



Comprehensive Targeted and Non-Targeted Analysis of Various Indoor Dust Samples Using LC-HRMS with Ion Mobility

Mullin L.^{1,2}, DiLorenzo R.A.³, Simmons D.B.D⁴, Jobst K.⁵, Ladak A.¹,
Plumb R.¹, Diamond M.⁶, Reiner E.⁵, Rosnack Kenneth¹

¹Waters Corporation, 34 Maple Street, Milford, MA 01757, USA

² MTM Research Centre, Örebro University, 701 82 Örebro Sweden

³Department of Physiology and Experimental Medicine, The Hospital for Sick Children, Mouse Imaging Centre, Toronto, ON, Canada

⁴McMaster University, Department of Chemistry, Hamilton, ON, Canada

⁵Ontario Ministry of Environment and Climate Change, Laboratory Services Branch, Etobicoke, ON, Canada

⁶University of Toronto, Toronto, ON, Canada

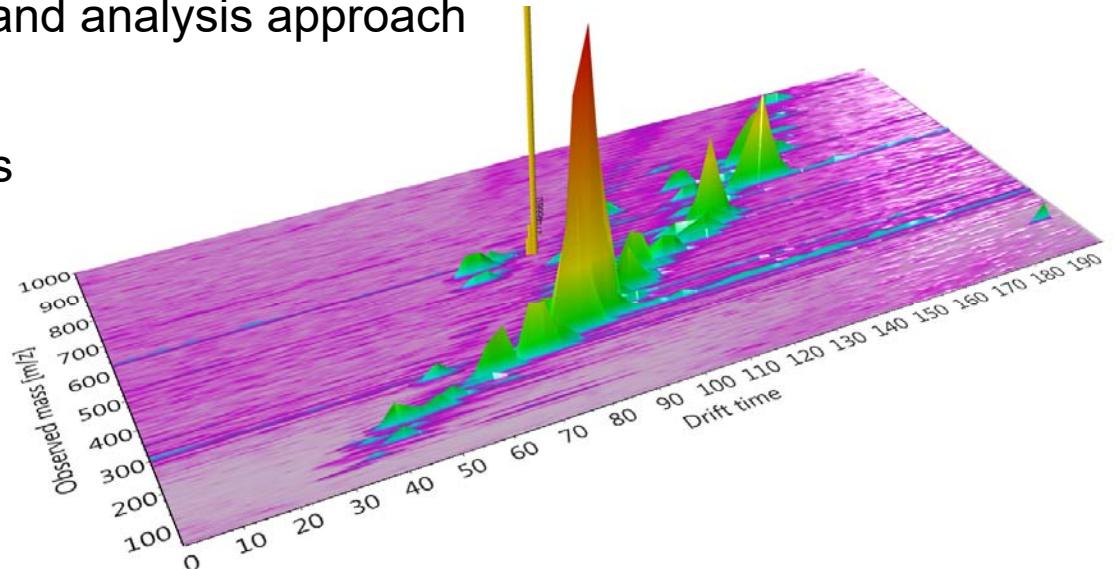


NEMC

2018

Overview

- Introduction to samples and analytes
- LC-HRMS-Ion Mobility system and analysis approach
- Targeted Screening List Results
- Non-Targeted Results
- Conclusions



Introduction to Study

Environ. Sci. Technol. 2009, 43, 2276–2281

Perfluoroalkyl Compounds (PFCs) in Indoor Dust: Concentrations, Human Exposure Estimates, and Sources

JUSTINA AWASUM BJÖRKLUND,
KAJ THURESSON, AND CYNTHIA A. DE WIT*

have reported that dust is a depot for PCBs and representing a potential source of exposure to them pounds in the indoor environment (16). This may be a case for PFCs as household dust samples from Japan and the United States have been found to contain measurable amounts of PFOS and PFOA (4, 17, 18).

Ingestion of house dust may therefore be a potential pathway for human exposure to the PFAs. No data for PFC concentrations in dust in Sweden exist. PFOA concentrations in house dust collected from day care centers, offices, houses, apartments, and office buildings have been analyzed.



Chemosphere 166 (2017) 433–437

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere



Non-target analysis of household dust and laundry dryer lint using comprehensive two-dimensional liquid chromatography coupled with time-of-flight mass spectrometry

Xiyu Ouyang ^{a,*}, Jana M. Weiss ^b, Jacob de Boer ^a, Maria H. Lamoree ^a, Pim E.G. Leenards ^a

* Institute for Environmental Studies (IVM), VU Universiteit Amsterdam, De Boelelaan 1087, 1087 HV, Amsterdam, The Netherlands.

³⁰ Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, SE-106 91, Stockholm, Sweden



■ Samples

- eWaste (4), Canadian Household dust and Canadian eWaste Facility

■ Data Independent Acquisition (DIA)

- Accurate mass measurement
 - Ion mobility separation (IMS)
 - Targeted and non-targeted data processing approach

LC Method

LC System:
Column:
Column Temp:
Sample Temp:
Flow Rate:
Mobile Phase A:
Mobile Phase B:
Total Run Time:

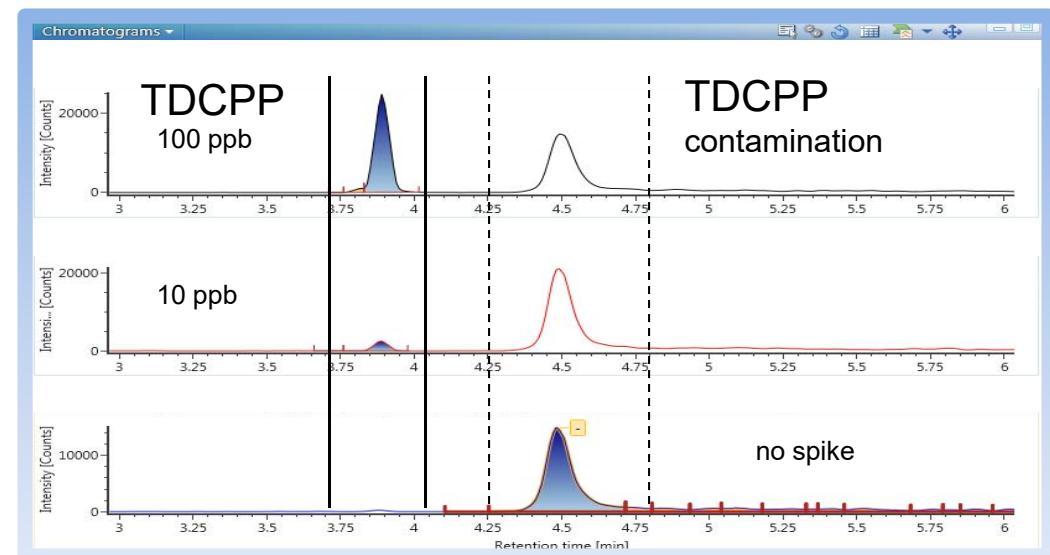
Waters ACQUITY I-Class (with **Isolator Column** in flow path)
ACQUITY UPLC BEH C18 2.1 x 50 mm, 1.7 µm
65 °C
4 °C
0.450 mL/min.
2mM ammonium acetate in 98:2 water:MeOH
2mM ammonium acetate in MeOH
8.5 min.

