



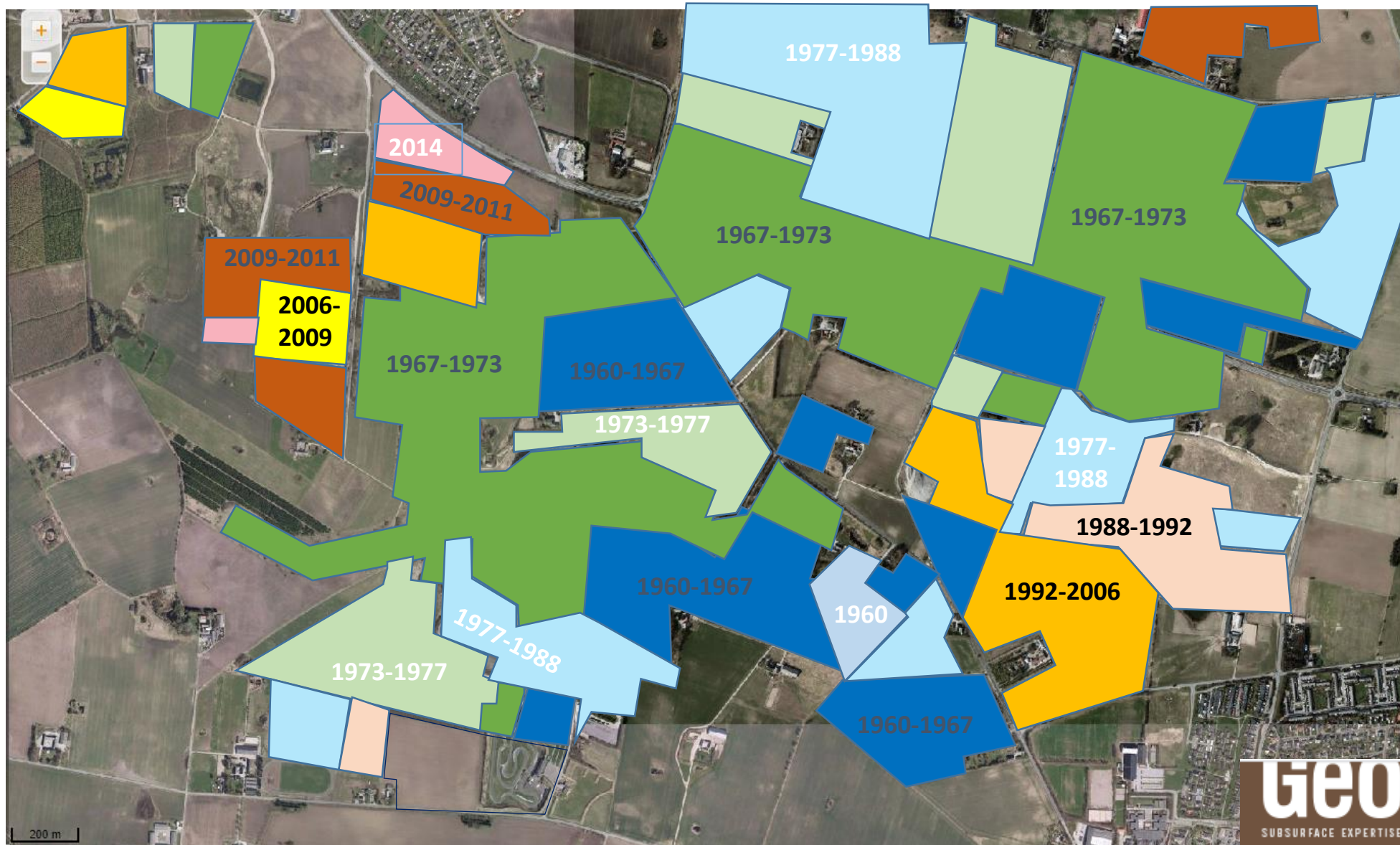
Non-target analyser ved Region Sjællands største grundvandsforekomst, Hedeland

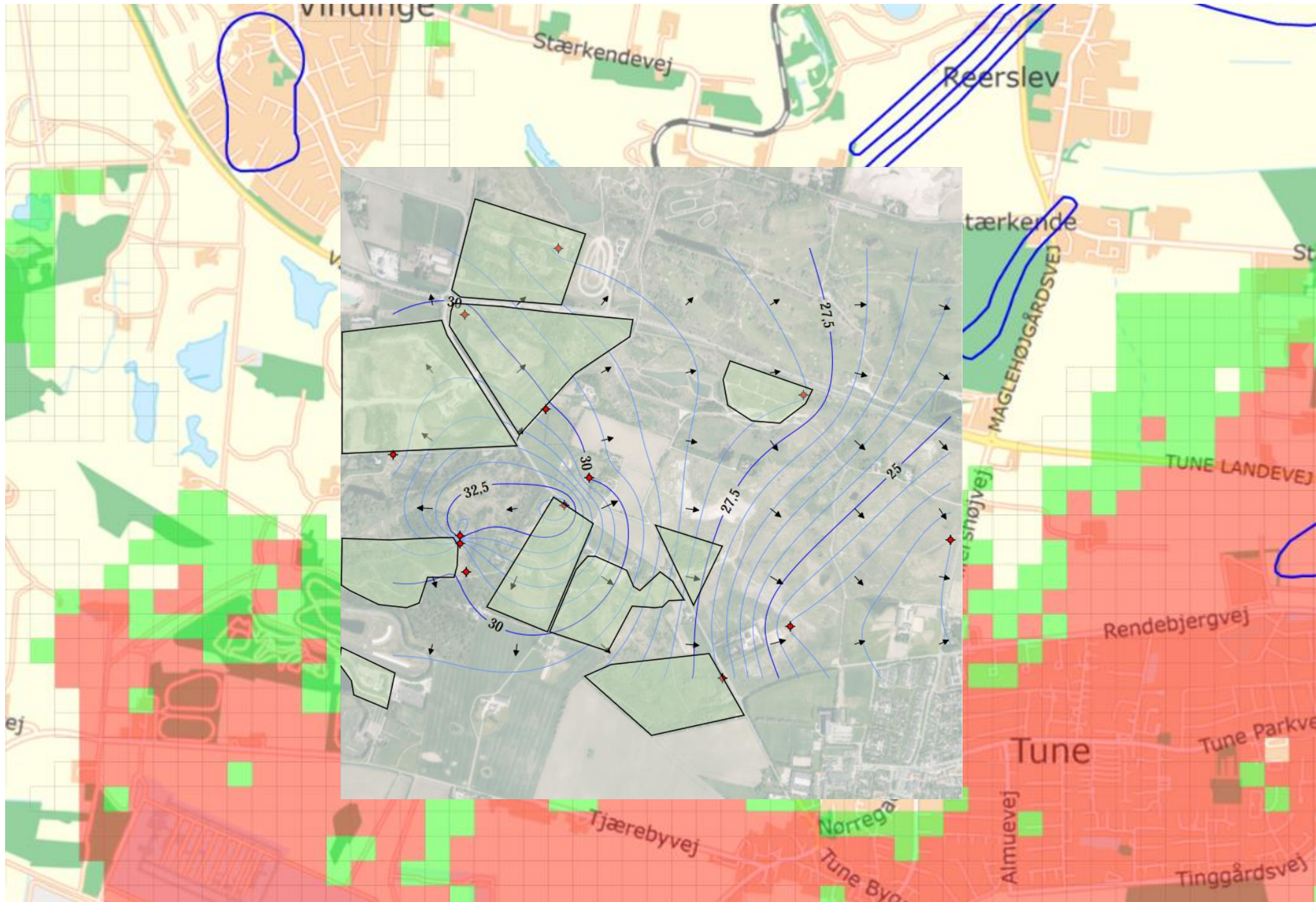
Nanette Schouw, Region Sjælland

Martin Hansen, Emil Frøkjær, Anders Johansen, Robert Young, Århus Universitet
ATV Vintermøde, 9/3-2021

