



How can non-target screening techniques support environmental monitoring and chemicals management?

Hands-on experience with large contaminant data sets: NORMAN approach

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Many chemicals in the environment but only few determine the risk. Example: mixture toxicity of 15 anti-androgenic compounds in typical environmental concentrations



Five chemicals explain 80% of the risk Efficient management needs to focus on these chemicals



NORMAN approach –

www.norman-network.net

- Cross-Working Group Activity Non-target Screening (NTS)
 - WG Prioritisation
- NORMAN
 - Suspect List Exchange: <u>https://www.normandata.eu/normansusdat/</u>
 - Close collaboration with the US EPA CompTox Chemistry Dashboard team
 - Digital Sample Freezing Platform:
 - http://www.norman-data.eu/
 - MassBank: <u>http://massbank.eu/MassBank/</u>
- Supporting and closely cooperating with NTS projects
 - APEX, JDS4, EMBLAS, SOLUTIONS...
- Collaborative trials
 - Surface water, Indoor environment dust...





NTS in the Joint Danube Survey 4 (ICPDR) and Joint Black Sea Survey in June 2019 (EU/UNDP EMBLAS-Plus)





Status quo of identification approaches for LC/GC-MS





NORMAN CT – non target screening *Received datasets*

		Name of organization / institute	Name of laboratory	Total DCTs	LC-MS	GC-MS
	1	IAREN- Water Institute of the Northern Region	Laboratory of Chromatography			
2 NIVA		NIVA	NIVA Oslo	1	1	
	3 SUEZ Environment		CIRSEE	1	1	1
			Reference Laboratory for Environment			
	4	T. G. Masaryk Water Research Institue	Components and Waste			
	5	University of Antwerp	Toxicological Centre	1	1	
	6	Technische Universitaet Muenchen	Chair of Urban Systems Engineering	1	1	
7 University Jaume I (UJI)		University Jaume I (UJI)	Research Institute for Pesticides and Water	1		1

LC-HR-MS: T&S 1072; NT&Unknown 21380 GC-MS: T&S 348; NT&Unknown 116 Less then 5% overlap

14	Ministry of the Environment of Canada	Laboratory Services Branch			
15	BRGM	Laboratory Division			
16	IRSTEA	LAMA	1	1	
17	Environmental Institute (EI), SK	Analytical Laboratory	1		1
18	Helmholtz-Centre for Environmental Research - UF	Æffect-directed analysis	1	1	
19	University of Padua / Department of Chemistry	Group of Analytical Chemistry	1	1	
20	University of Bordeaux	team LPTC, laboratory EPOC (UMR 5805 CNRS)			
21	Masaryk University / Faculty of Science	RECETOX			
22	Bundesanstalt für Gewässerkunde	Gewässerchemie	1	1	
23	Zweckverband Landeswasserversorgung	Betriebs- und Forschungslaboratorium	1	1	
24	Croatian Waters	Central Water Management Laboratory	1	1	
25	University of Tuebingen	Environmental Chemistry	1	1	
26	University of Umea	Department of Chemistry	1		1
			18	16	7



JDS3 - Distribution of 7767 different mass spectral processed features through the Danube river and

its tributaries; Danube countries are shown on x-axis and normalised signal intensity values are represented on y-axis; each single feature/compound is represented by a horizontal bar at a fixed position on the chart (position given by a unique combination of retention time, accurate mass spectrum, name, molecular formula, etc.) and the intensity of signal increase is indicated by blue (low) to red (high) colour



01 GERMANY 02 AUSTRIA 03 SLOVAKIA 04 HUNGARY 05 CROATIA 06 SERBIA 07 ROMANIA 08 BULGARIA 09 UKRAINE





How to collect data?



COOK BOOK



Size: Few GB-hundreds MB

Size: Few MB

Basic-Information

Sample-MetaData

Instrumental-MetaData

RTI_Calibration

Upload-Files

I have not injected these these calibrants OR I am using GC-HRMS

You have to input the RT of the calibrants. Let the cells empty for compounds without RT.