Gradient:

Min.	Flow Rate	%A	%B
Initial	0.650	90.0	10.0
0.5	0.650	90.0	10.0
5.10	0.650	0	100
6.60	0.650	0	100
6.70	0.650	90.0	10.0
8.50	0.650	90.0	10.0



Waters
THE SCIENCE OF WHAT'S POSSIBLE.®

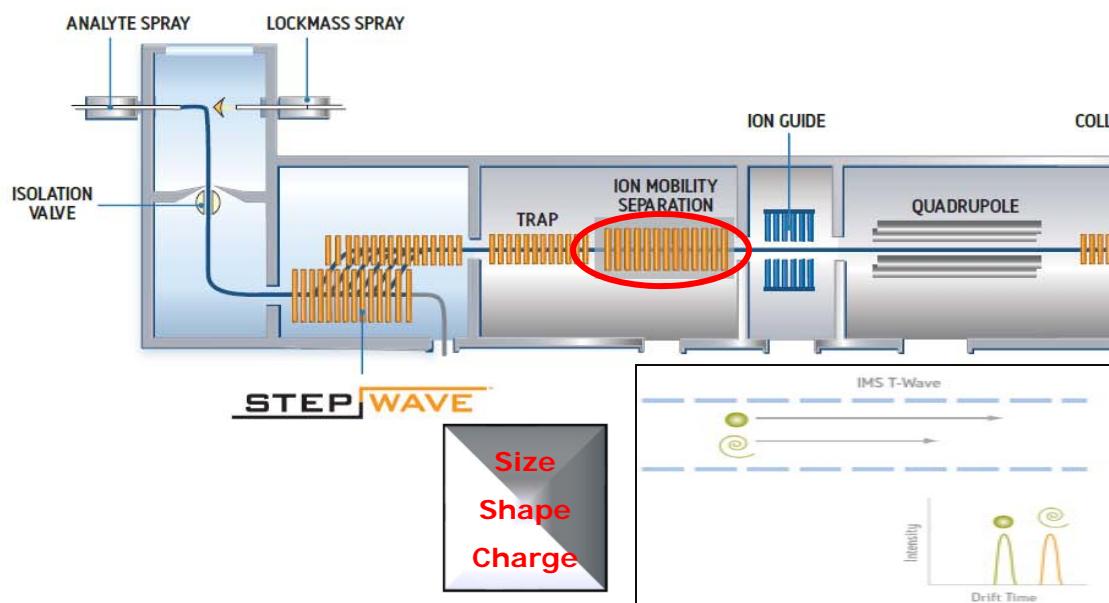


DIA HRMS-IMS conditions: HDMSE

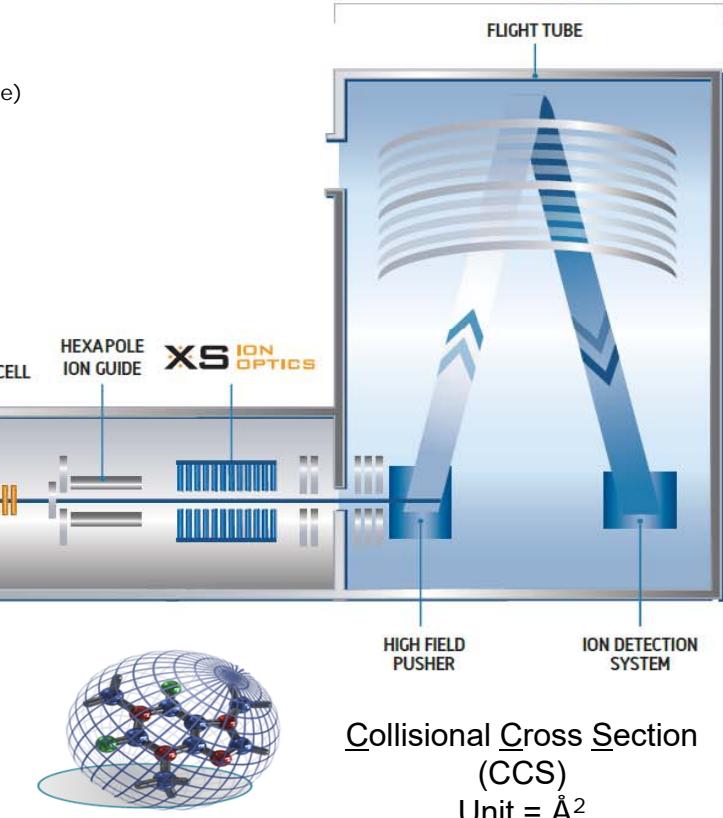
Waters
QUANTOF 2

Acquisition Settings

Ionisation Mode: ESI negative and positive polarity
Capillary Voltage (kV): 1.0 (positive mode); 0.5 (negative mode)
Collision Energy (LE): 3 eV
Collision Energy (HE ramp): 20-55 eV
Scan Time: 0.25 sec
Acquisition Range: 50-1000 m/z
Drift Gas: N₂



©2018 Waters Corporation



Collisional Cross Section
(CCS)
Unit = Å²

Ion Mobility Spectrometry (IMS)



**Small
Compact**

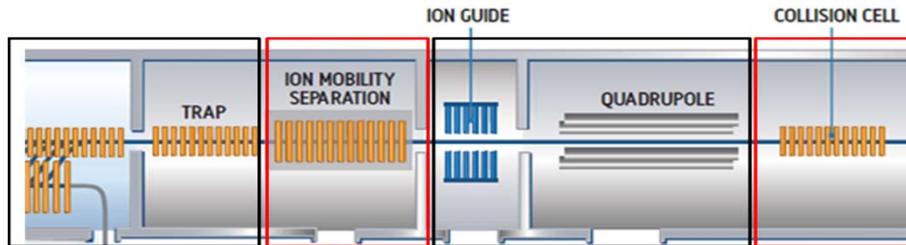
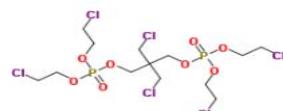
Slide courtesy of Severine Goscinny, ISP-WIV, Belgium