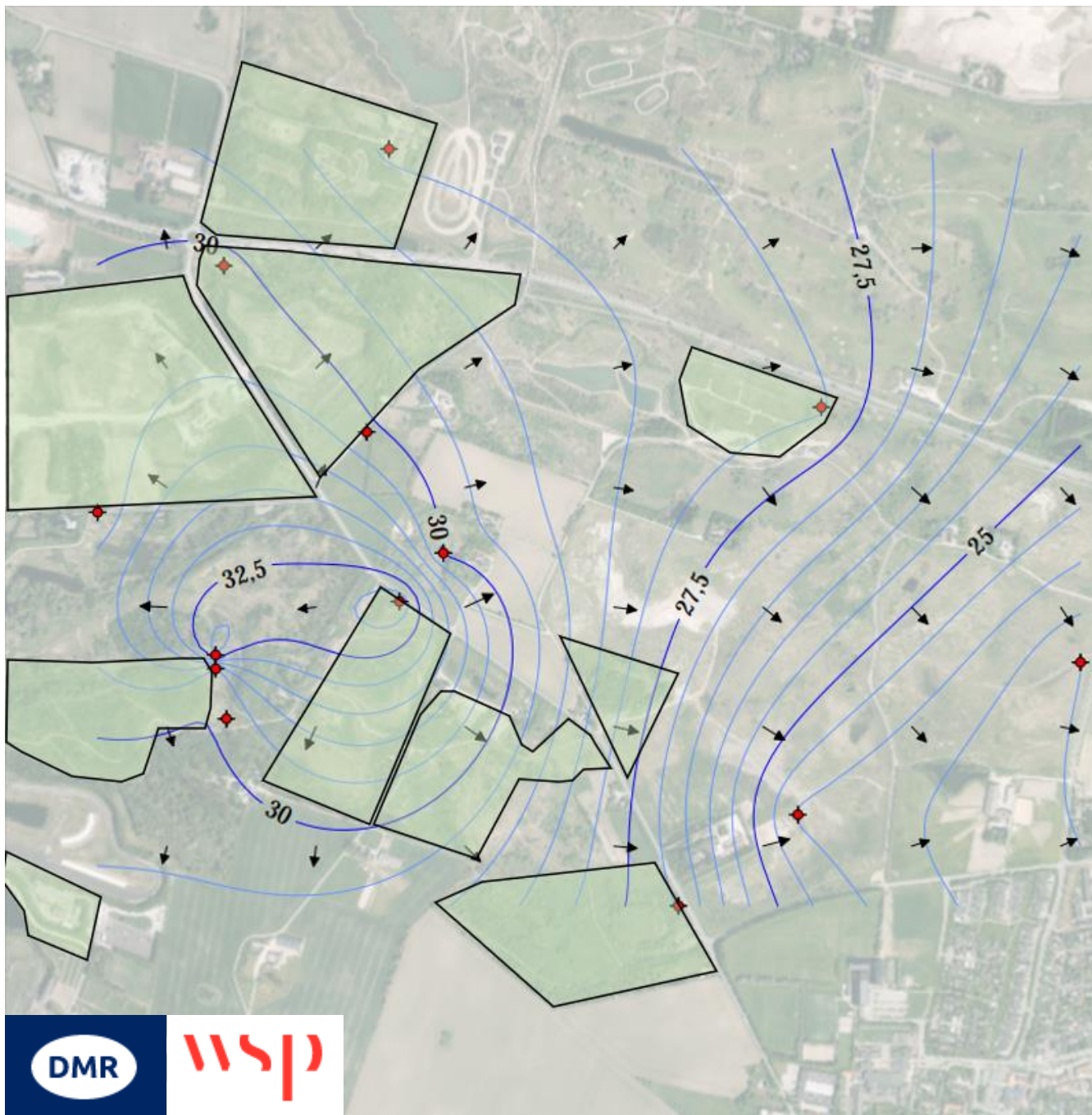


Råstofindvindinger





- Grundvandsdannende opland til
aktuel forsyning < 100 år
- Grundvandsdannende opland til
aktuel forsyning < 150 år
- Grundvandsdannende opland til
aktuel forsyning > 150 år
- BNBO



Target analysepakker:

Pesticider og metabolitter (233)

Phenoler og Chlorphenoler (20)

Chlorerede opløsningsmidler og metabolitter (15)

Polære opløsningsmidler (16)

BTEX og kulbrinter (15)

Boringskontrol, uorganisk (19)

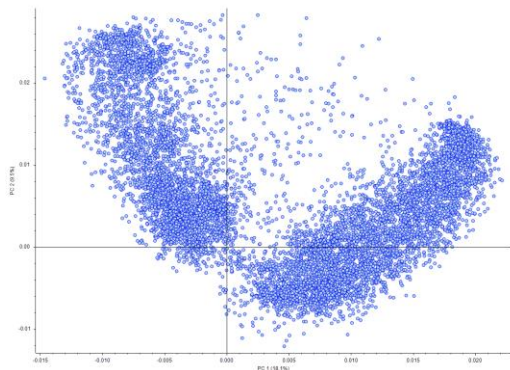
Bisphenol A

PFAS (12)

Redox parametre (15)

Holistic non-targeted and suspect screening

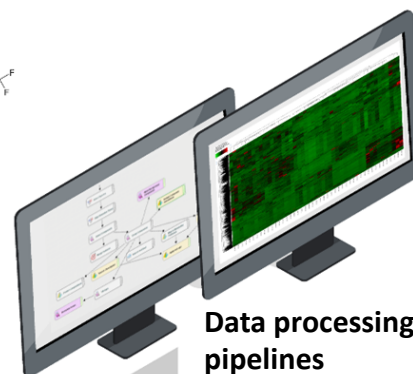
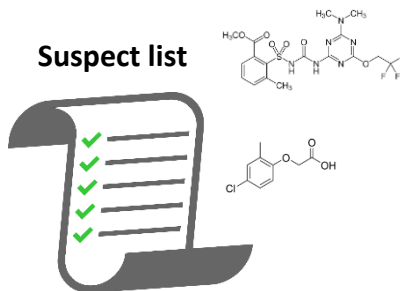
Non-targeted screening analysis