1 Guanylurea 1.325 141-83-3 C2H6N4O 103	0614
2 Amitrol 1.392 61-82-5 C2H4N4 85	0509
3 Histamine 1.642 51-45-6 C5H9N3 112	0869
4 Chlormequat 1.875 999-81-5 C5H13CIN 122	0731
5 Methamidophos 2.625 10265-92-6 C2H8NO2PS 142	0086
6 Vancomycin 3.192 1404-90-6 C66H75Cl2N9O24 724	7224
7 Cefoperazone 4.342 62893-19-0 C25H27N9O8S2 646	1497
8 Trichlorfon (Dylox) 5.142 52-68-6 C4H8Cl3O4P 256	9299
9 Butocarboxim 5.992 34681-10-2 C7H14N2O2S 191	0849
10 Dichlorvos 6.908 62-73-7 C4H7Cl2O4P 220	9532
11 Tylosin 7.975 1401-69-0 C46H77NO17 916	5264
12 TCMTB 9.208 21564-17-0 C9H6N2S3 238	9766
13 Rifaximin 10.025 80621-81-4 C43H51N3O11 786	3596
14 Spinosad A (Spinosyn A) 11.525 131929-60-7 C41H65NO10 732	4681
15 Emamectin B1a 12.475 121124-29-6 C49H75NO13 886	5311
16 Avermectin B1a (Abamectin) 13.674 71751-41-2 C48H72O14 890	5260
17 Nigericin 13.908 28380-24-7 C40H68O11 725	4834
18 Ivermectin B1a 14.458 70288-86-7 C48H74O14 892	5436

Select Chromatogram

UoA_LC-ESI-QTOF_Seawater UA07_Black Sea_Ukraine_19.05.2016_EMBLAS II_17856.xlsx

Interactive	table
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2e4

	mz	accuracy_mDa	chromatogram	show		
1	254.0594	0.0020	UoA_POS_4eV_LC-ESI-QTOF_Seawater UA07_Black Sea_Ukraine_19.05.2016_EMBLAS II_17856.mzML	· 8		
2	156.0114	0.0020	UoA_POS_25eV_LC-ESI-QTOF_Seawater UA07_Black Sea_Ukraine_19.05.2016_EMBLAS II_17856.mzML	· 🖉		
3	108.0444	0.0020	UoA_POS_25eV_LC-ESI-QTOF_Seawater UA07_Black Sea_Ukraine_19.05.2016_EMBLAS II_17856.mzML	· 🖉		
4	92.0495	0.0020	UoA_POS_25eV_LC-ESI-QTOF_Seawater UA07_Black Sea_Ukraine_19.05.2016_EMBLAS II_17856.mzML	- 2		

Submit (Press the button everytime changes are done to the table above)

--- 254.0594 ± 0.002

RTI=155.5	RT region where sulfomethoxazole is	RTI=362.5	
PT-3 34 min	expected to elute	RT=6.05 min	

Retention Time Index – calculated automatedly for each feature/substance in the mass chromatogram

GAME CHANGER



RMAN Digital S	ample Freezing Pla	atform Main Page	Batch mode	Contribute	More 🗕		
Basic-Information	Sample-MetaData	Instrumental-MetaDat	a RTI_Calibr	ation Uplo	ad-Files		
Positive Ionization							
(Subtracted) Full Scan							
Browse 4_9878_bbCID_POS_GC4_01_28547.mzML							
		Upload con	nplete				

It is difficult to upload mass chromatograms into DSFP?

Browse 25,9878, bbCID, POS, GC4, 01, 28547, mzMI	scan data. Please walt
Upload complete	Creating DCT Isotope elimination
	Creating DCT Adduct search
	× Creating DCT Creating component list
Do you have data-dependent file to submit? No	Creating DCT Transforming component list to DCT database
	Creating DCT Peak-picking of data- independent
Lownload the DCT	Creating DCT Generating excel file
EI_LC-ESI-QTOF_Dxlsx ^	Creating DCT Storing information to the database



DEET detected in many seawater samples from the Black Sea

http://www.normandata.eu/ Example of point and widespread detection

Monensine detected only at 1 sampling station

Create Results Visualization



On-line interface for results of all analyses [Chemical/Effects/ARGs]

www.norman-data.eu/EWW_DANUBE



On-line interface for results of all analyses [Chemical/Effects/ARGs]



Retrospective screening GC-HR-APCI-MS Bis(4-chlorophenyl) sulphone in Black Sea samples

Intens

2000

4000 2000

500

1000

6000

2000 2000 2000

2000

1000

20.7

20.8

20.9 Time (min)



20.2

20.4

20.6

20.8

21.0

21.2

21.4



^c Cut-off: 4 countries, 100 sites detected



Conclusions

- NORMAN SusDat
 - European (global??) suspect list regular update
- NORMAN DSFP
 - Fast retrospective screening of many samples for thousands of emerging substances
 - Need for international cooperation continuous update of the mass fragments' list
- NORMAN MassBank
 - Mass spectra of environmentally relevant substances mass fragments used by DSFP
 - Need for more by all interested parties!



Coming soon

• DSFP

It is not possible to develop the necessary knowledge and methodologies solely at the national scale