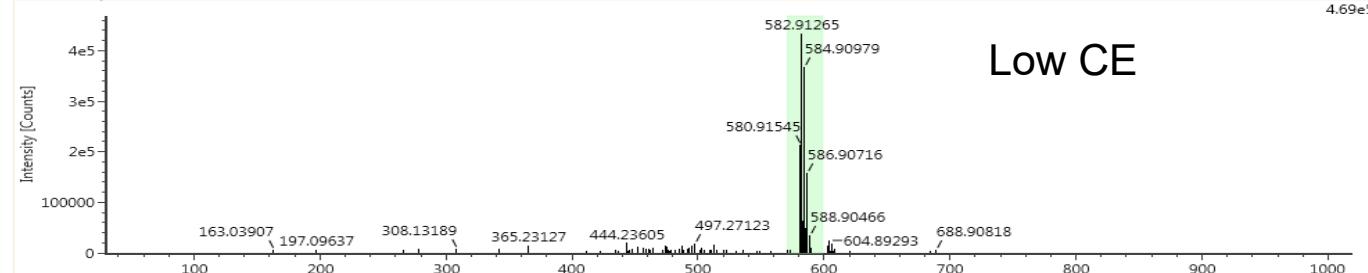
**Large
Extended**

©2018 Waters Corporation

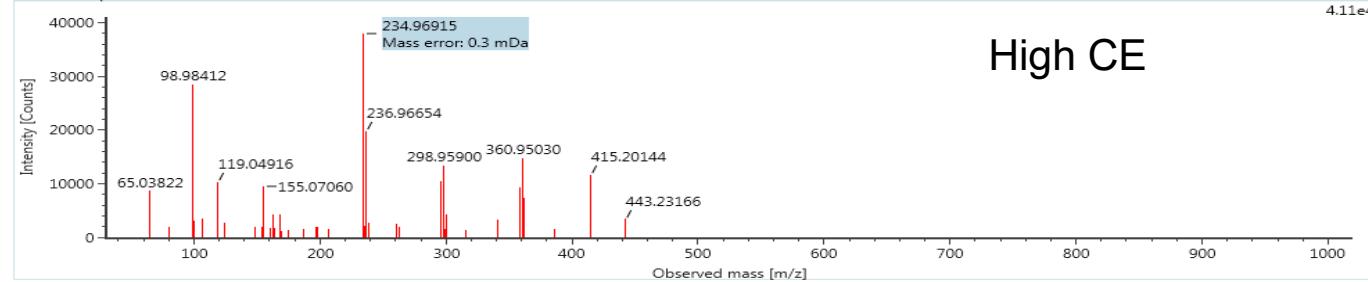
Drift Time Alignment of Spectra



Item name: Canadian eWaste Facility dust_32
Item description:

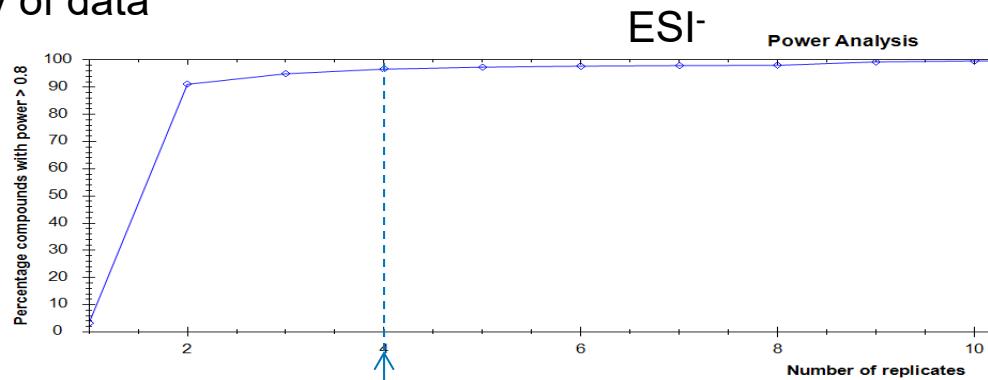


Item name: Canadian eWaste Facility dust_32
Item description:



Analysis Considerations and Approach

- QC and blank injections ensure quality of data
- Sample analysis
 - Randomized replicate injections
 - MVA
 - Targeted search using library



Component name	Label	Expected RT (min)	Expected neutral mass (Da)	Expected fragment (m/z)	Adducts	Excluded	Formula
7 Perfluooctanesulfonic acid		3.89	499.9375	79.9574, 168.9894, 129.9535, 197.9779	-H		C8HF17O3S
8 Perfluoroundecanoic acid		4.27	563.9641	518.9568, 168.9894, 118.9926	-H		
9 Perfluoropentanoic acid		2.11	263.9833	218.9861	-H		
10 Perfluoroctanoic acid		3.60	413.9737	368.9766, 168.9894, 118.9926	-H		

CCS input in
"Adduct" entry

Edit Adducts

Edit the adducts expected for target 'Perfluooctanesulfonic acid':

Add Delete

Adduct	Mass	Charge	CCS
1 -H	-1.00...	-1	166.8...