Retrospective analysis

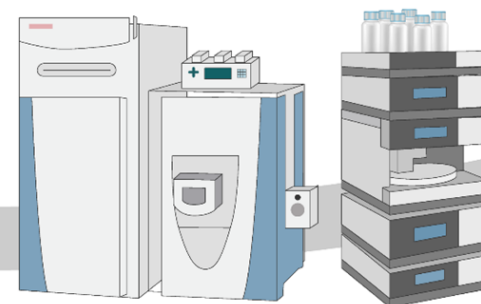


Suspect list



Data processing
pipelines

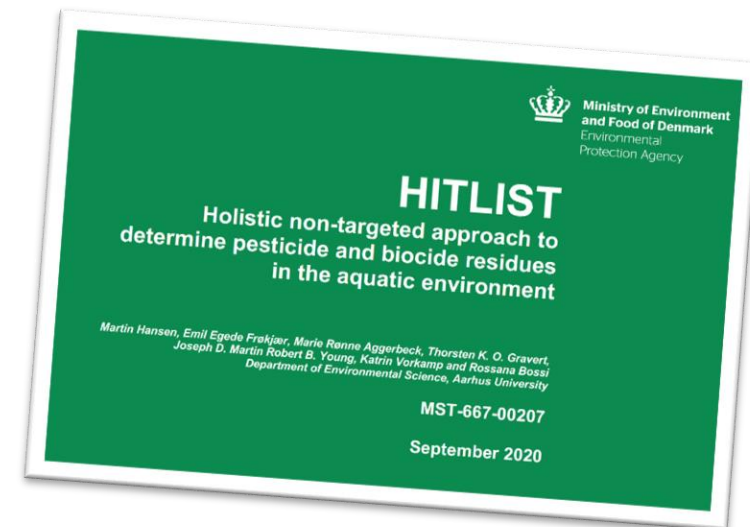
High-resolution mass spectrometry



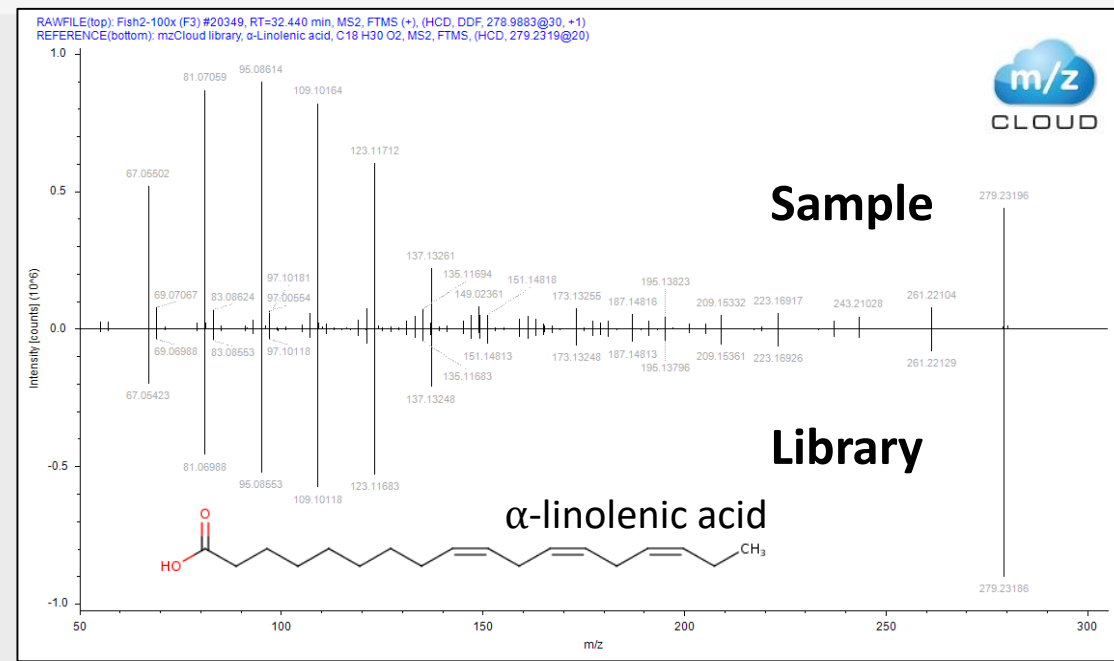
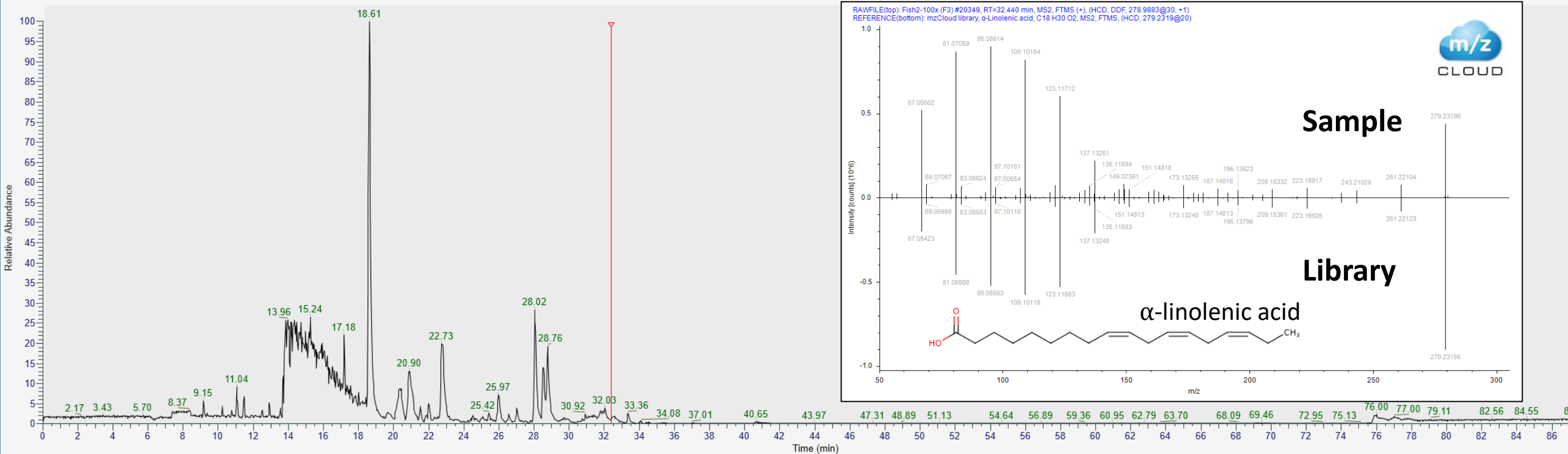
Sample preparation



