Non-target screening
First results from Norway

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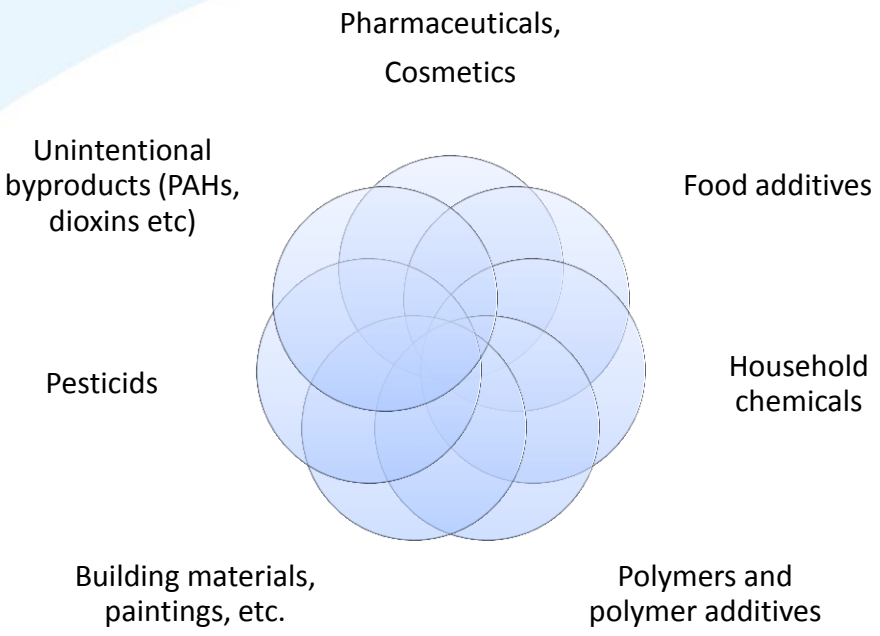
Umeå University

Daily exposure to chemical cocktail

- Modern live based on chemicals
- Most chemicals are mobile and find their way to environment and humans



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Exposure

Digestive system:

food, drinks, drugs, dust , soil

Lungs: Air pollution (gases, volatile and semi-volatile compounds, dust)

Skin: Cosmetics, drugs, other.

Ingestion

Inhalation

Skin absorbtion

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New requirements to analytical chemistry

Rapid change in chemical products requires flexible analytical methods

”Non target” or non specific screening

New instrumental techniques available (for example: time-of-flight MS)

Advantages:	Simultaneous analyses of 1000 of compounds (~100 in targeted methods)
Challenges:	1. Treatment of HUGE data files
	2. ”Separating the wheat from the chaff”

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Analytical approaches

- Traditional – *targeted* screening approach

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

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Targeted screening

- ✔ Developed specifically for a certain group of substances gives good sensivity and reliable identification and quantification of the target compounds
- ✖ Will miss all compounds which were not selected at the beginning
- ✖ Concentrations of known compounds are not high enough to explain some of toxic potentials of the samples

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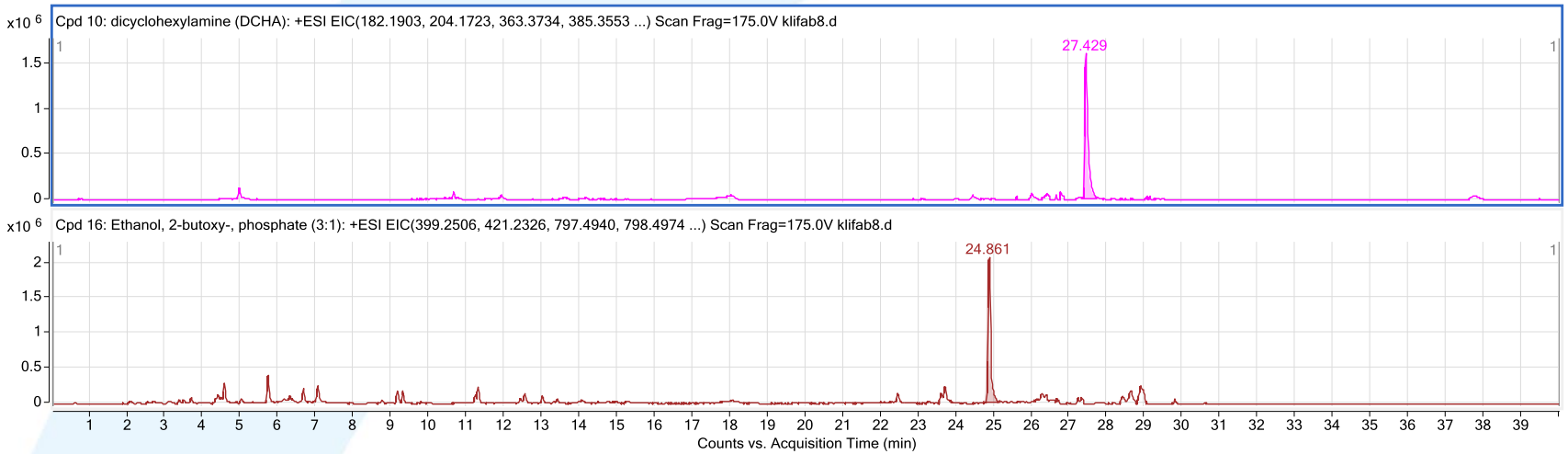
Targeted screening



