How to analytically detect and identify emerging substances?

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NORMAN

Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

"Emerging substances" can be defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programmes at EU level and whose fate, behaviour and (eco)toxicological effects are not well understood.

"Emerging pollutants" can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments.

Examples from the **LIST OF EMERGING SUBSTANCES** are surfactants, flame retardants, pharmaceuticals and personal care products, gazoline additives and their degradation products, biocides, polar pesticides and their degradation products and various proven or suspected endocrine disrupting compounds (EDCs).

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Adapted from: http://www.norman-network.net/?q=node/19

Emerging substances

"Emerging contaminants" can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and(or) human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants.

Adapted from US National Geological Survey http://toxics.usgs.gov/regional/emc/

Emerging substances:

- Detected in the (indoor)environment but not a subject of a routine monitoring, with a potential for legal regulations
- Not detected earlier because of:

I. the lack of the analytical methodology

II. the synthesis of new chemicals or changes in use and disposal of existing chemicals created new sources of emerging contaminants

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Indoor environment

- We spend, on average, **85-90% of our time indoors** at home, in school, at work or during leisure time.

- Reductions in ventilation rates to limit energy consumption and extensive use of new building materials are releasing chemical substances with unknown toxic properties.

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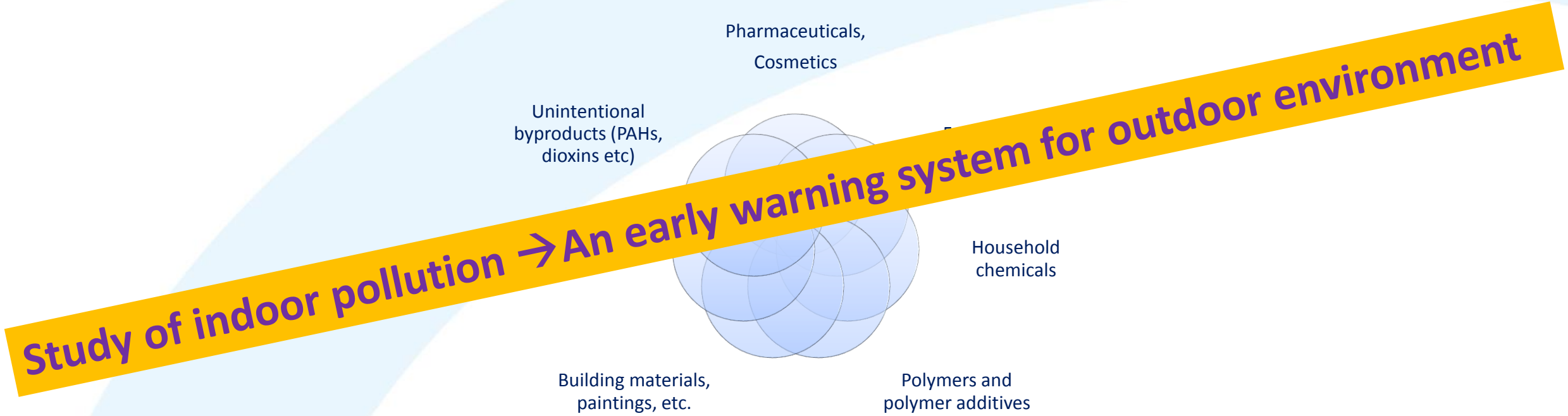
Daily exposure to a cocktail of chemicals