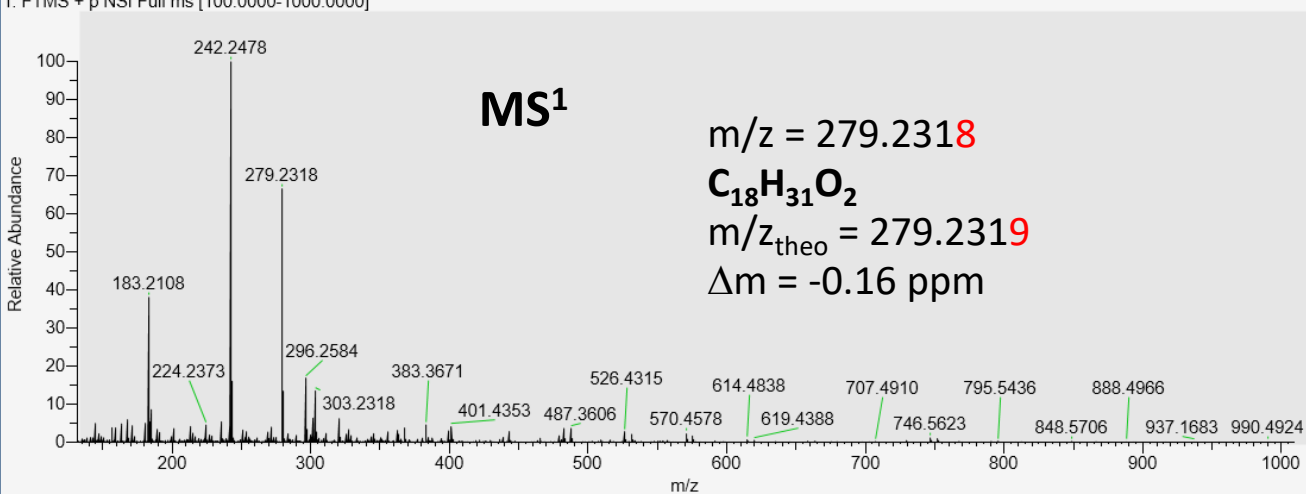
Sampling



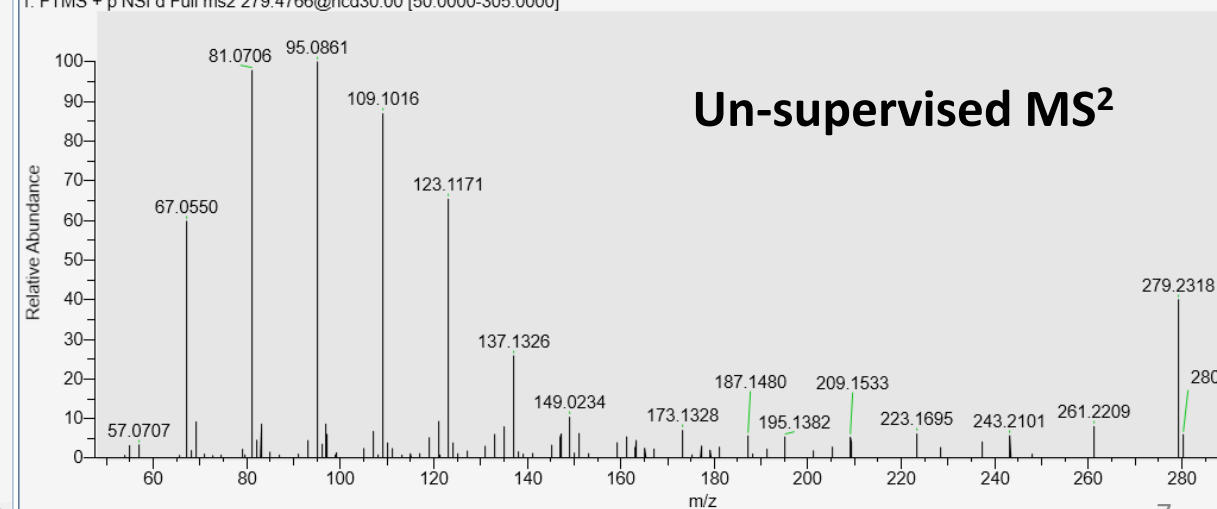


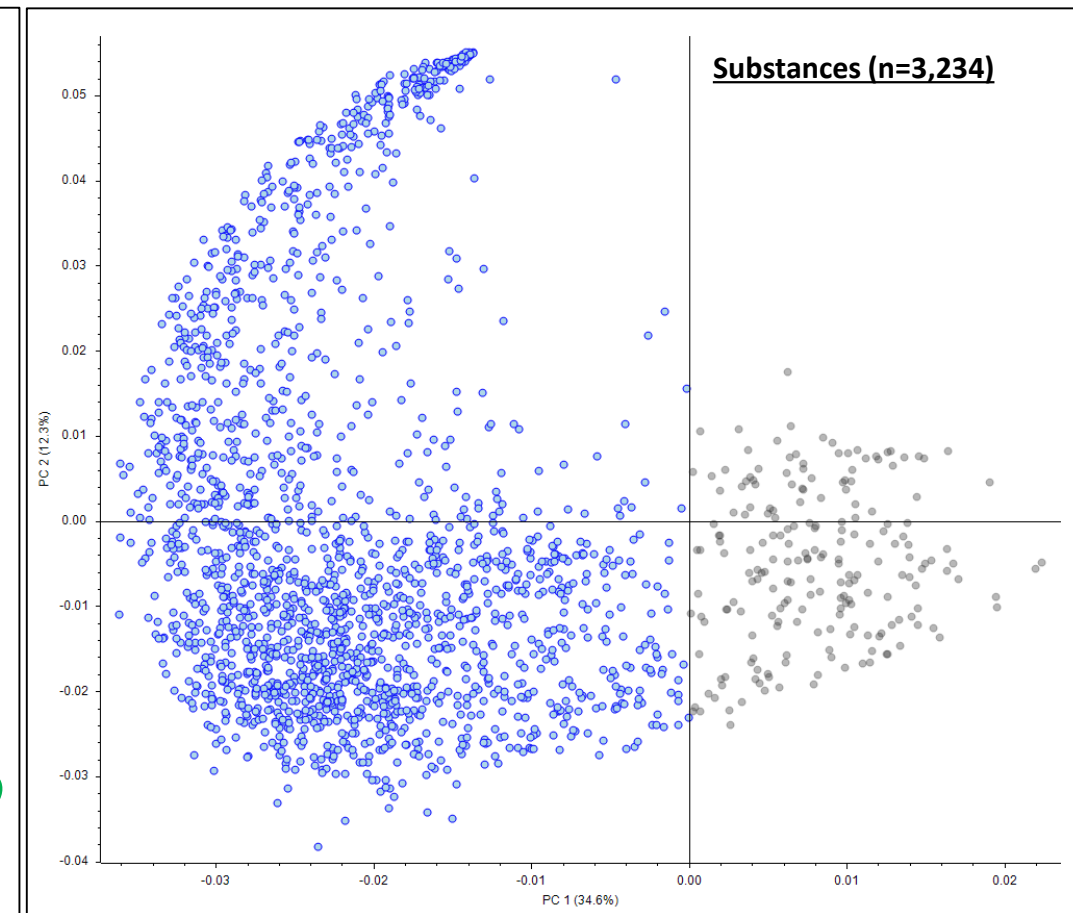
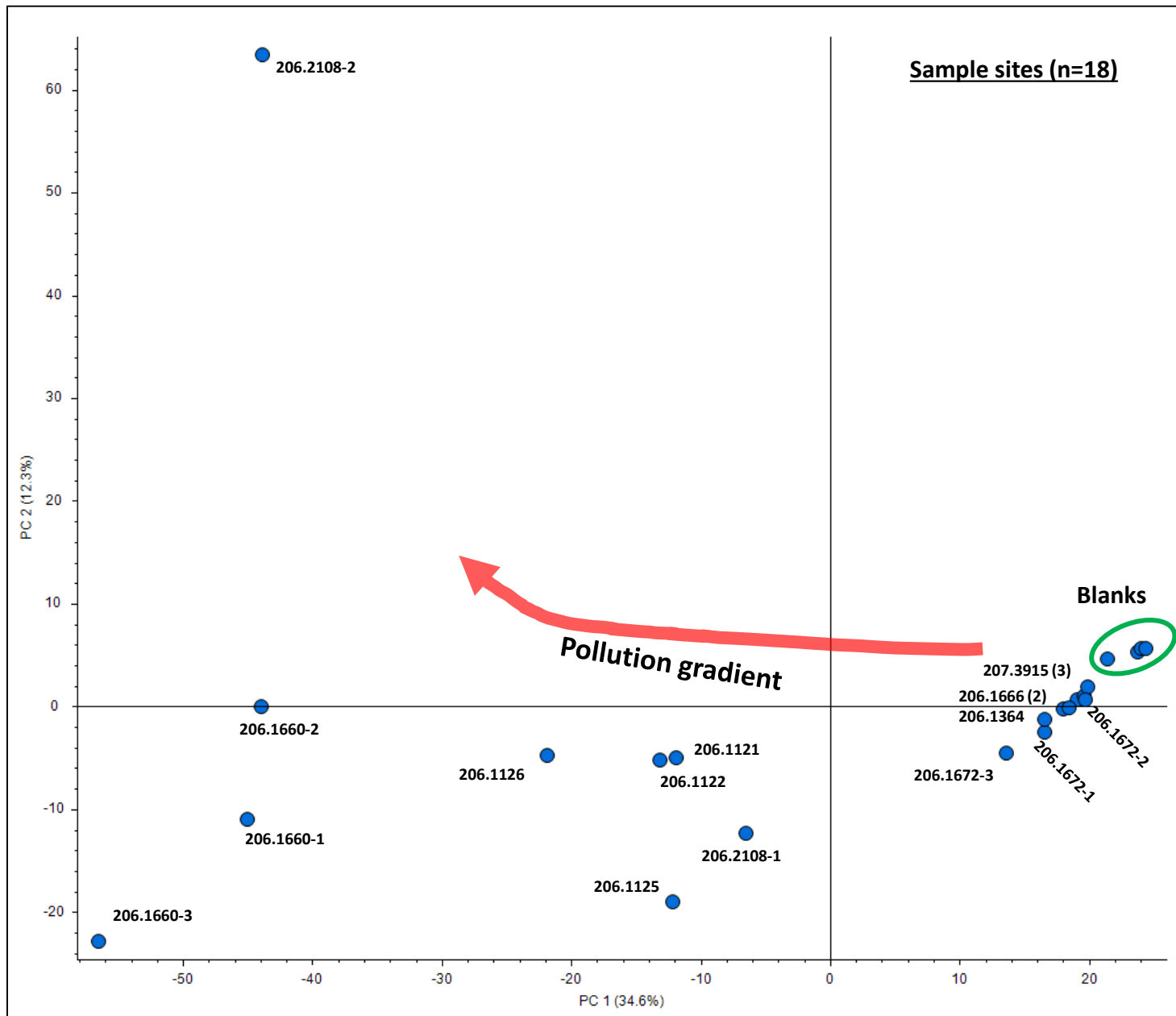