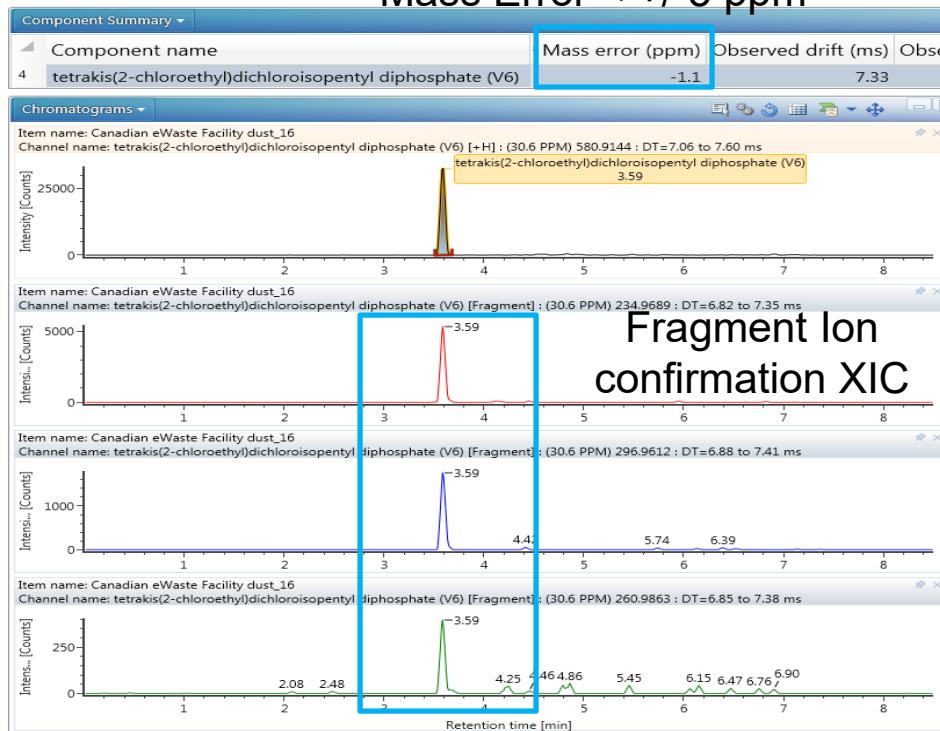
Targeted Results



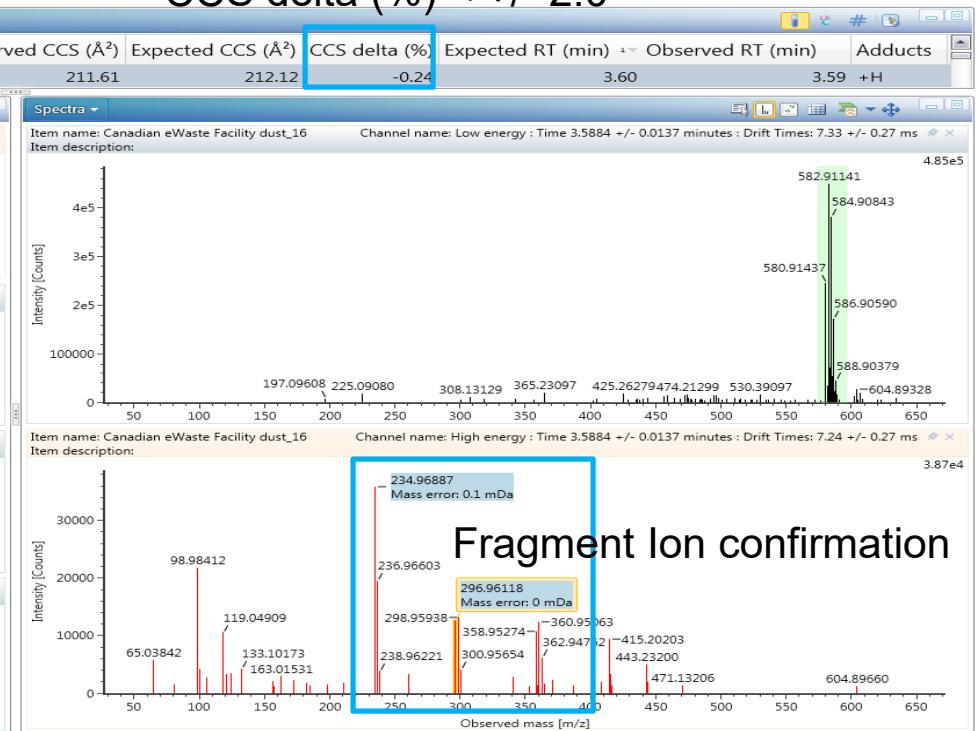
Identification Criteria

Waters
THE SCIENCE OF WHAT'S POSSIBLE®

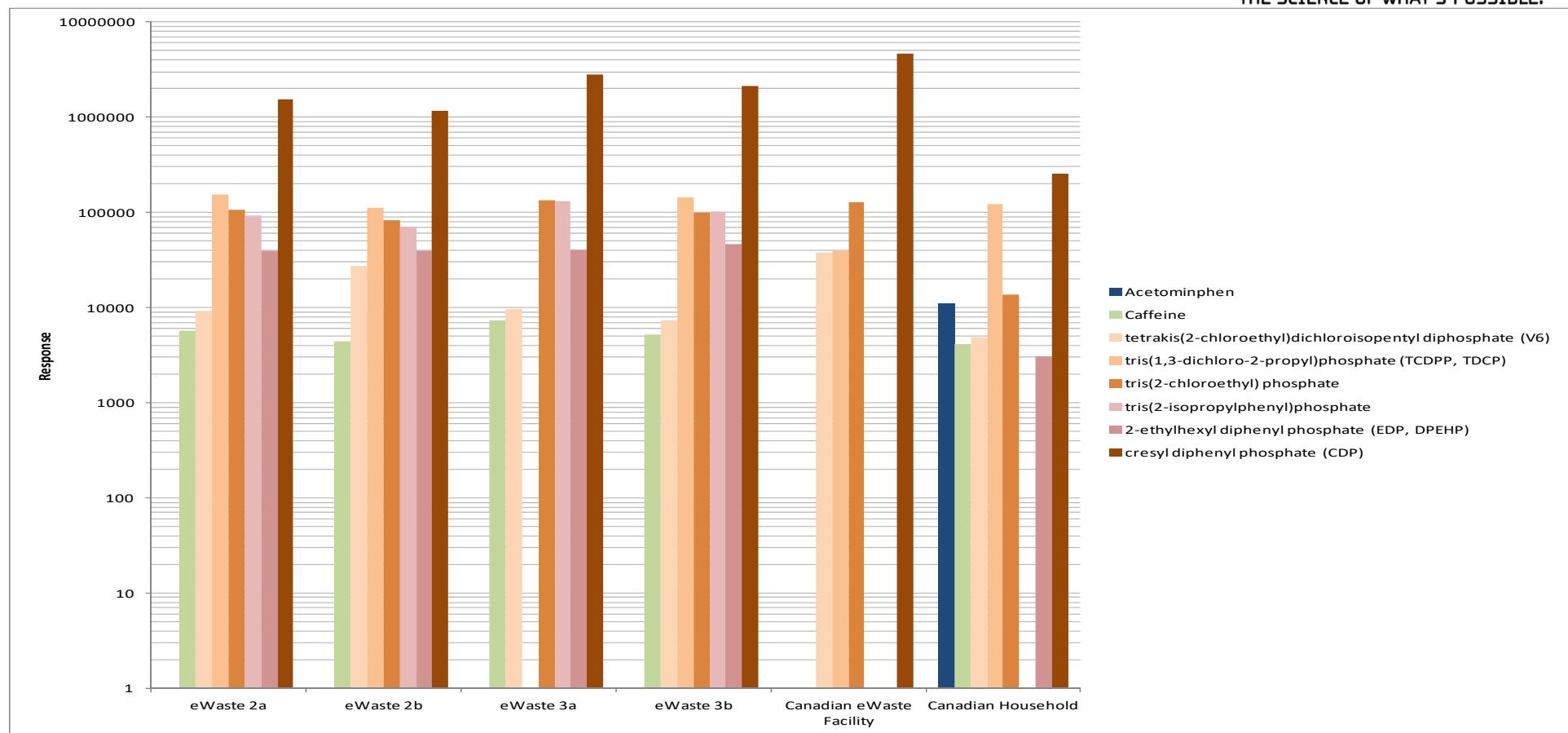
Mass Error < +/- 5 ppm



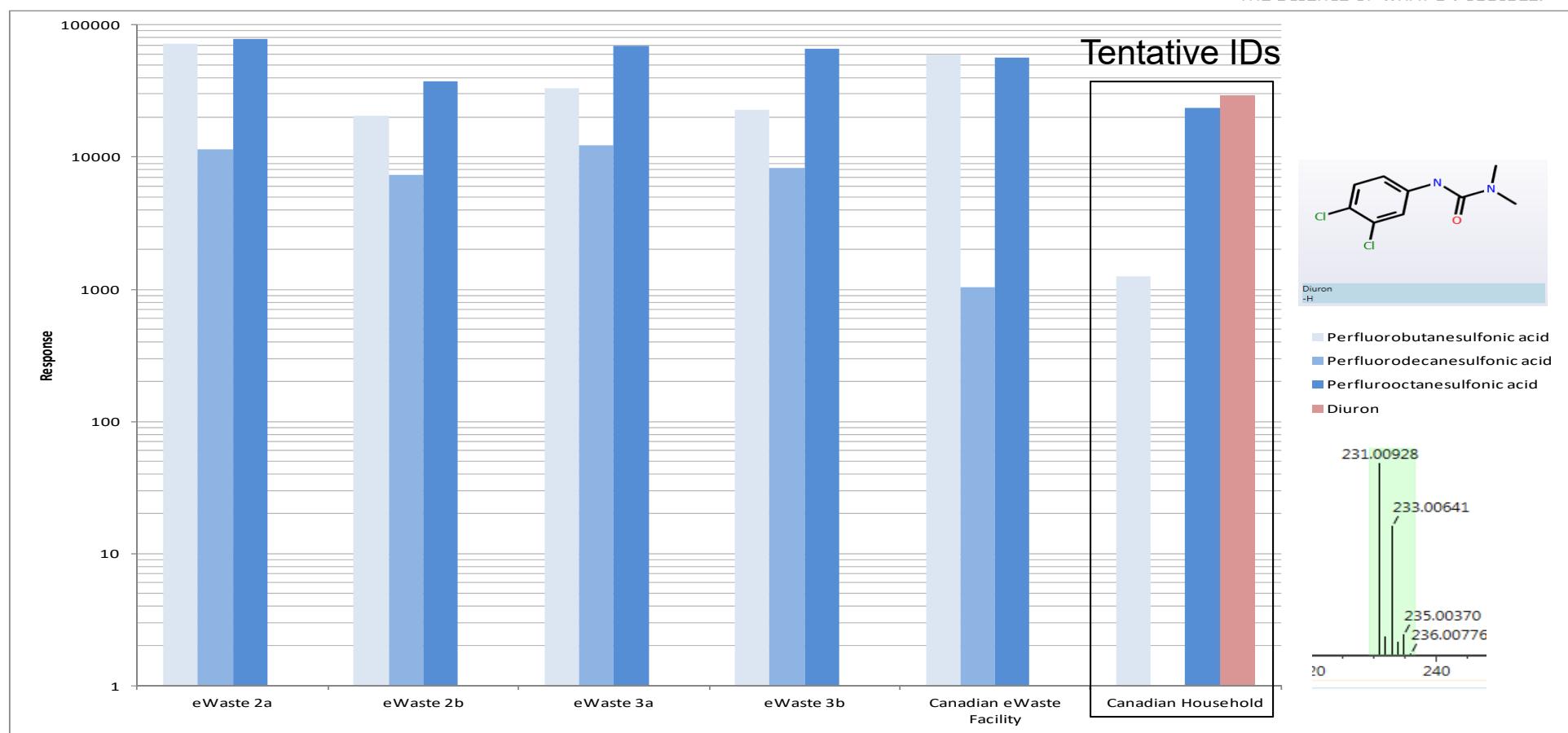
CCS delta (%) < +/- 2.0



ESI⁺ Confident IDs



ESI- Confident IDs



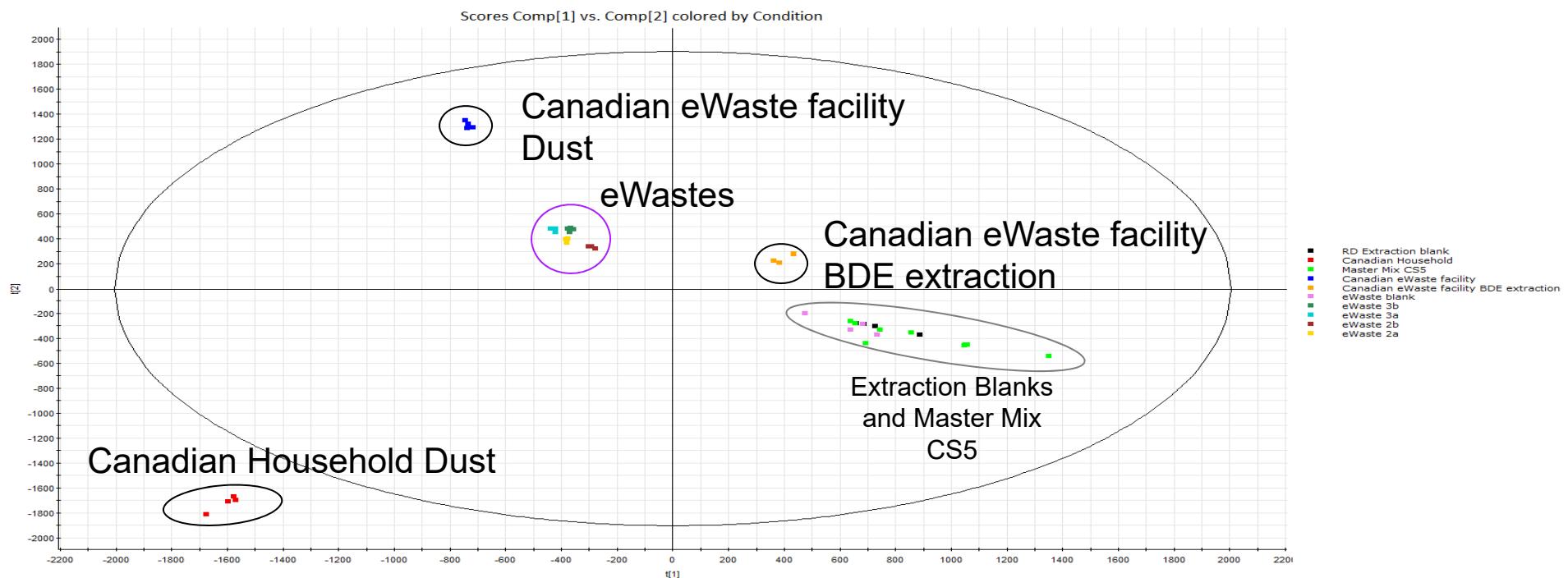