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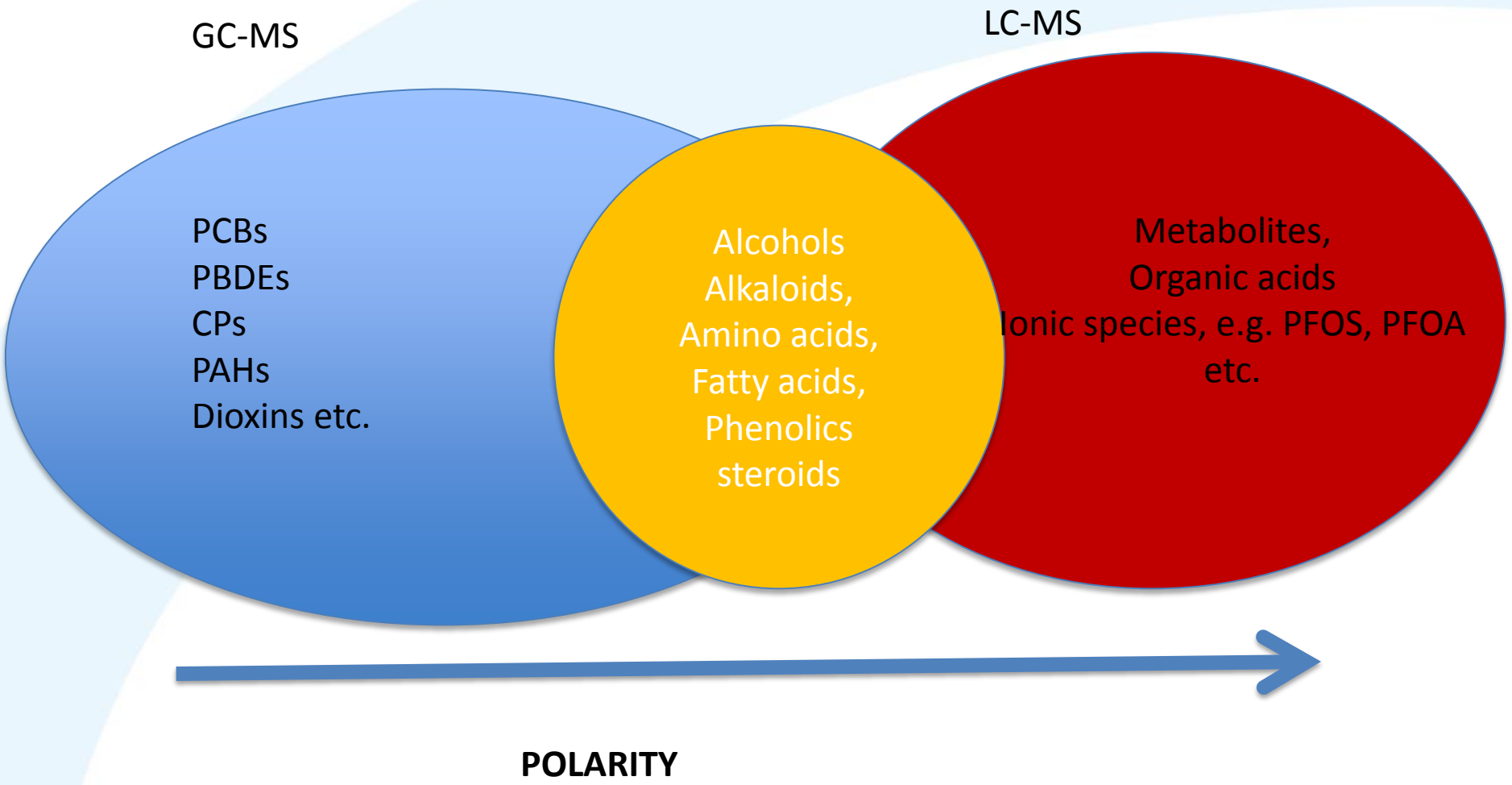
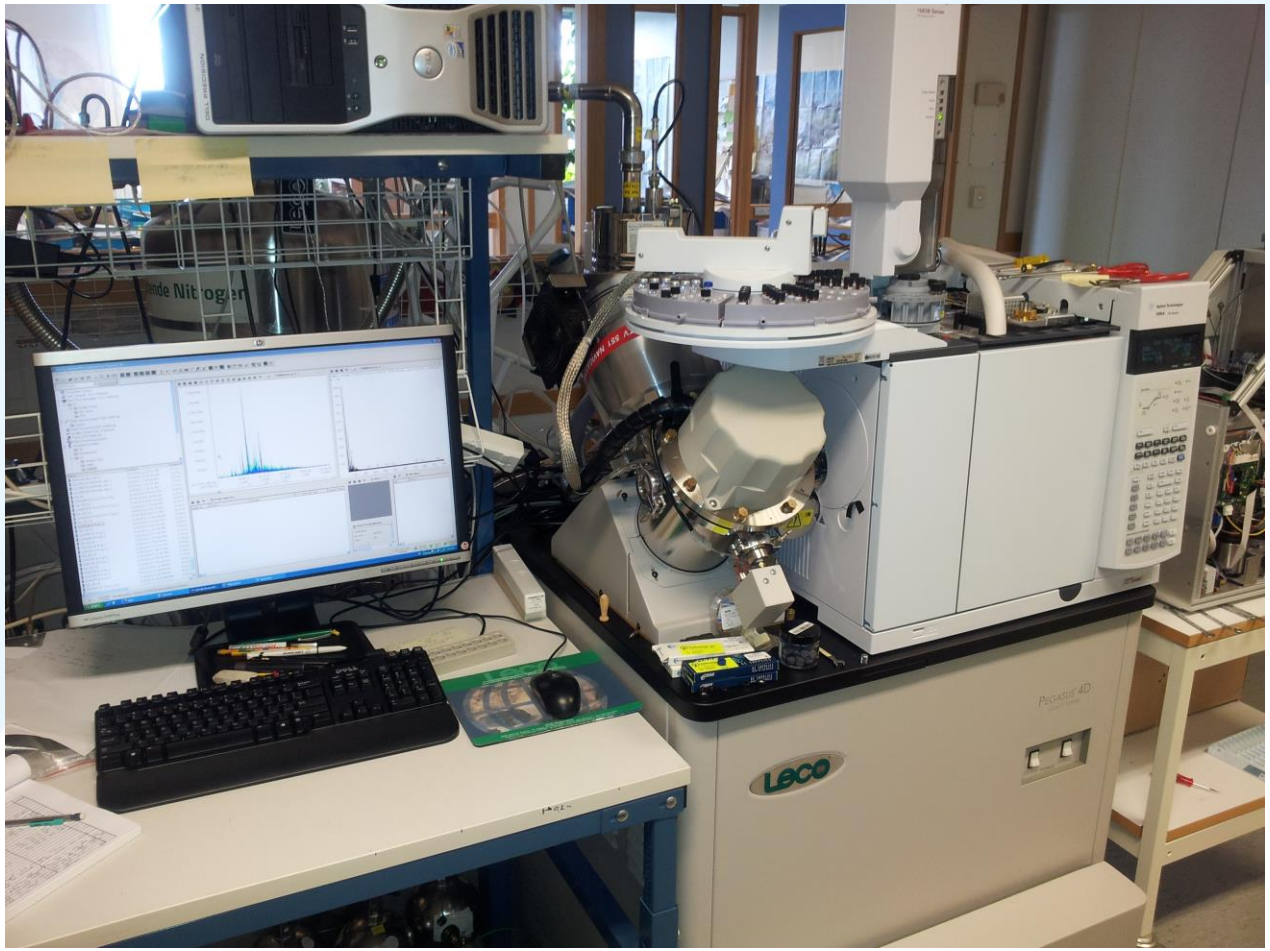
Properties of chemicals and the analytical techniques with which they are the most compatible