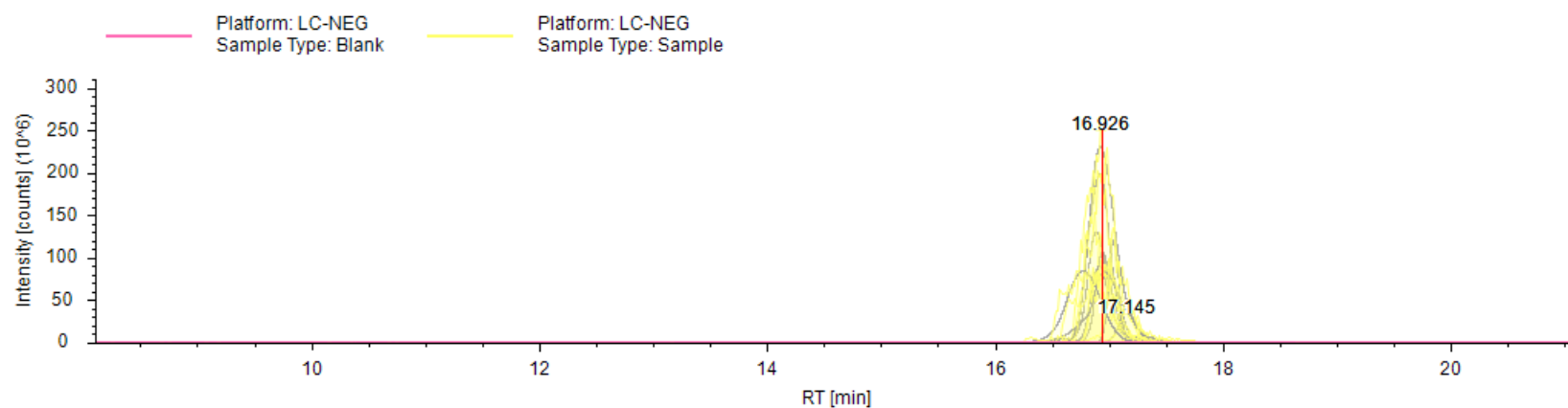
Spectrum 1 20329 - Fish2-100x
Fish2-100x #20329 RT: 32.41 AV: 1 NL: 6.94E+006
T: FTMS + p NSI Full ms [100.0000-1000.0000]