Non-targeted Results





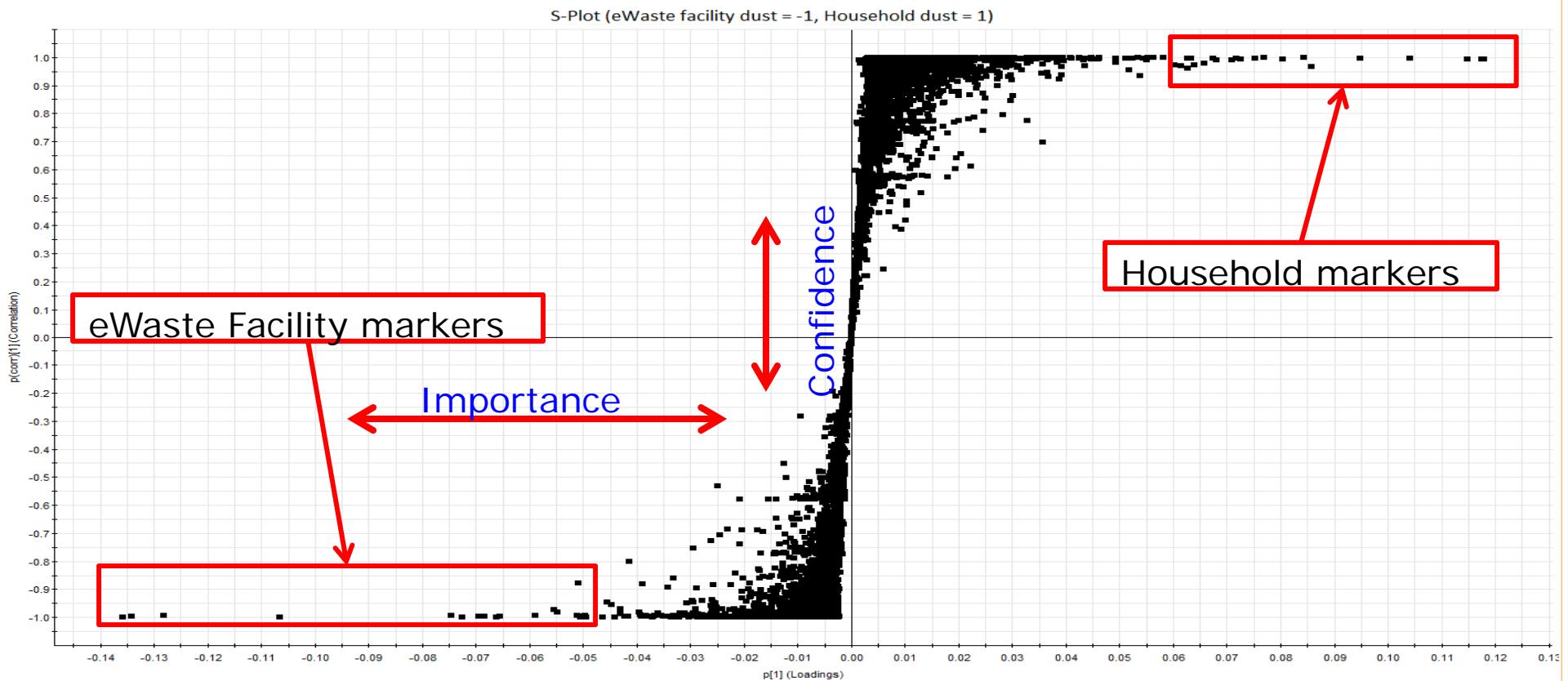
Principle Component Analysis: ESI-

Waters
THE SCIENCE OF WHAT'S POSSIBLE.[®]



FOCUSED QUESTION: Compare Canadian eWaste facility dust to Canadian Household Dust.

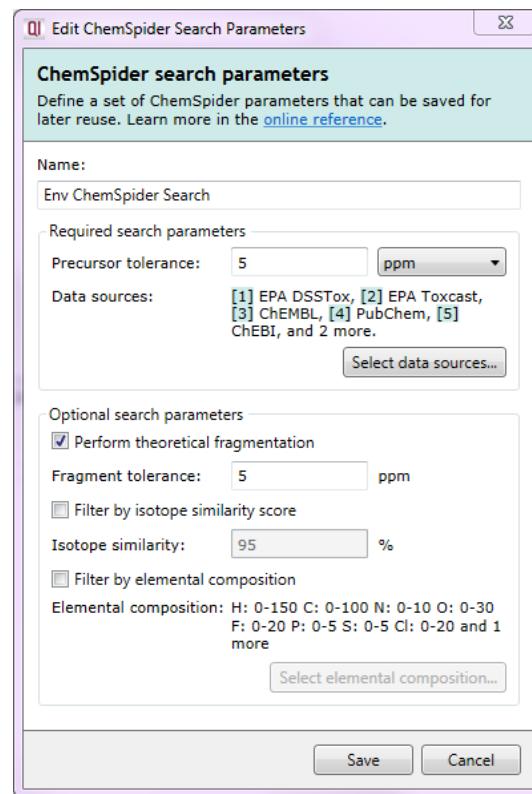
S-Plot: Comparing Canadian eWaste Facility and Household Markers



Database searching