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

Agilent 7200 GC-HR-QTOF- MS

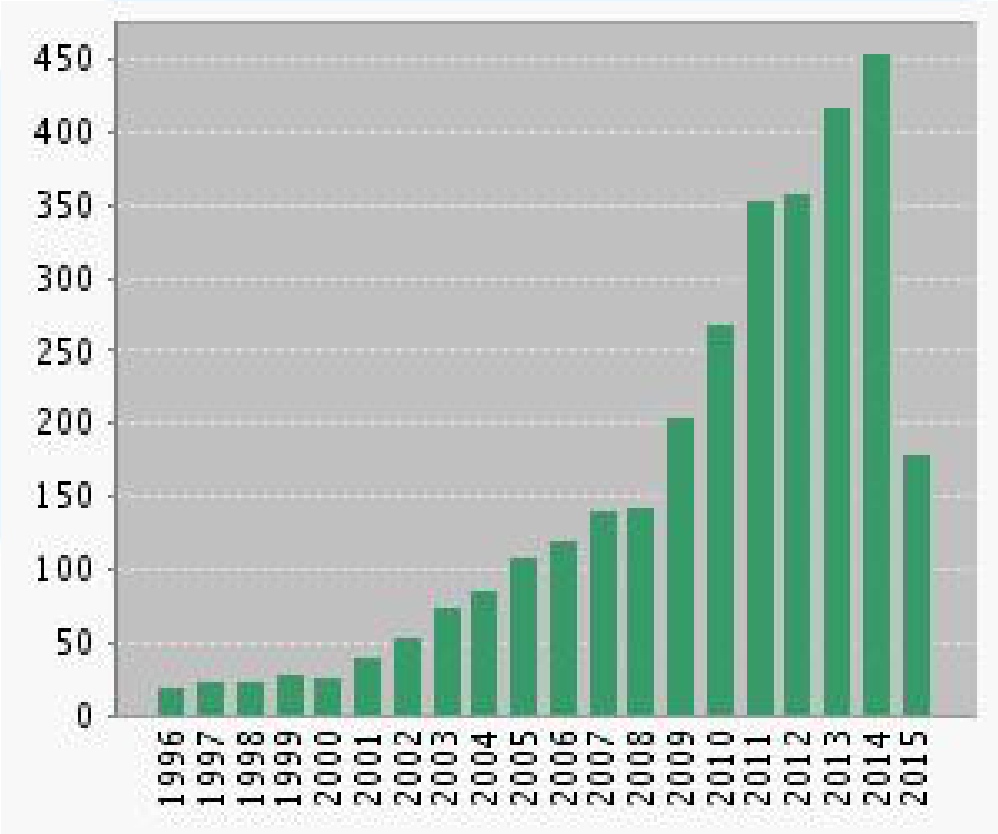
Leco GCxGC-LR-TOF



What we find in the (indoor)environment often depends on what we look for and how hard we look.