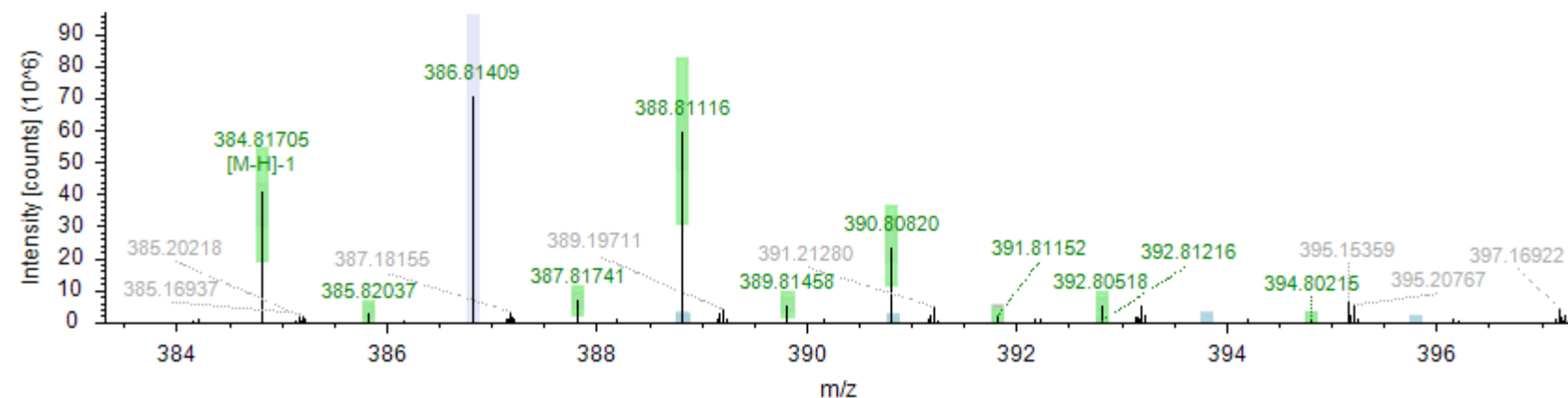
Spectrum 2 20341 - Fish2-100x
Fish2-100x #20341 RT: 32.43 AV: 1 NL: 7.55E+005
T: FTMS + p NSI d Full ms2 279.4766@hcd30.00 [50.0000-305.0000]



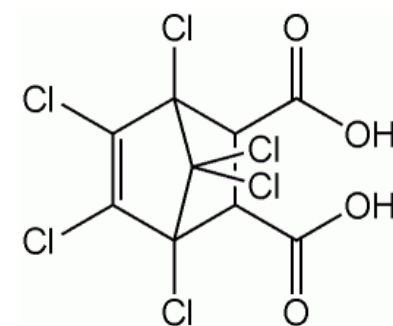
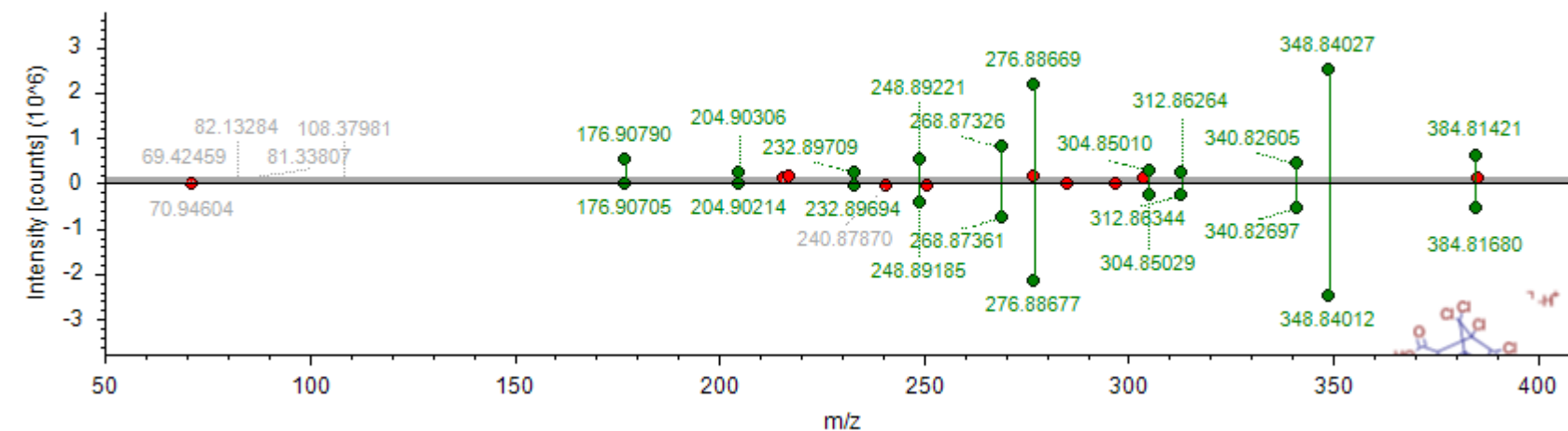




G33 #6261, RT=16.900 min, MS1, FTMS (-)
C9 H4 Cl6 O4 as [M-H]⁻¹



RAWFILE(top): G33 (F151) #6341, RT=17.082 min, MS2, FTMS (-), (HCD, DDA, 384.8171@(15;50), -1)
REFERENCE(bottom): mzCloud library, Chlorendic acid, C9 H4 Cl6 O4, MS2, FTMS, (HCD, 384.8168@10)



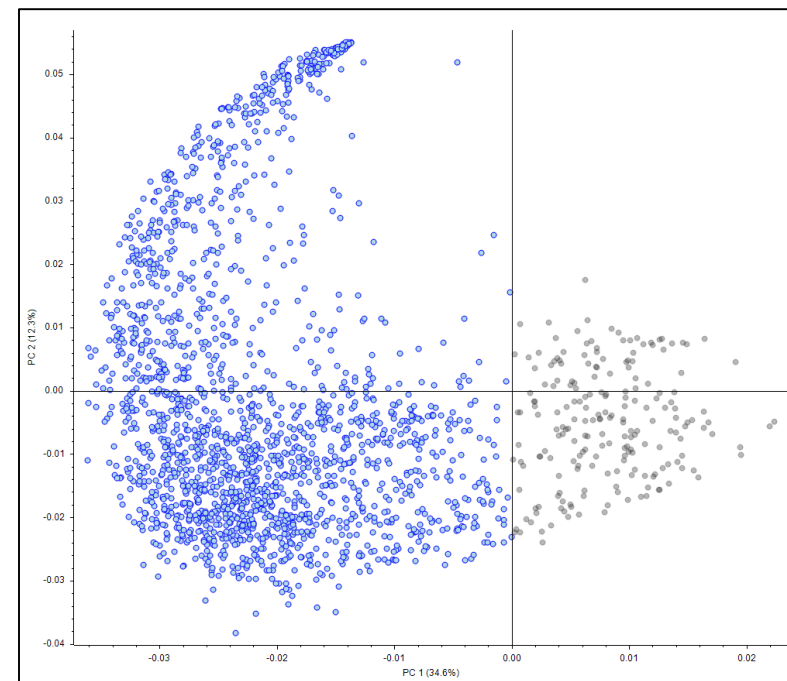
Chlorendic acid

(synthesis of flame retardants, polymers, breakdown product of several organochlorine insecticides)

Suspect list (n=14)