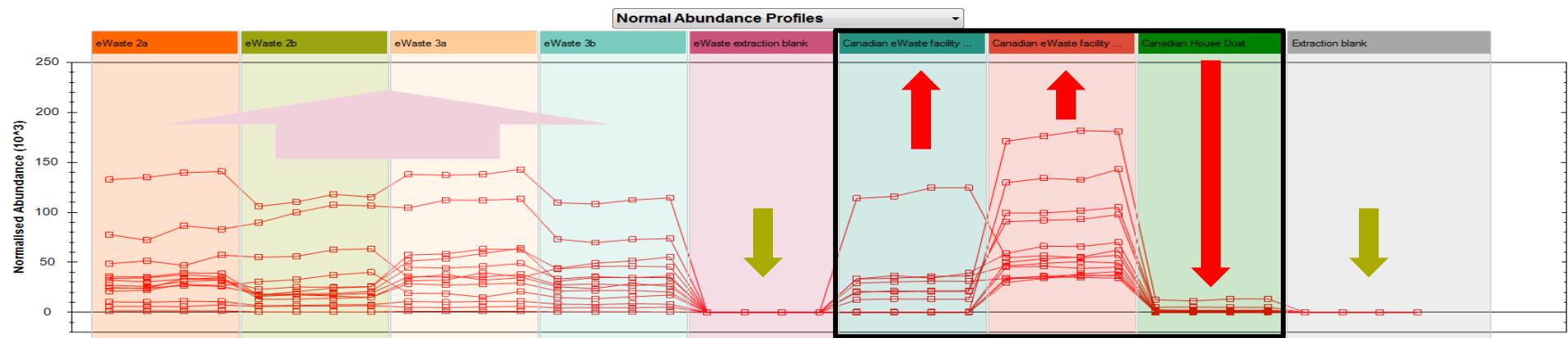


- These significant compounds (markers) were then subjected to a ChemSpider database search:
 - KEGG
 - Chemspiderman
 - PubChem
 - EPA DSSTox
 - EPA Toxcast
- 1000s of compounds to be searched and structures compared to the fragmentation pattern



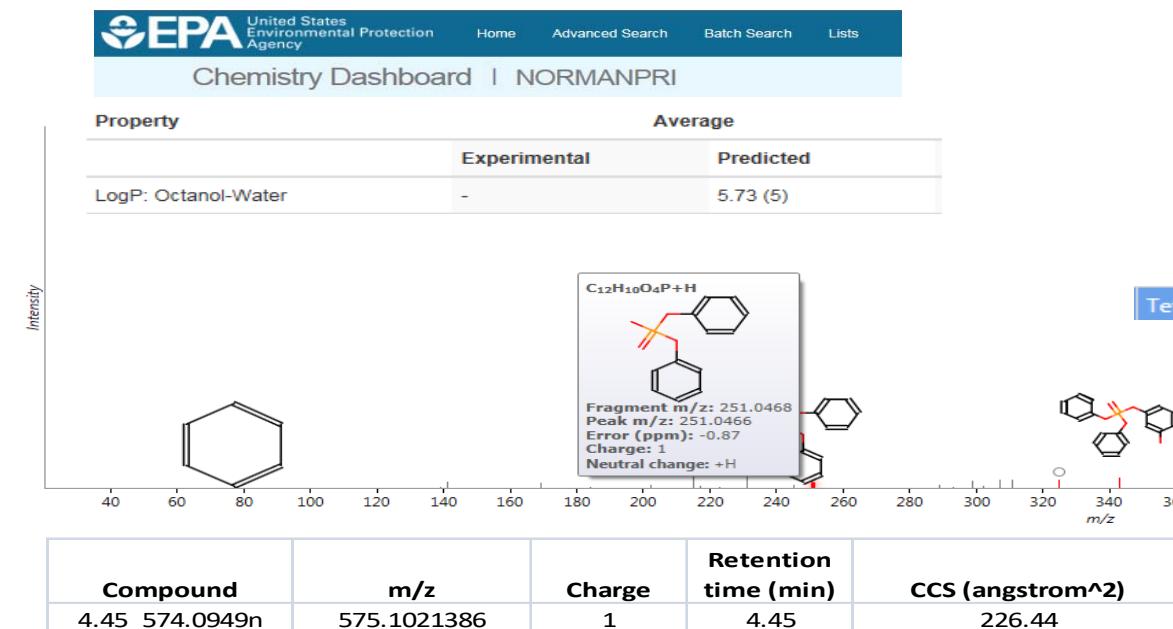
Proposed ID summary: ESI⁺ eWaste Facility