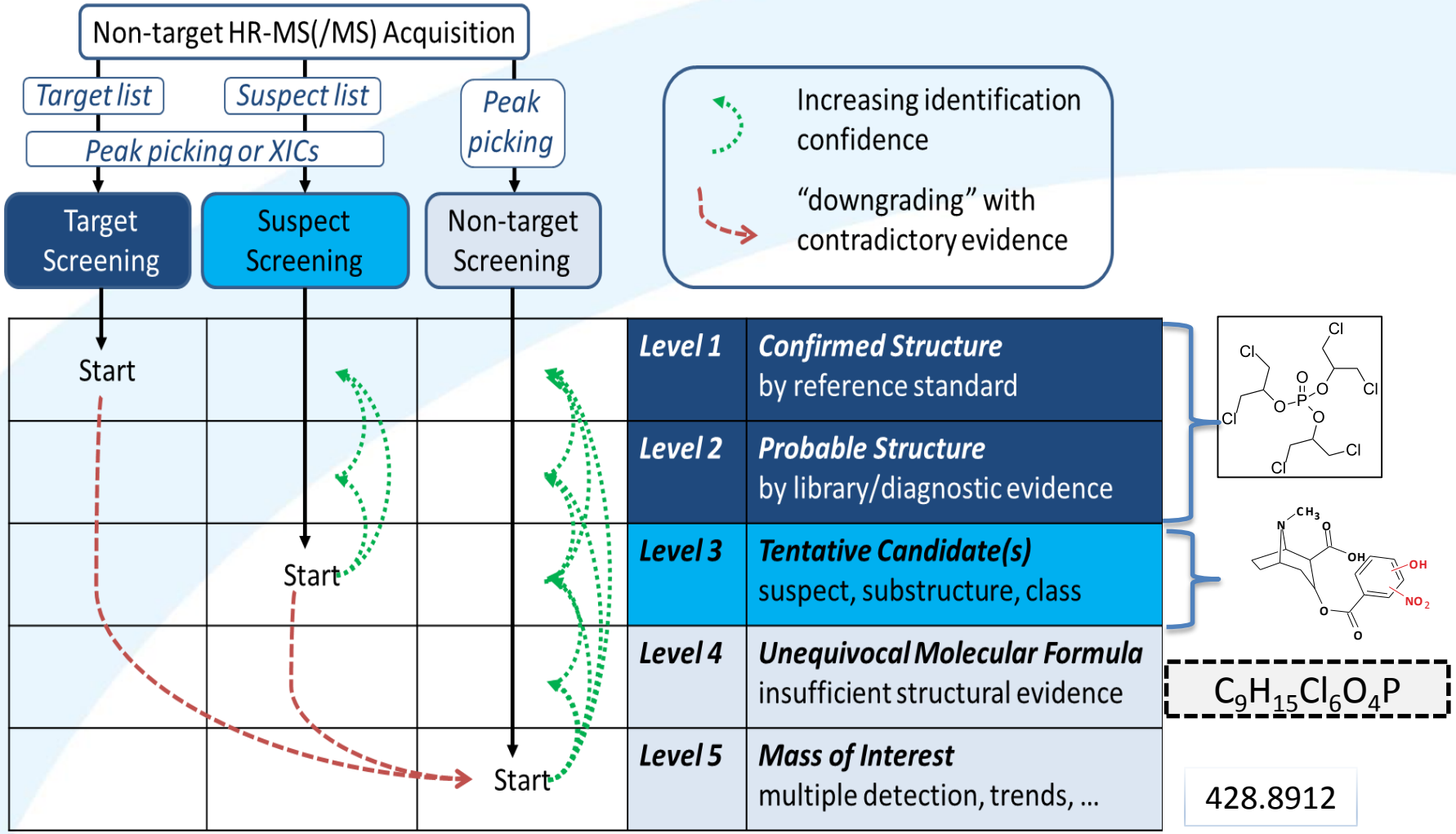
Increasing interest in non-target analyses

Search Web of Science for: Non target* AND mass spectrometry OR non-target* AND mass spectrometry (7 June 2015)