Non-targeted screening

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Non-targeted screening

“environmental forensics”

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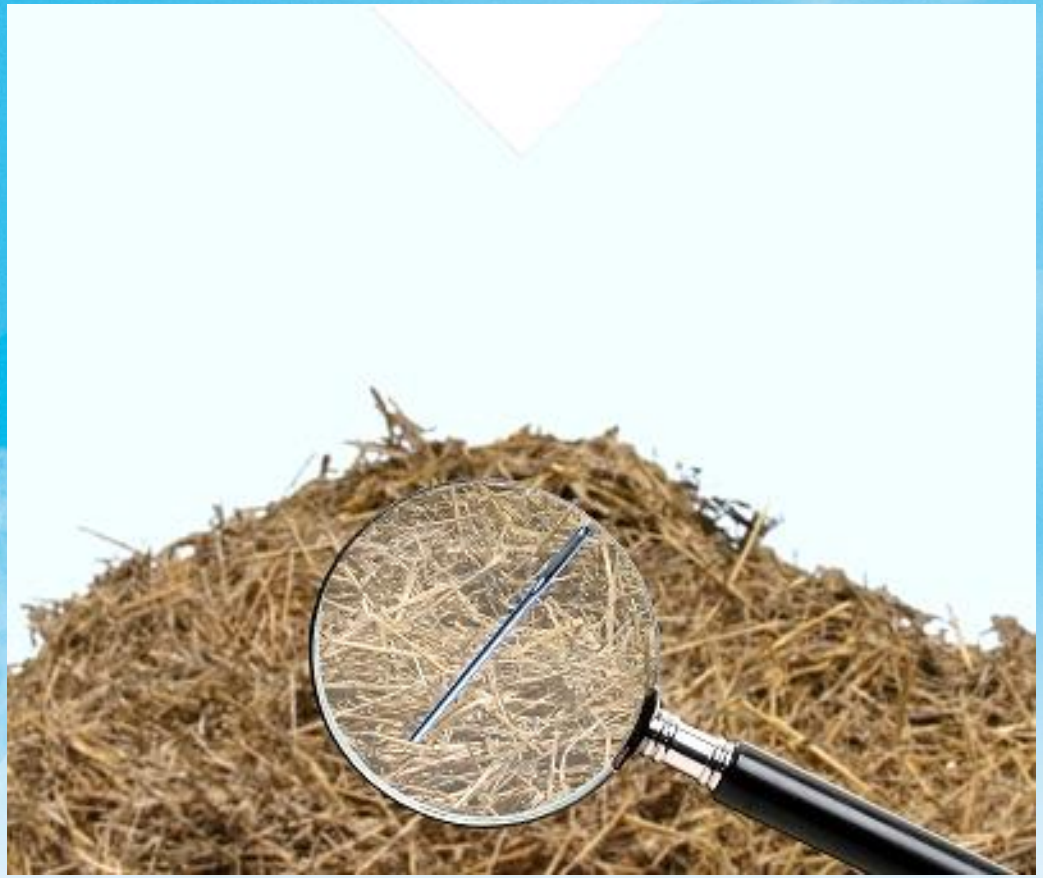

NILU Norsk institutt for luftforskning

Aim of the study

Pilot study initiated by Norwegian Environment Agency and conducted by NILU and UMU

Is non-target screening a good tool to select environmental contaminants?

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Samples

- Air filters (urban and remote),
- Sludge (processed and not-processed),
- Wastewater (influent and effluent),
- Sediment,
- Biota (cod liver, eggs, shrimps).

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Extraction

- Methods:

➢ Wastwater – SPE (OASIS HLB)

➢ Sediment, sludge and biota samples – ultrasonic extraction

- Solvents used:

✓ for the LCMS – methanol: acetonitrile (50:50)

✓ For the GCMS - dichloromethane

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Agilent 6550 UHPLC-HR-(Q)TOF-MS