Waters



- Increased relative abundance of various **organophosphate** molecules
 - Additional to target screening library
 - Decreased or not present in household dust
 - Shared abundance with eWaste replicates
- Common fragments with targeted OPFRs recognized

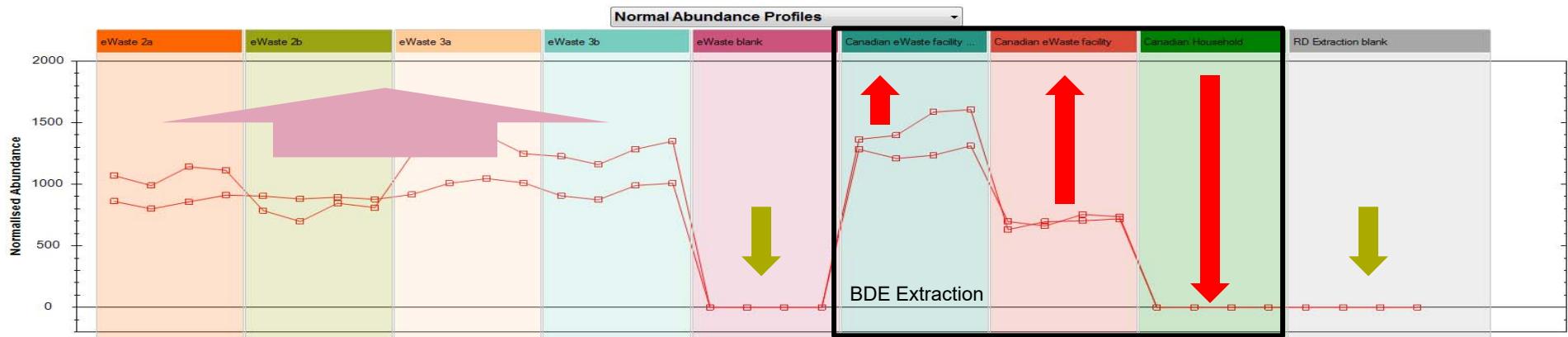
Additional OPFR Example



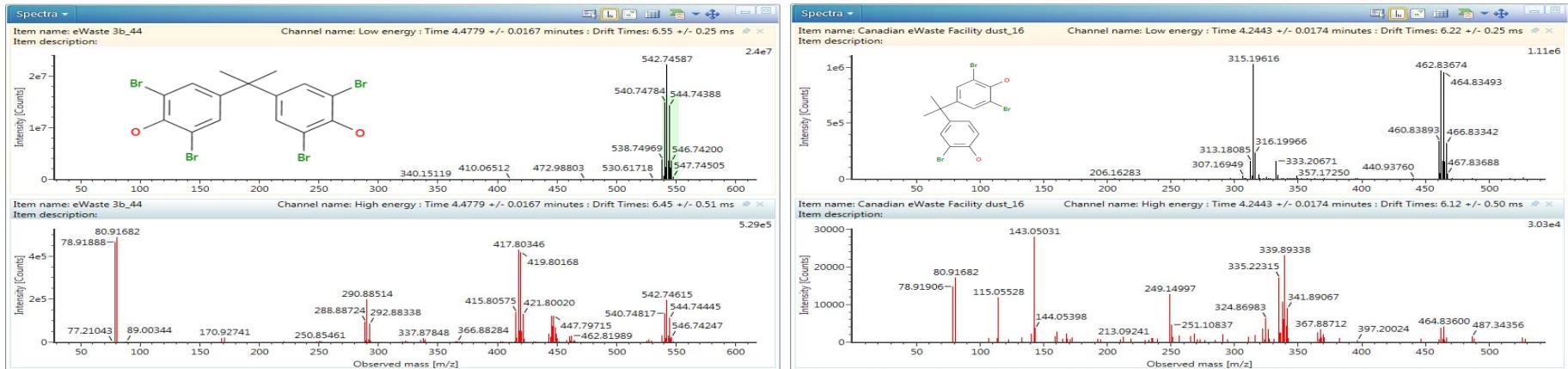
Anova (p)	q Value	Max Fold Change	Highest Mean	Lowest Mean
<1.1E-16	<1.1E-16	47304.6176	eWaste facility dust	eWaste extraction blank

