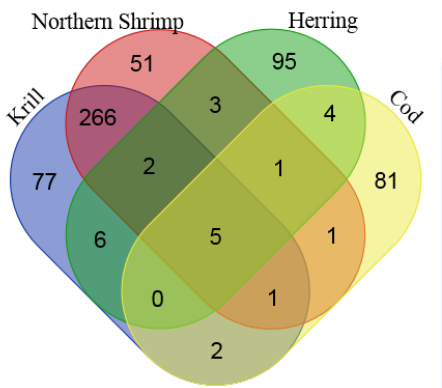
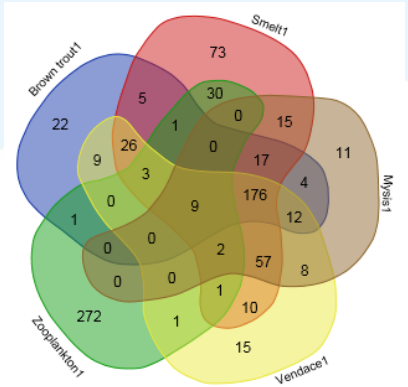
# Interesting compounds – Norwegian NTS




| Matrix combination | Compounds |
|---|---|
| Cod, Herring, Krill, Northern Shrimp | Galaxolide, Hexachlorobiphenyl, p,p'-DDE, PFOS, PFOSA |
| Herring, Krill, Northern Shrimp | Tonalide, carbenoxolone |
| Cod, Krill, Northern Shrimp | Diethyl phthalate |
| Cod, Herring, Northern Shrimp | Pentachlorobiphenyl |

| Matrix, combination | Compounds |
|---|---|
| Brown trout, Mysis, Smelt, Vendace, Zooplankton | 1-[1,6-dimethyl-3-(4-methylpent-3-enyl)-3-cyclohexen-1-yl]ethan-1-one; Hexachlorobiphenyl; stearic acid, monoester with glycerol; Buprenorphin; OTNE; Phenol, dodecyl-, branched; p,p'-DDE; p,p'-DDT; nitrophenylhydrazine |
| Mysis, Smelt, Vendace, Zooplankton | 4-(5,5,6-Trimethylbicyclo[2.2.1]hept-2-yl)cyclohexanone<br>3-(5,5,6-Trimethylbicyclo[2.2.1]hept-2-yl)cyclohexanone<br>Degradation-Product |
| Brown trout, Smelt, Vendace, Zooplankton | Diethyl phthalate<br>2,2-dimethyl-1,3-propanediyl dioctanoate<br>Trospium |

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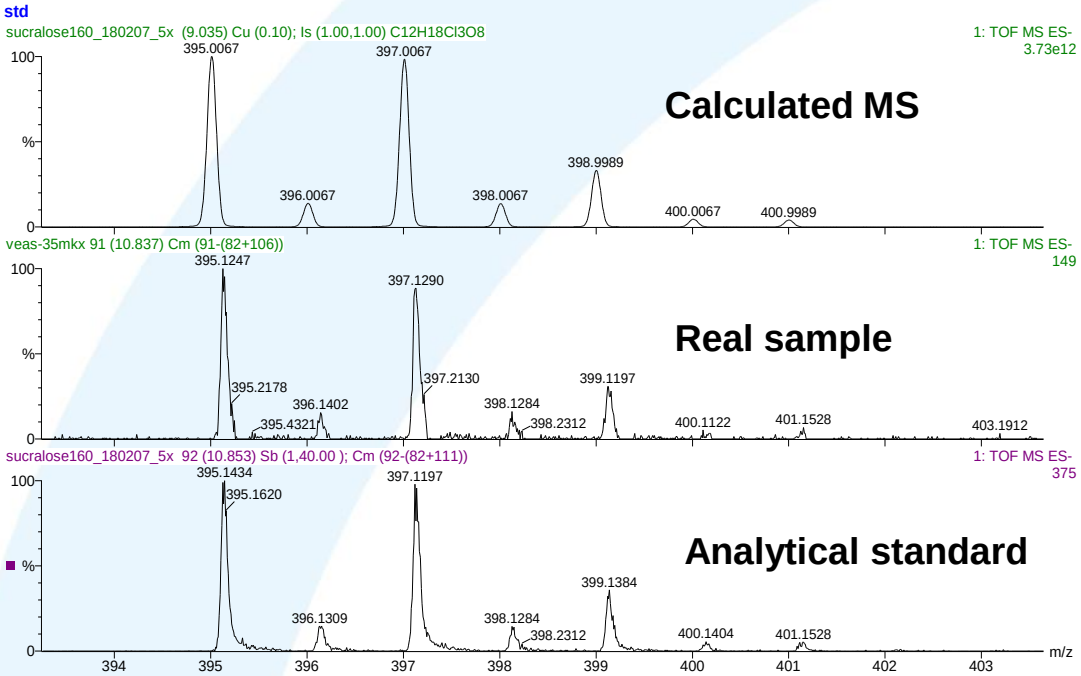
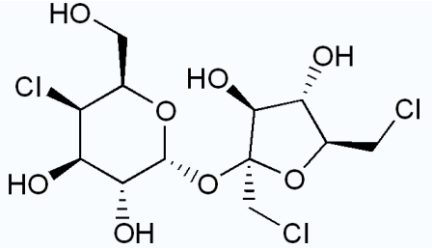
# Suspect/Non-target screening

- ✔ Allows to detect wide range of compounds in a single analysis,
- ☹ but is often less sensitive than *targeted screening* and often not quantitative
- ✔ Important tool for identification of emerging compounds
- ✔ Retrospective analyses possible

# Retrospective analysis - The sucralose case

- 2007 NILU was asked about sucralose in environment?
- 2006 NILU analysed PPCPs in environmental samples with LC-HRToF-MS
- **New** treatment of **old raw data** revealed sucralose as an environmental pollutant

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# Retrospective analysis

- ✓ Possible in many, but not all cases
- ✓ Could easily be part of routine monitoring
- ✓ No sample storage needed
- ☹ Limited sensitivity
- ☹ Often not quantitative
- ☹ Extraction, clean-up & detection not optimized
- ☹ Huuuuge datafiles to be stored
- Which fileformat to use (instrumental or third part software)

# Environmental specimen banking

- ✓ Original sample material available
- ✓ Best sensitivity
- ✓ Quantitative and full quality assurance
- ☹ Sample storage needed
- ☹ Extra sample handling and administration
- ☹ Limited storage space

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# Conclusions

- ✔ Wide range of compounds in single analysis
- ✔ Only some harddisks contra big freezing room
- ☹ Often less sensitive than targeted screening
- ☹ Not suitable for all compounds
- ☹ Normally not quantitative

- ✔ Retrospective analyses as a supplement to ESBs
- ✔ Tool for selection of environmental contaminants and planning targeted analysis

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# Further plans

- National and International collaboration
- NORMAN network:
  - Libraries & Databases
  - Interlaboratory studies
  - Common approach & protocols

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# Thank you for your attention!

**Questions?**

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