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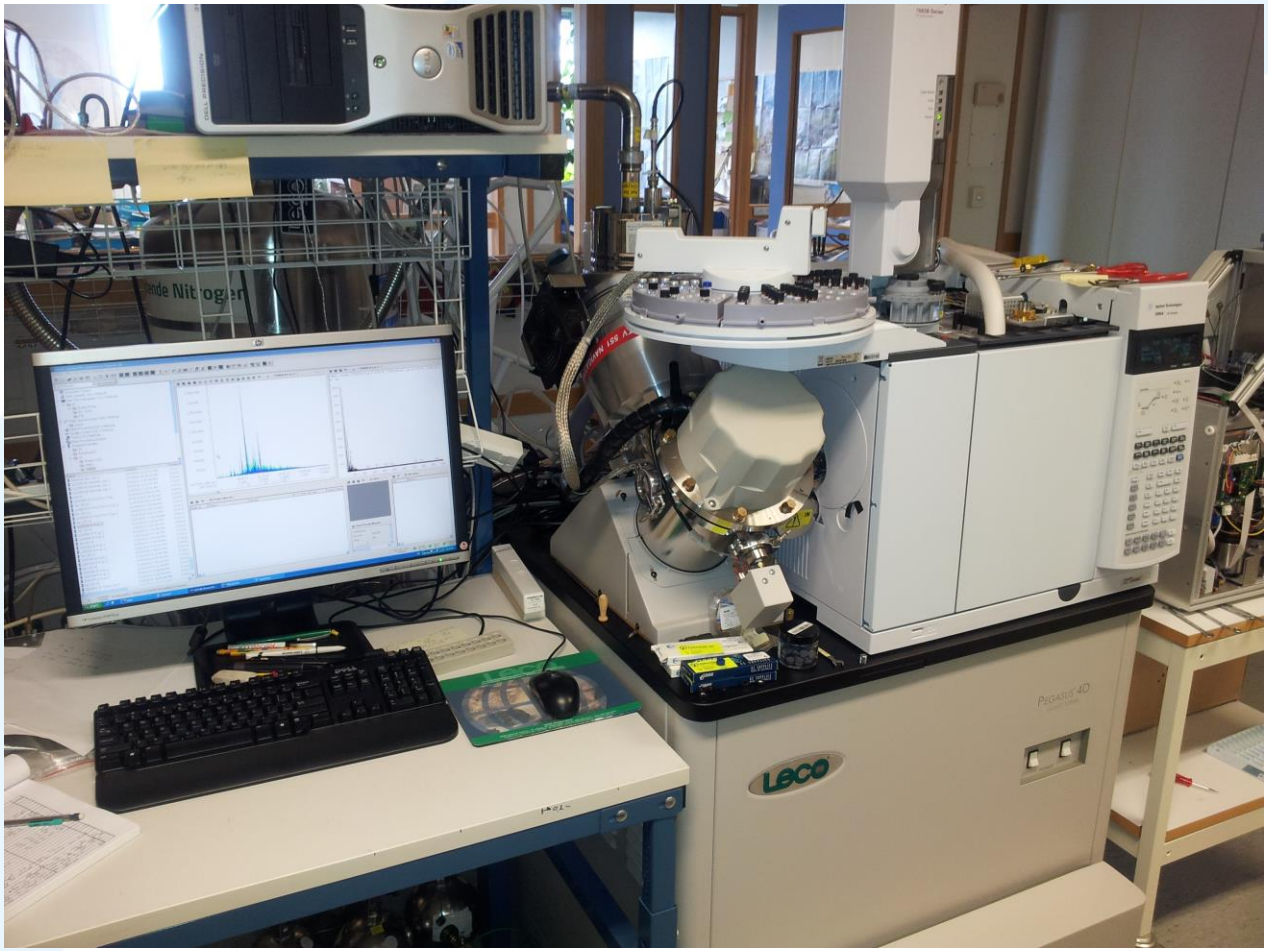
Leco GCxGC-LR-TOF



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Why both LC and GC MS screening is needed?

- Non-target screening = wide variety of compounds with different properties

Single method will not cover the whole range!