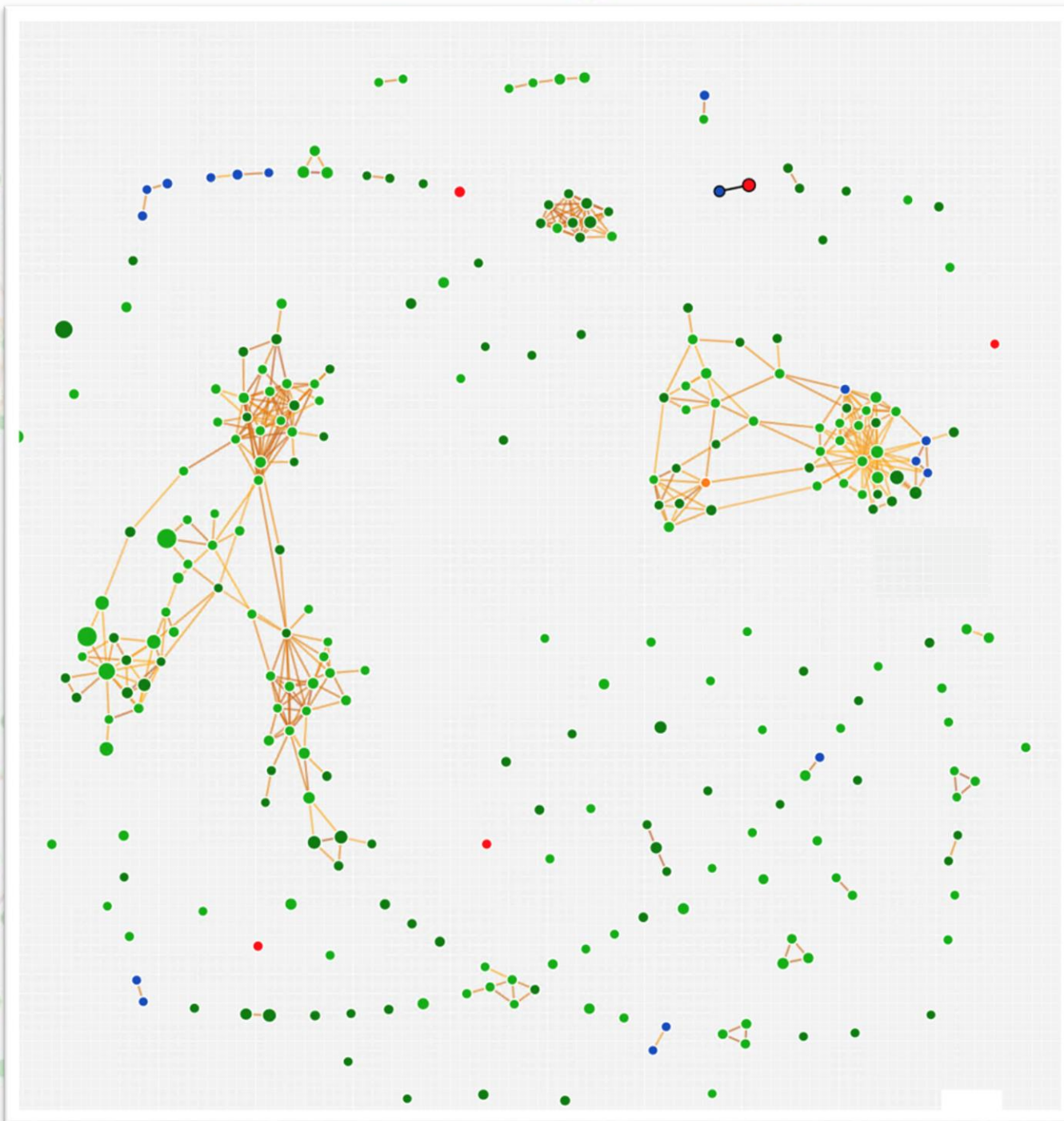
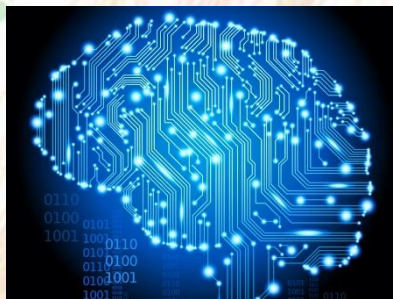
2,4-Dichlorophenol	C6 H4 Cl2 O
2,4-Dichlorophenoxypropionic acid	C9 H8 Cl2 O3
4-Chloro-3-methylphenol	C7 H7 Cl O
4-Chlorophenol	C6 H5 Cl O
6:2 Fluorinated telomer sulfonate	C8 H5 F13 O3 S
alachlor oxanilic acid	C14 H19 N O4
Bisphenol A	C15 H16 O2
DEET	C12 H17 N O
Ethofumesate	C13 H18 O5 S
kresoxim-methyl	C18 H19 N O4
Mecoprop	C10 H11 Cl O3
Napropamide	C17 H21 N O2
Perfluoro-1-octanesulfonic acid (PFOS)	C8 H F17 O3 S
Terbutylazin	C9 H16 Cl N5

Non-targeted list:
~3234 unknown substances



Molecular network analysis

Machine learning

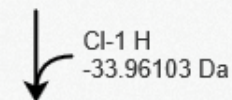
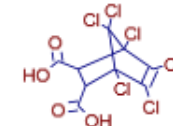


Reductive Dechlorination

Change Cl-1 H
Mass -33.96103 Da
Score 69 %
Coverage 75 / 63 %
Matches 21 / 12

Chlorendic acid

Formula C₉H₄Cl₆O₄
RT 16.921 min
MW 385.82429 Da
Max. Area 3,945,419,231
Fragments 28



Unknown Compound

Formula C₉H₅Cl₅O₄
RT 16.066 min
MW 351.86319 Da
Max. Area 564,649,678
Fragments 19

Target < > Non-target, overensstemmelse?

	Target [µg/L]	Flest detektioner?	NTA - detekteret og identificeret [Ja/Nej]		Target [µg/L]	Flest detektioner?	NTA - detekteret og identificeret [Ja/Nej]
MCPP	3,5	=	Ja	BAM	0,26	>	Nej
Dichlorprop	0,11	=	Ja	Metaldehyd	0,26	>	Nej
Napropamid	<0,01	<	Ja	Dithiocarbamater	0,26	>	Nej
Ethofumesat	<0,01	<	Ja	Pyrimidinol	0,26	>	Nej
Alachlor o.a.	<0,01	<	Ja	4-CPD	0,26	>	Nej
4-Chlorophenol	<0,01	<	Ja	4-Chlorophenol	0,04	>	Nej
2,4-Dichlorphenol	<0,01	<	Ja	2,4-Dichlorphenol	0,25	>	Nej
Kresoxim-methyl	<0,01	<	Ja	Kresoxim-methyl	11	>	Nej
Terbutylazin	<0,01	<	Ja	Terbutylazin	0,1	>	Nej
DEET	Begge	<	Ja	DEET	2,1	>	Nej
Bisphenol A	0,58	<	Ja	Desethyl-hydroxy-atrazin	0,17	>	Nej
PFOS	0,034	>	Ja	Formaldehyd	36	>	Nej
FTS 6:2	0,019	>	Ja	BTEX	0,27	>	Nej
4-chlor-3-methylphenol	<0,02	<	Ja	Total-C	7,9	>	Nej
Target: 345 analyseparametre				Chlorerede opl. Sum	0,8	>	Nej
				4-methyl-Phenol p-cresol	2,2	>	Nej
				Phenol	0,63	>	Nej