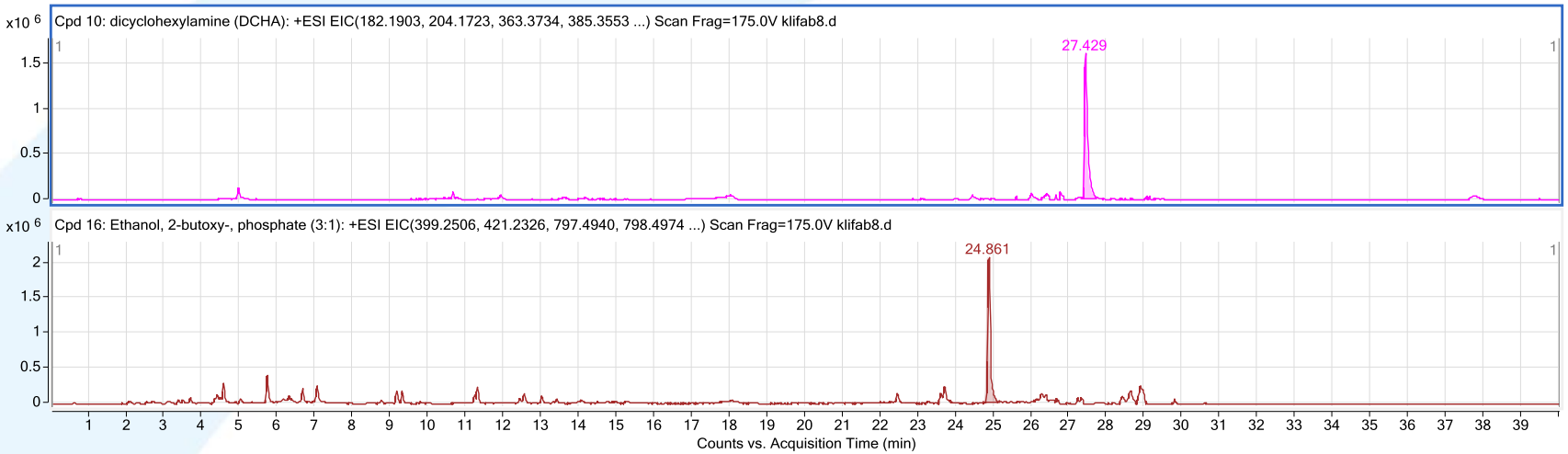
Approx. 4600 publications

Norman network approach



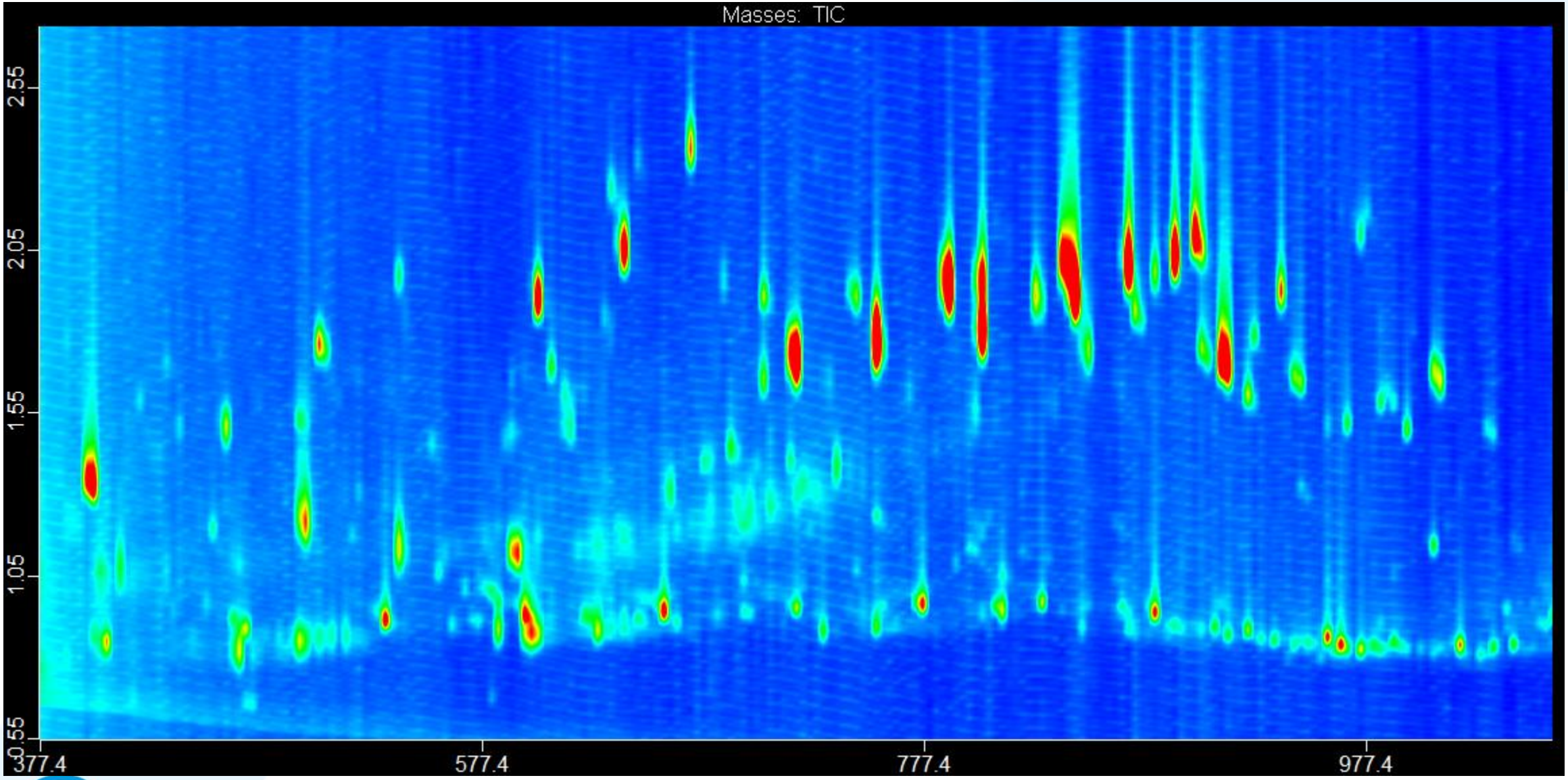
Adapted from Schymanski et al., 2015

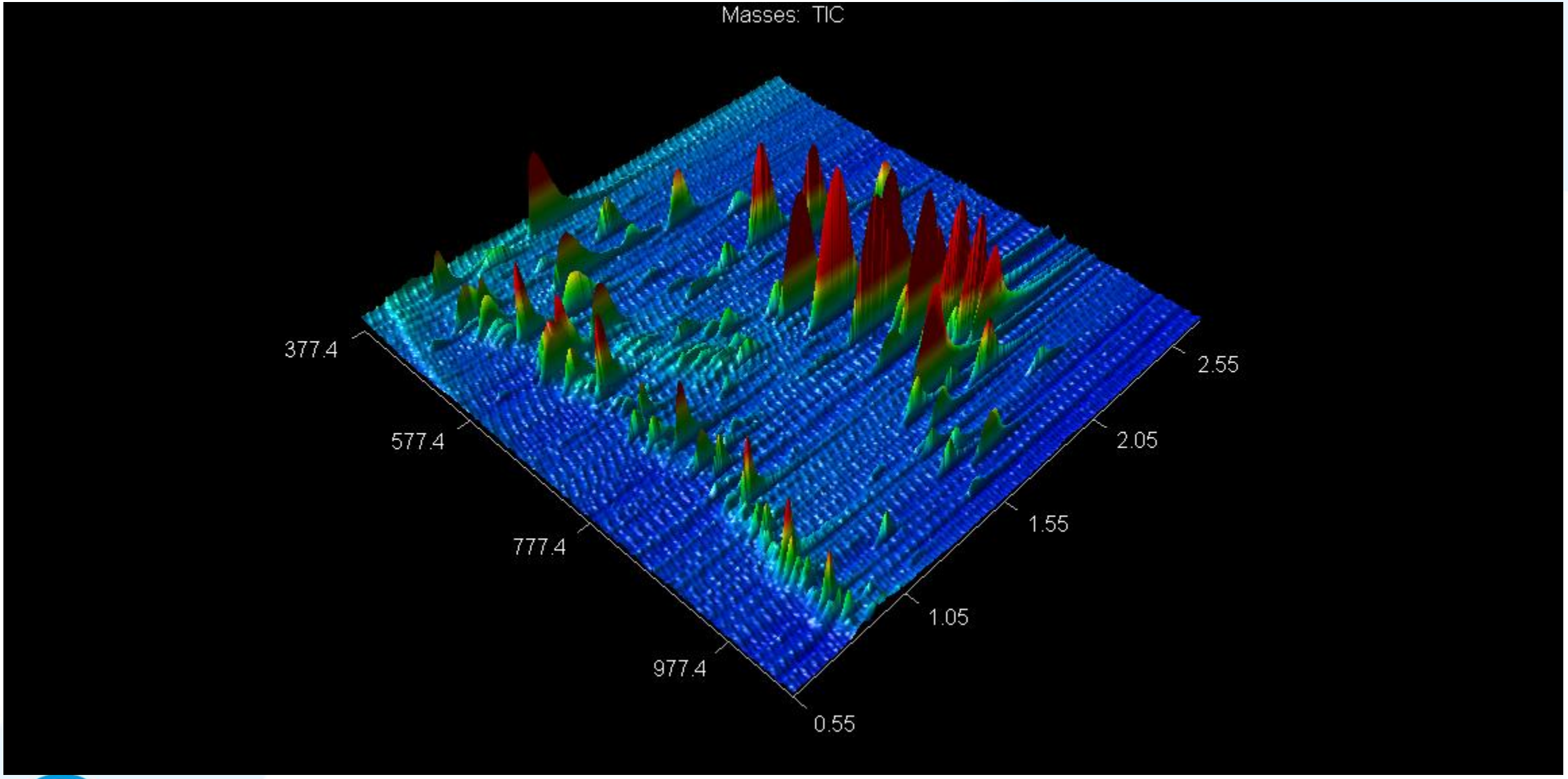
Targeted screening



Full scan

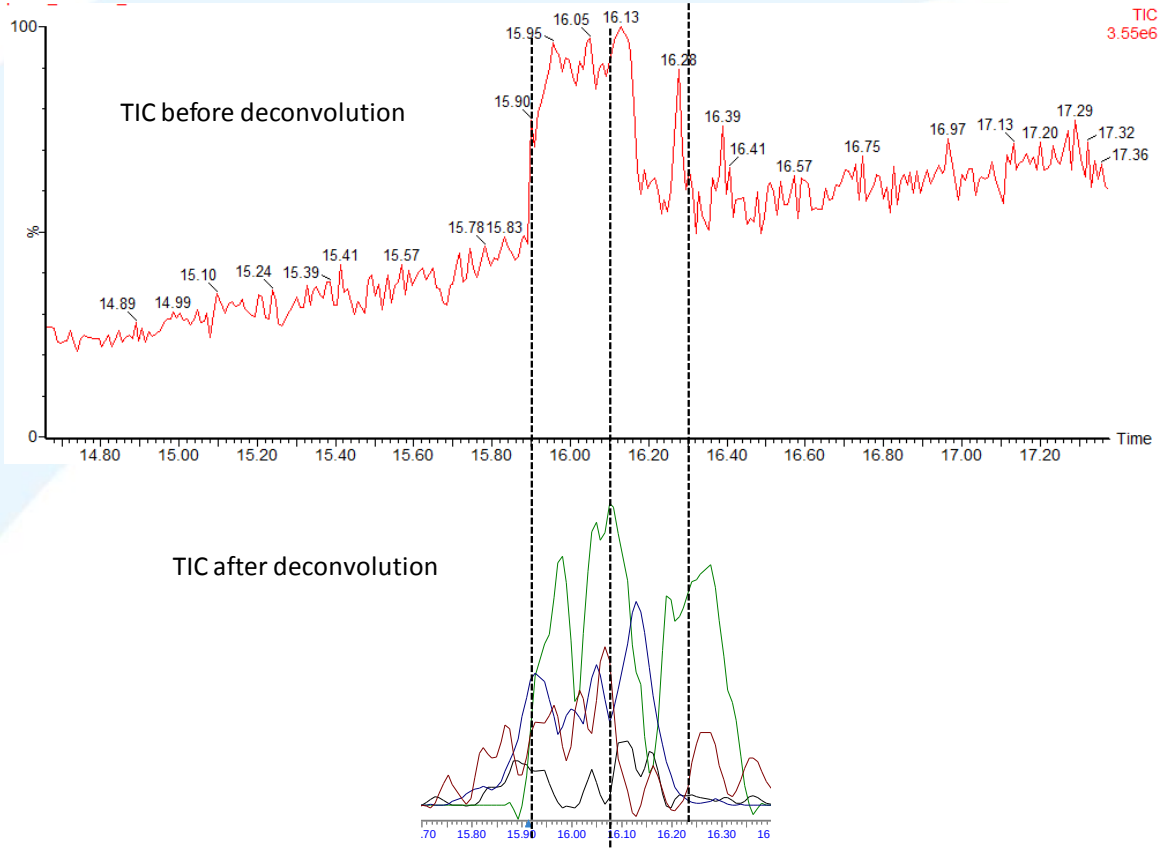
Target + suspect + non-target screening


Masses: TIC
2.55
2.05
1.55
1.05
0.55
377.4
577.4
777.4
977.4

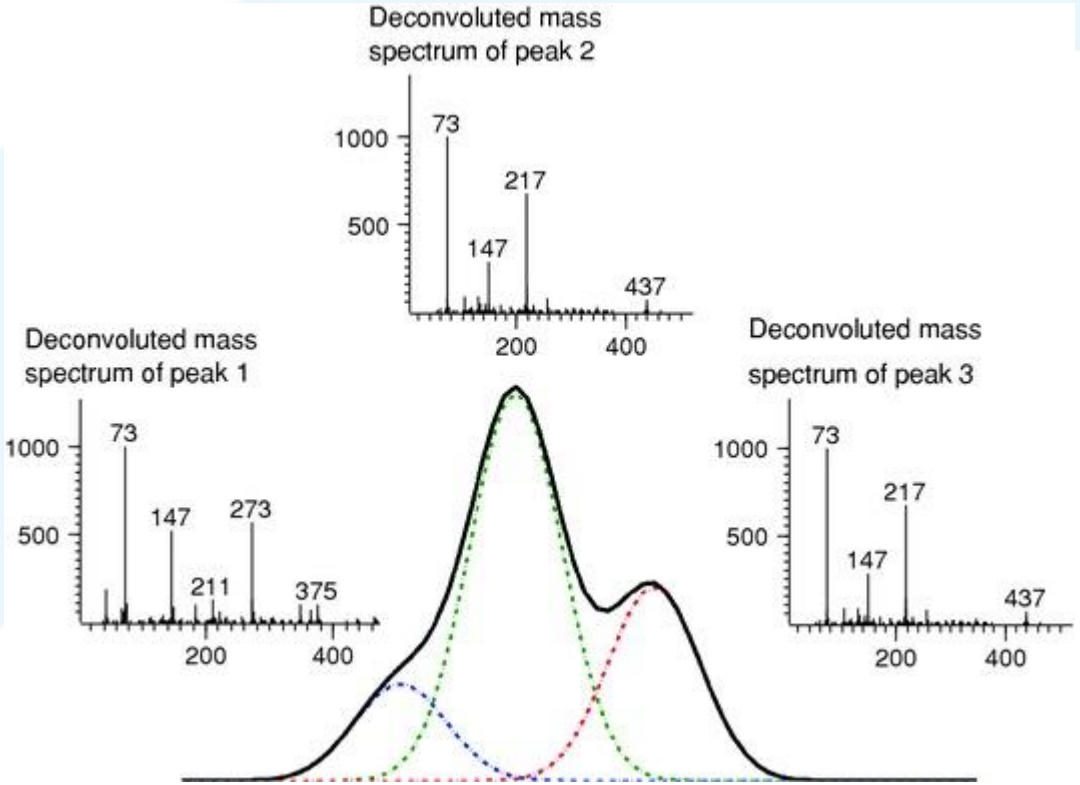

Masses: TIC
377.4
577.4
777.4
977.4
0.55
1.05
1.55
2.05
2.55

Data processing

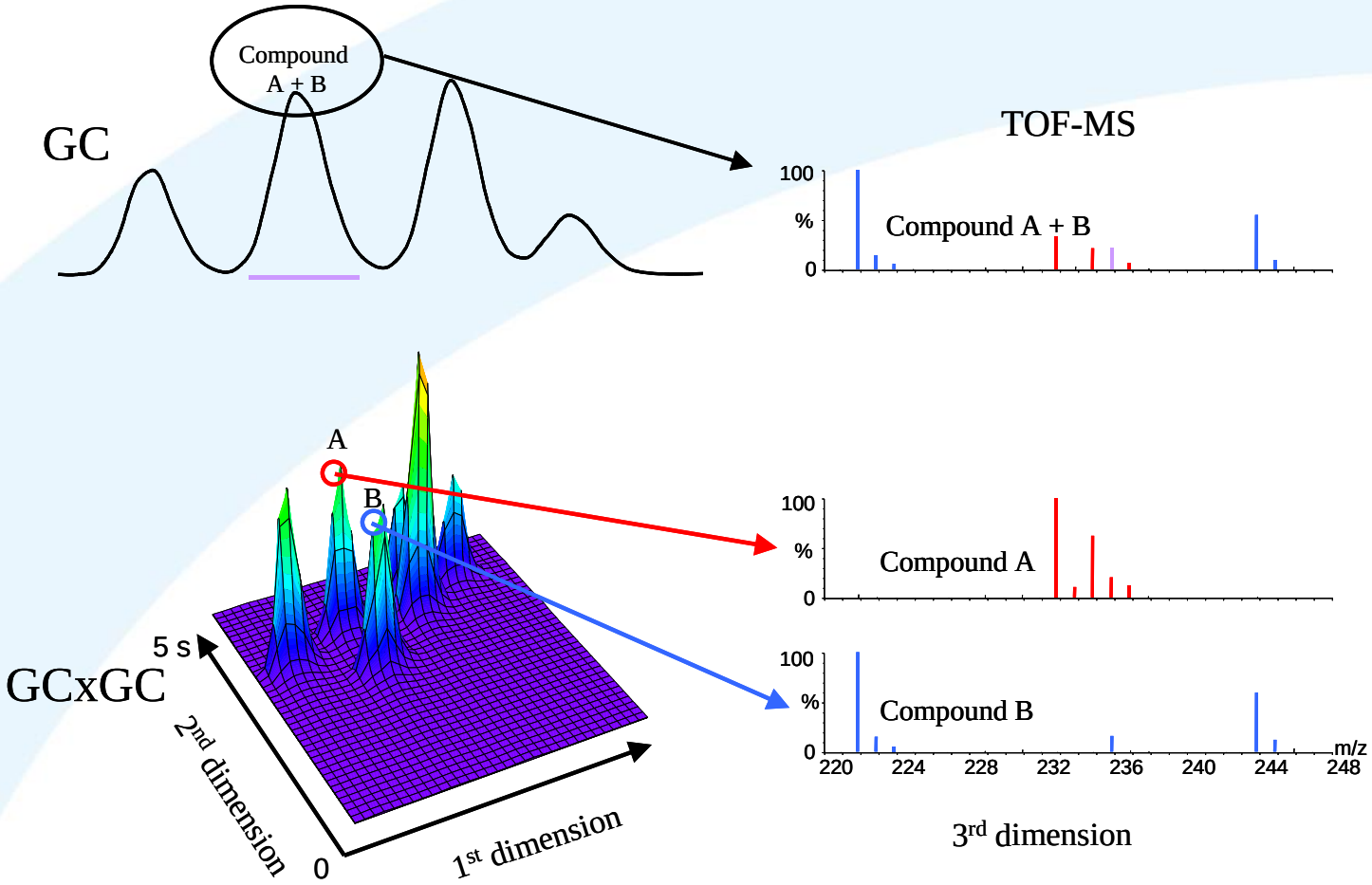
- Deconvolution



Deconvolution



GCxGC-TOF-MS


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

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

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Examples

I. A pilot non-target screening of indoor dust from personal houses and kindergarten in Norway (2012):

- A number of target emerging compounds found: phthalates, PFRs, PFCs, benzotriazoles, DEET, siloxanes → on average 40 known substances /per sample
- Approx. 300 substances per sample identified tentatively
- **On average 3000 substances per sample not identified in the duration of the study.**

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Examples

- Analyses of phthalates and bisphenol A in dust samples in collaboration with NHI → ExBisphA funded by NRC

Details from Dr Amrit Sakhi (NHI) tomorrow 10.25

Examples

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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Target/Suspect/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
- Effective tool in analyses and identification of emerging compounds

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What could we do to be more effective?

- International and national collaboration
- Exchanging list of suspect compounds
- Sharing in house generated spectra to free public mass spectral database, for example Norman Mass Bank

Acknowledgments

NHI and NRC for collaborative work in ExBisphA

NILU OrgSpec

Norwegian Environment Agency

Thank you for your attention!

Questions?

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