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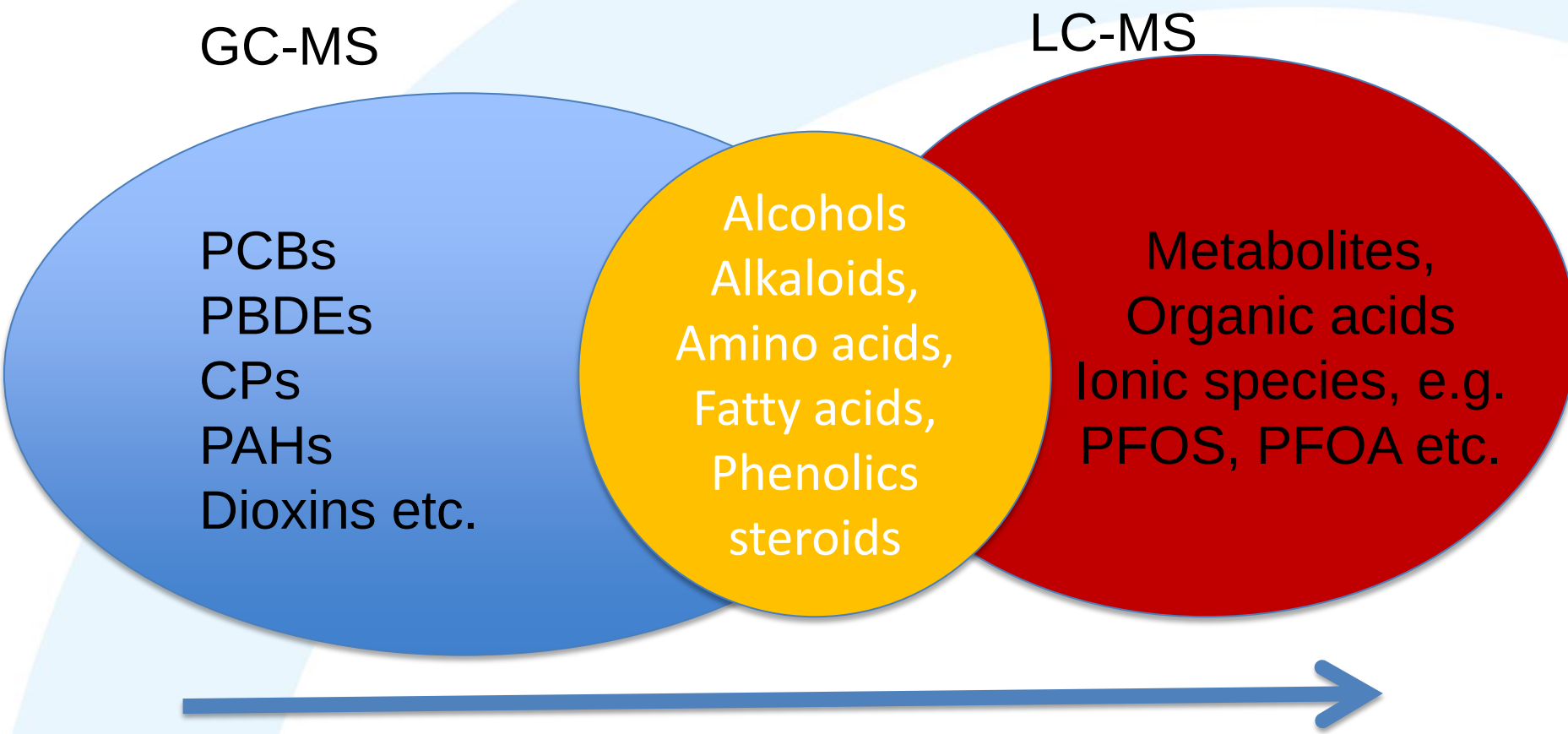
Properties of chemicals and the analytical techniques with which they are the most compatible



POLARITY

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Approaches:

- LC-HR-MS/MS

Identification of «known unknowns» using ChemSpider, automated MS/MS structure correlation and library searches