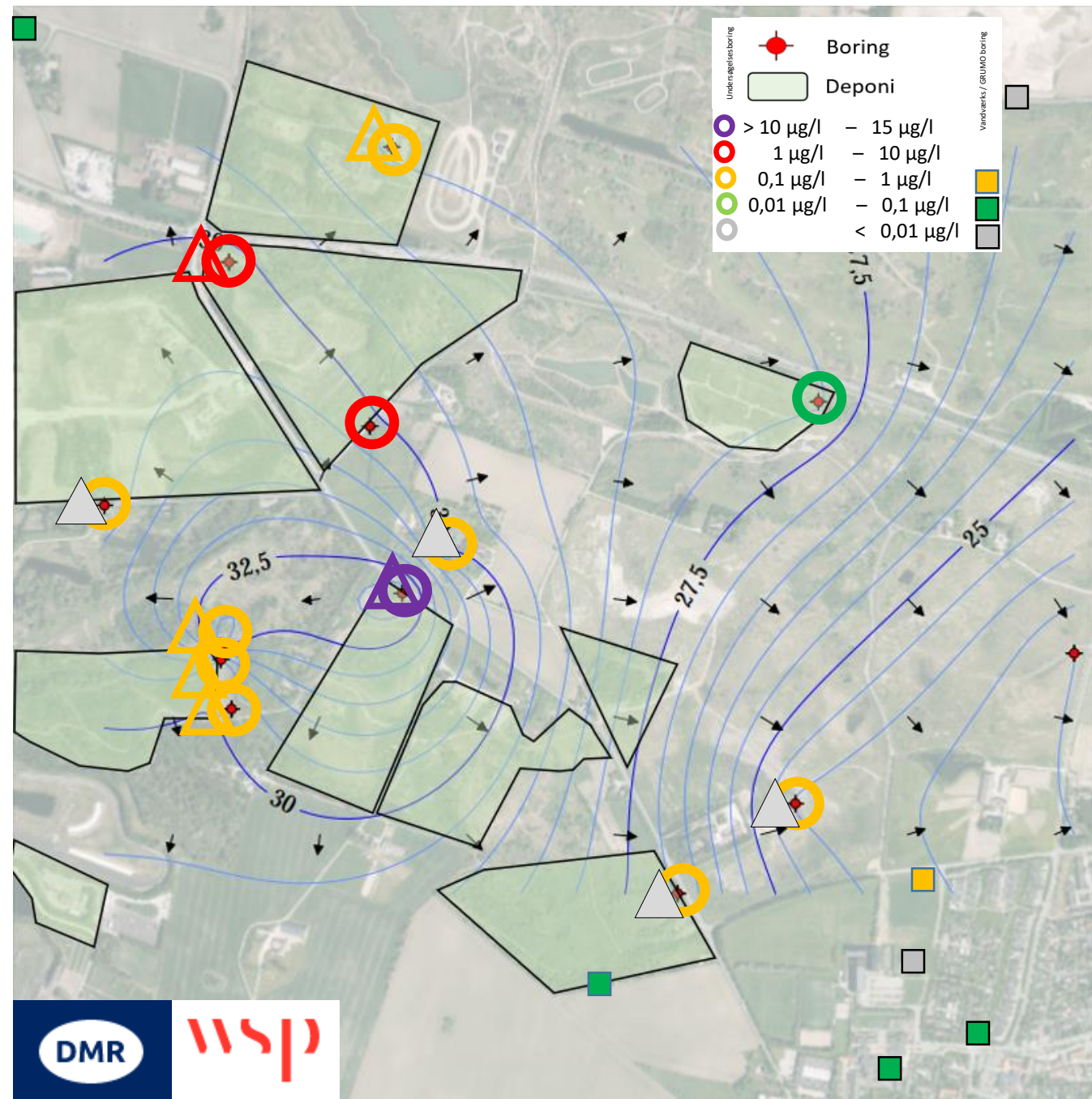
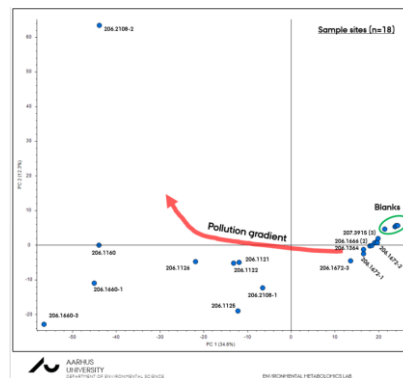
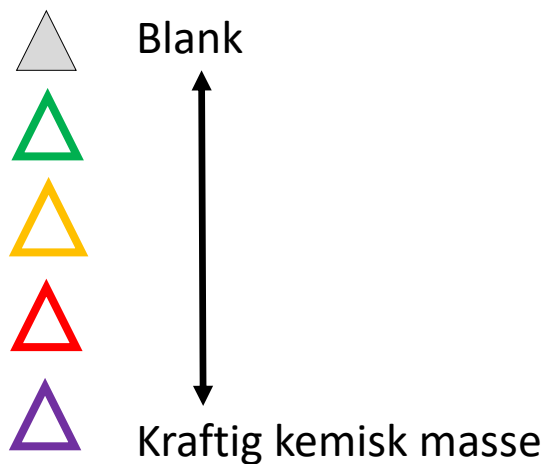
Non-target: 269 ekstra stoffer identificeret
I alt 3234 ekstra stoffer detekteret

Pesticider

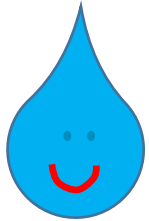
Forurenings-trykket er størst ved vandspejl

Særligt: MCPP, Dichlorprop, 4-CPP, DMS, BAM, DPC

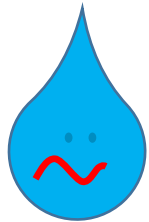
Forureningsmassen baseret på NTA følger *nogenlunde* target pesticidanalyseresultaterne



Administrative overvejelser



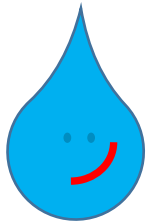
Grundvandets DNA – sikring af fuldt overblik, regionens indsats kan medtage alt relevant af én omgang



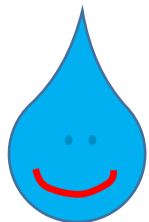
Men kan vi følge med: administrativt og lovgivningsmæssigt?



Vil vi vide 'alt'? < - > hvad er alternativet – lukke øjnene?



Viden giver handlemuligheder - handleforpligtelser





Miljø- og Fødevareministeriet

Miljøstyrelsen



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