- GCxGC-TOF-MS

Library based identifications, GC-HR-TOF confirmations

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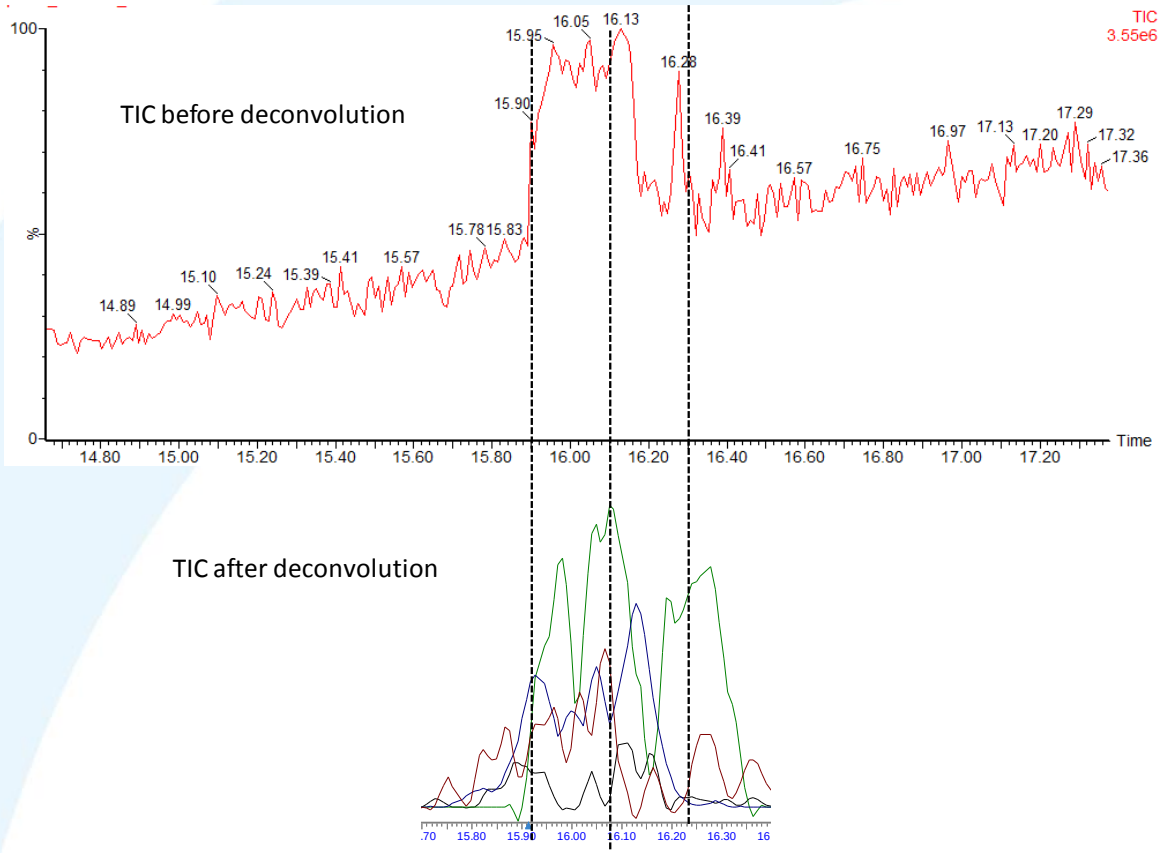
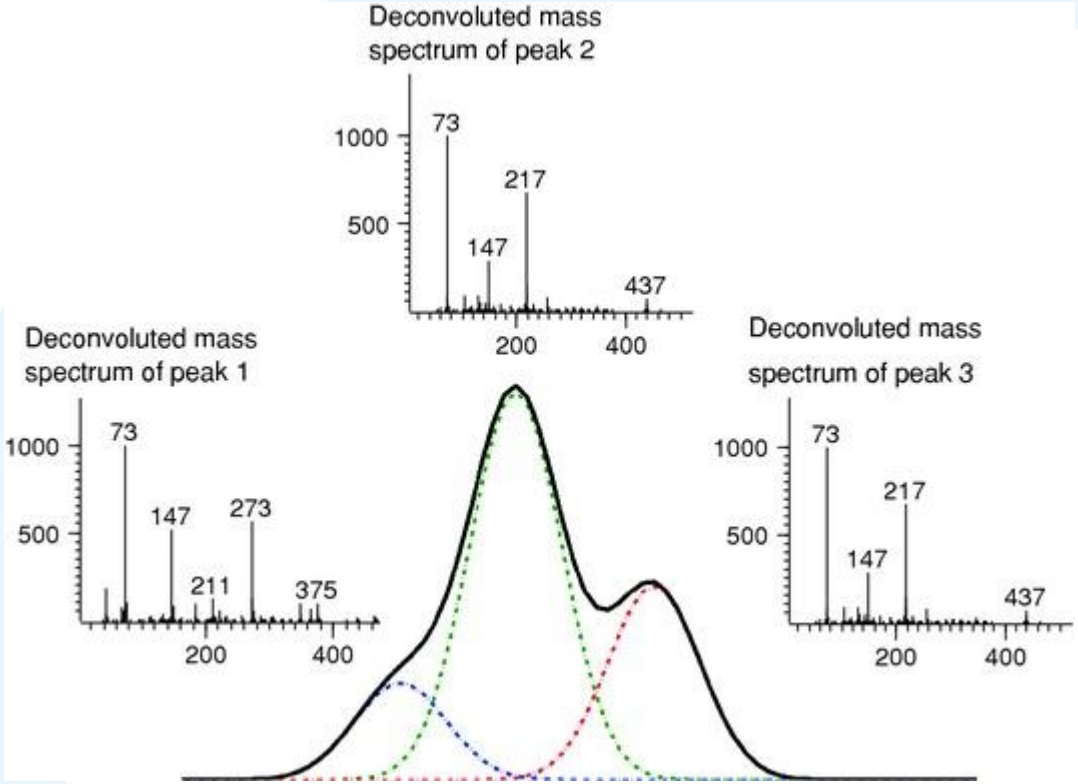
Data processing

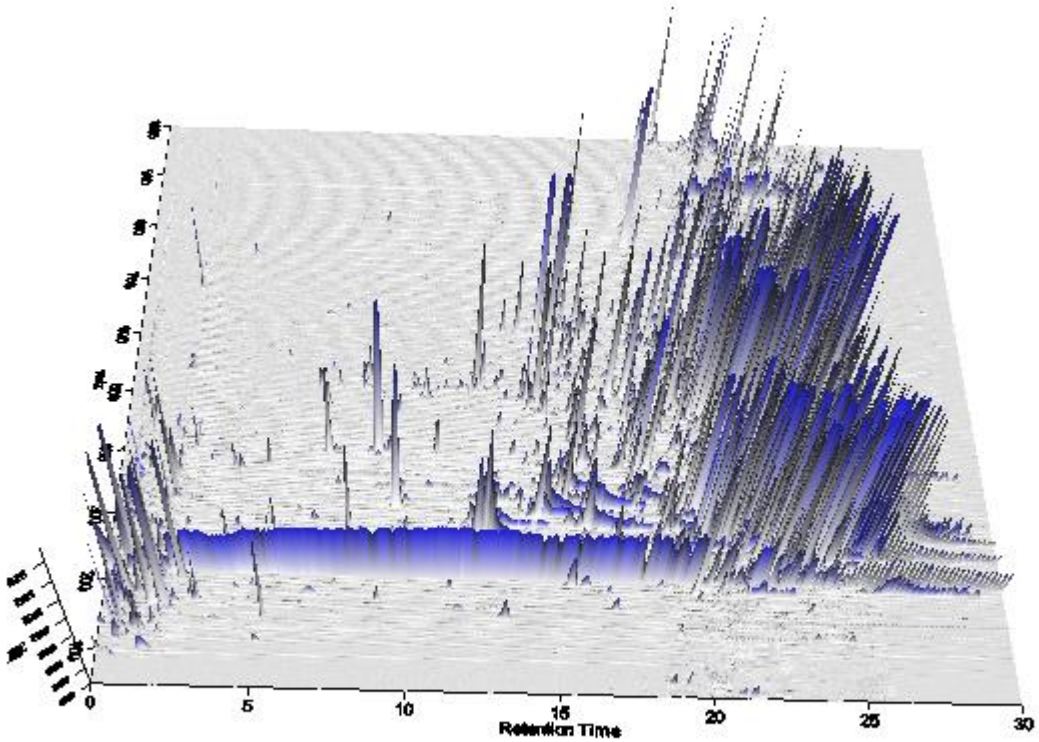
- Deconvolution



Deconvolution



Results (LCMS)



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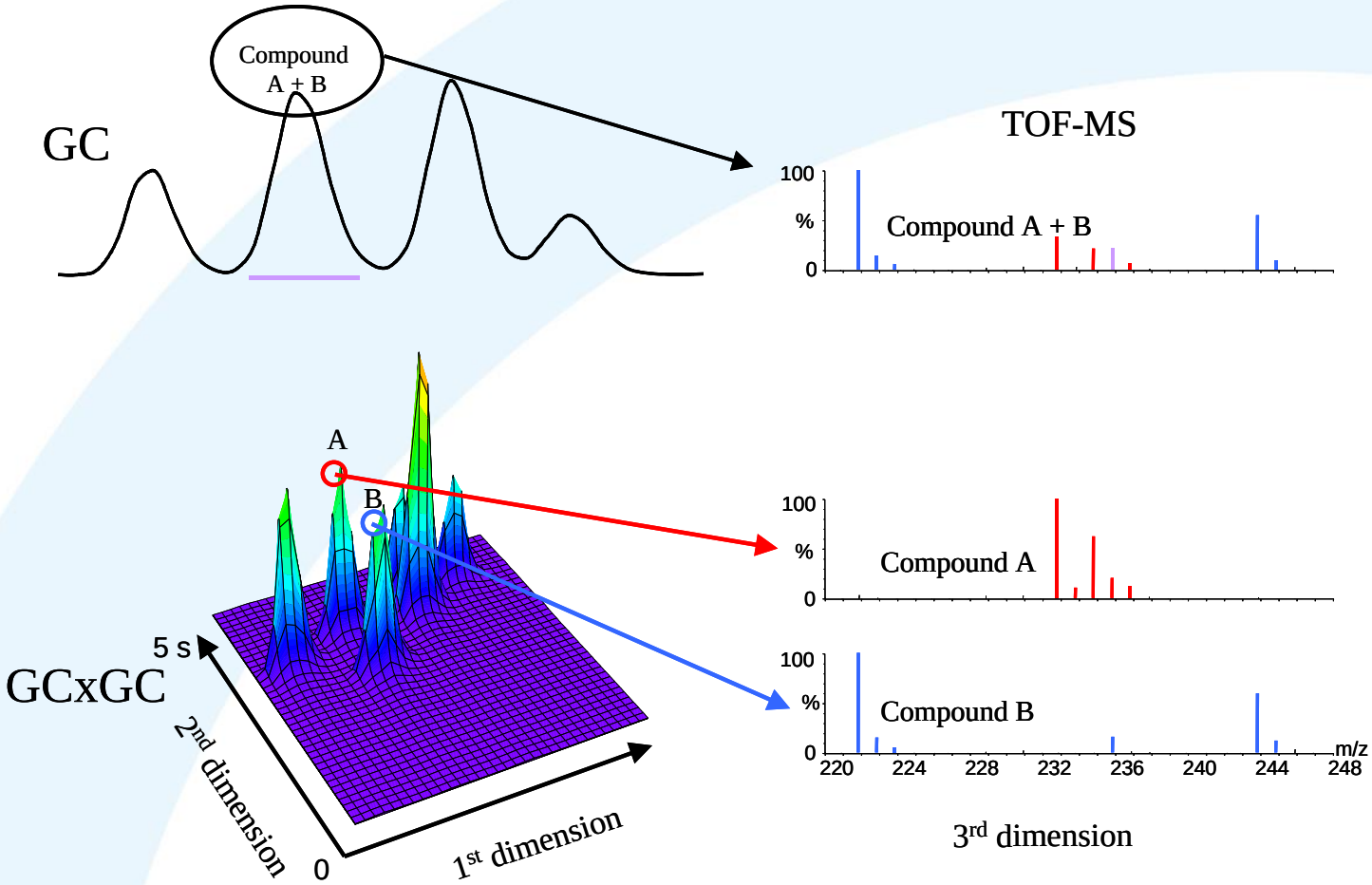
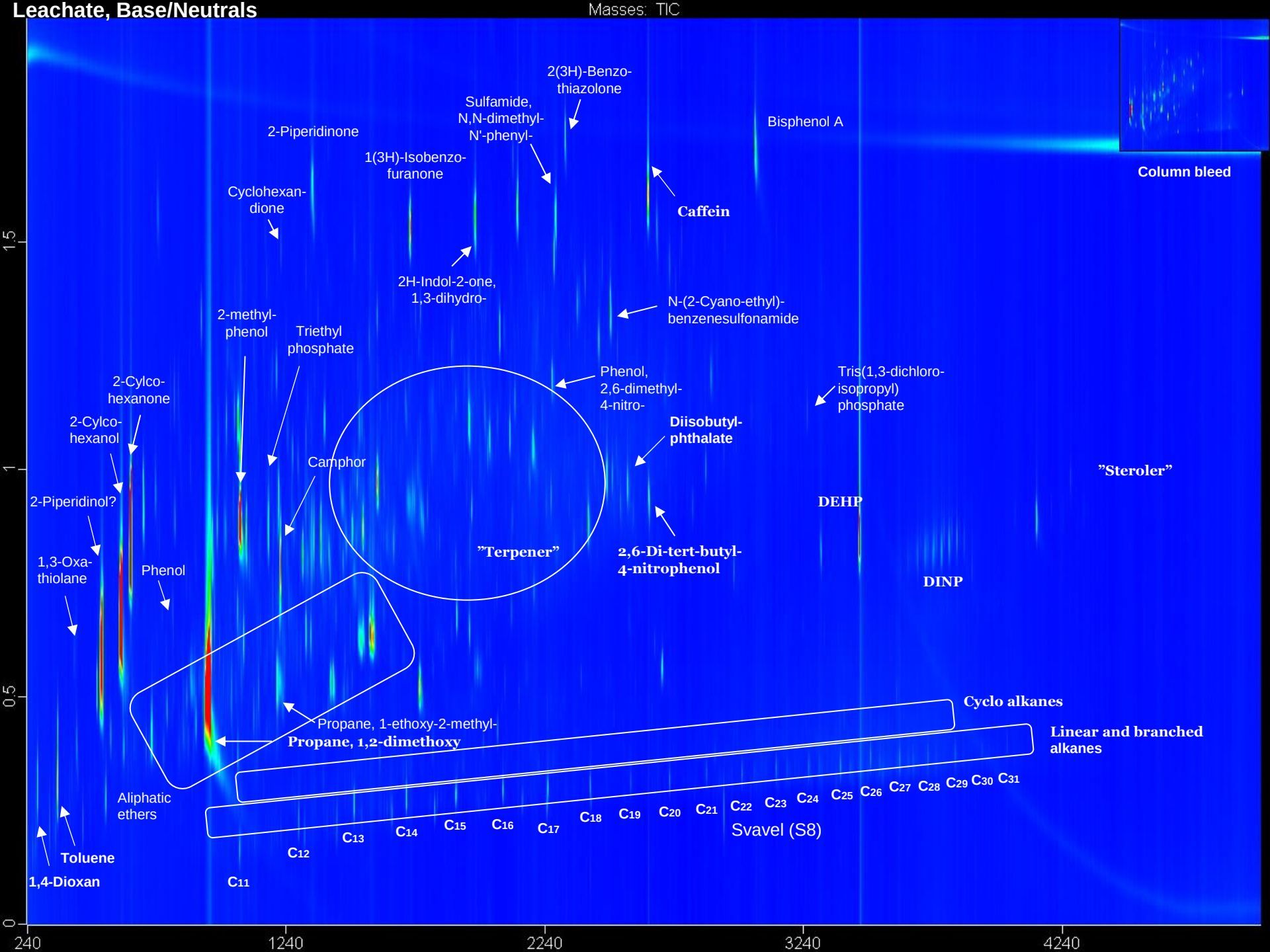
GCxGC-TOF-MS


Compound
A + B
GC
TOF-MS
100
%
0
Compound A + B
A
B
100
%
0
Compound A
100
%
0
Compound B
m/z
220
224
228
232
236
240
244
248
3rd dimension
5 s
GCxGC
2nd dimension
0
1st dimension


Leachate, Base/Neutrals
Masses: TIC
Column bleed
2(3H)-Benzo-thiazolone
Sulfamide, N,N-dimethyl-N'-phenyl-
Bisphenol A
2-Piperidinone
1(3H)-Isobenzo-furanone
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

Compounds detected

Many biogenic compounds

- Fatty acid derivatives
- “Steroles”
- Terpenoids
- Other phytochemicals

System impurities

- Column bleed
- Solvent impurities

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Compounds detected

Petroleum derivatives

- n-Alkanes
- Branched alkanes
- Oxidation products

Combustion products

- PAHs and Alkyl-PAHs
- N-, S-, O-heterocyclic aromatic compounds
- Oxidation products (primarily ketones and quinones)

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Compounds detected

Pharmaceuticals and Personal Care Products

- UV-screens
- Surface active compounds
- Fragrances
- Antioxidants
- Bleach activator

Plasticizers and flame retardants

- Phthalates and adipates
- Organophosphate esters
- PBDEs

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Compounds detected

Polymer additives

- Benzothiazoles
- Benzenesulfonamides and -amines
- UV stabilizers
- Antioxidants
- Photo initiators
- Plastic monomers

POPs

- PCBs
- DDTs
- HCB and HCHs
- Chlordanes and toxaphenes
- Mirex
- Dieldrin
- Permethrin

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Example:

Sample type	Air		STP					Sediment	Biota					
Compound group	Remote	Urban	Digested sludge	Raw sludge	Influent	Influent particles	Effluent	Contaminated fjord	Prawns	Cod liver	Common eider	Common shag	Herring gull	Sum
Unidentified	252	212	265	82	271	291	209	237	305	63	216	230	286	2919
PPCPs	26	18	39	25	33	15	242	25	39	54	33	4	34	587
PACs	1	9	50	94	9	3	4	96	45	0	4	2	2	319
Additives	12	15	27	42	34	15	28	15	9	6	8	3	5	219
Phthalates	9	8	8	8	7	8	8	17	1	1	0	0	1	76
Organophosphates	4	7	4	7	7	4	9	5	3	2	2	4	7	65
Pesticides	4	5	5	4	2	2	33	1	5	1	6	2	12	82
Halogens	0	0	6	6	0	1	0	12	0	14	2	10	29	80
Oxy-compounds	0	0	0	12	9	0	4	7	0	0	0	0	0	32
N-compounds	0	0	2	7	1	0	2	0	0	0	0	0	0	12
PFCs	0	0	0	0	3	0	0	0	1	0	0	0	0	4
Sum identified	56	62	141	205	105	48	330	178	103	78	55	25	90	1476
Sum	308	274	406	287	376	339	539	415	408	141	271	255	376	4395

- some of the compounds well known
- some of the compounds not monitored earlier

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Non-target screening

- Allows to detect wide range of compounds in a single analysis, but is often less sensitive for some compounds than *targeted screening*
- Retrospective analyses possible
- Tool for selection of environmental contaminants and planning traditional targeted monitoring campaigns

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Acknowledgments

MILJØ-
DIREKTORATET

NILU SIS OrgSpec

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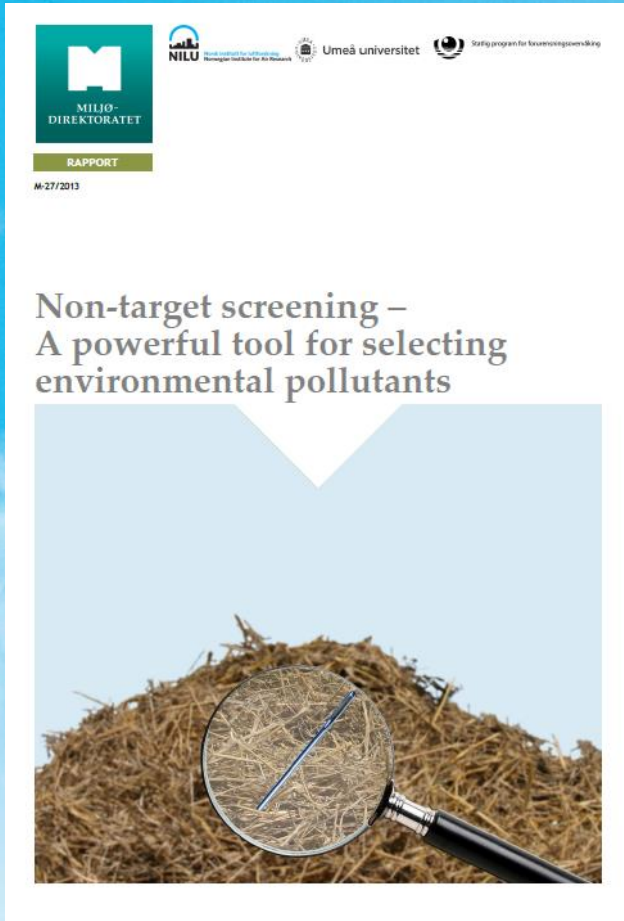
Thank you for your attention!



http://www.nilu.no/DesktopModules/NiluWeb.UserControls/Resources/File.ashx?filename=9-2013-msc-screening.pdf&filetype=file

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