Proposed ID summary: ESI- eWaste Facility

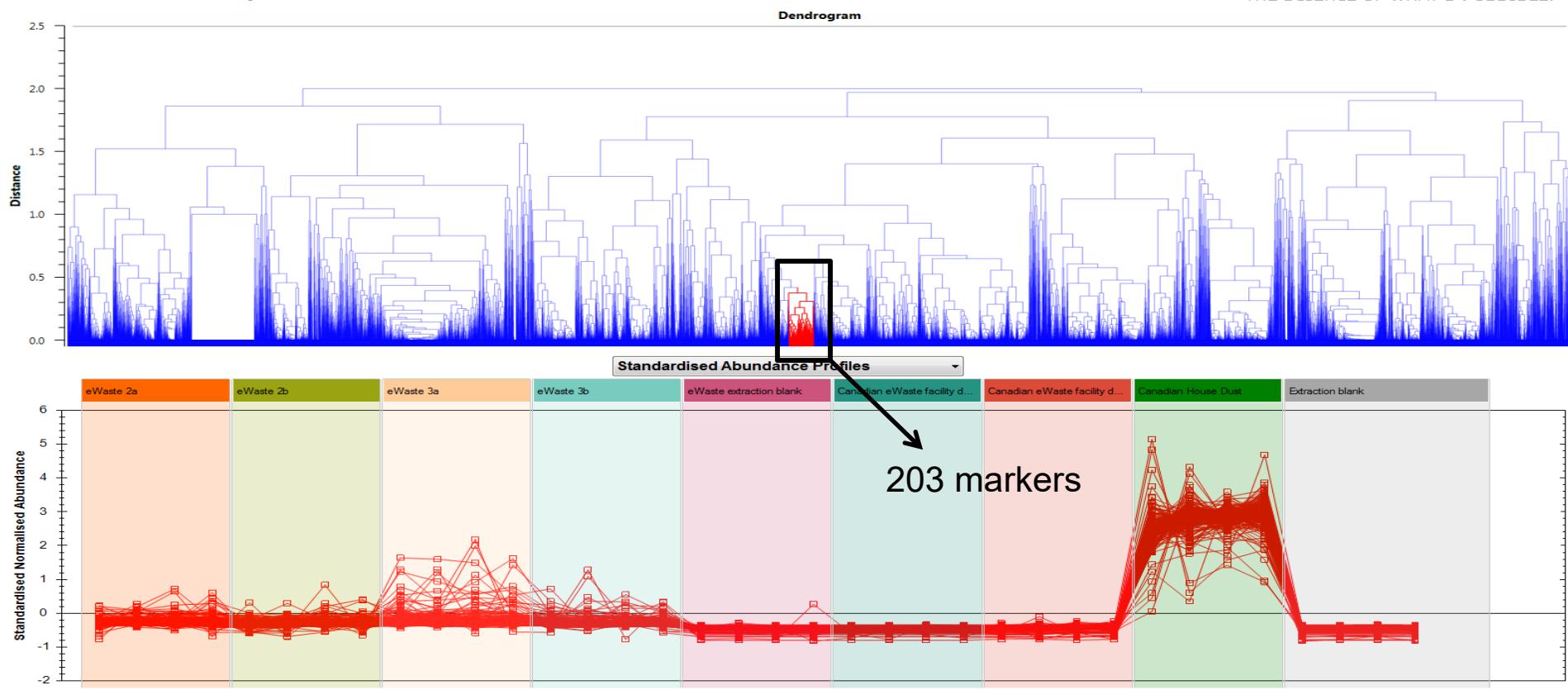
Waters



- eWaste facility: TBBP-A and additional -Br compound

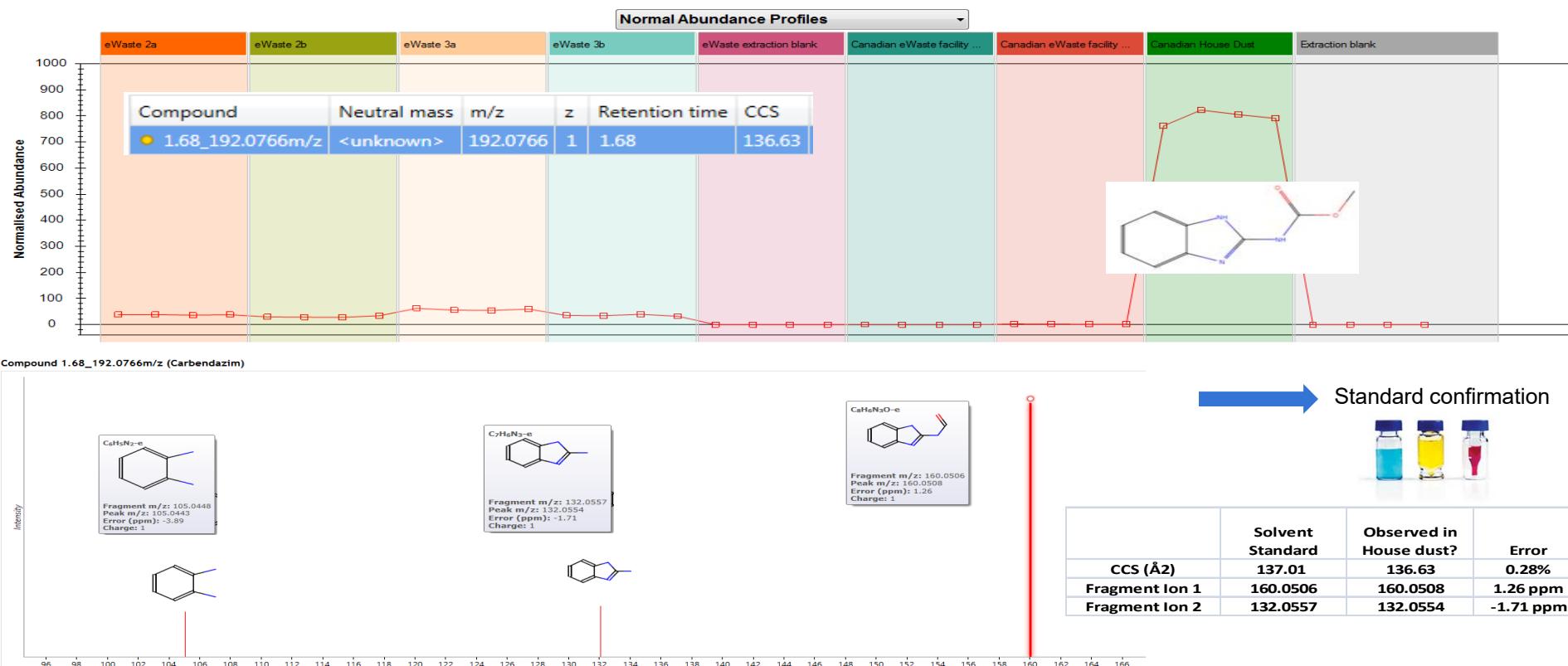


Canadian Household:compounds similar in trend to Acetaminophen



Carbendazim Confirmation

Waters
THE SCIENCE OF WHAT'S POSSIBLE®





Conclusions and Future Work

- IMS provides additional dimension to HRMS data set and adds additional measurement based on compound properties
- Non-targeted data acquisition approach is a powerful tool for rapid assessment of sample variation with respect to contaminant profiling

■ Future Work

— CCS modeling

- Potentially useful for where analytical standards don't exist?

analytical
chemistry

Article

pubs.acs.org/ac

Prediction of Collision Cross-Section Values for Small Molecules: Application to Pesticide Residue Analysis

Lubertus Bijlsma,^{†,‡,§} Richard Bade,^{†,‡,§} Alberto Celma,[†] Lauren Mullin,[§] Gareth Cleland,[§] Sara Stead,[§] Felix Hernandez,^{†,§} and Juan V. Sancho^{§,†}

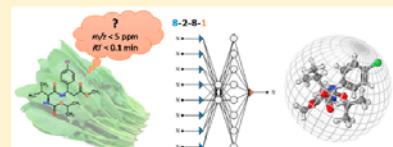
[†]Research Institute for Pesticides and Water, University Jaume I, Avda. Sos Baynat s/n, E-12071 Castellón, Spain

[‡]School of Pharmacy and Medical Sciences, University of South Australia, Adelaide, South Australia 5000, Australia

[§]Waters Corporation, 34 Maple Street, Milford, Massachusetts 01757, United States

Supporting Information

ABSTRACT: The use of collision cross-section (CCS) values obtained by ion mobility high-resolution mass spectrometry has added a third dimension (alongside retention time and exact mass) to aid in the identification of compounds. However, its utility is limited by the number of experimental CCS values currently available. This work demonstrates the potential of artificial neural networks (ANNs) for the prediction of CCS values of pesticides. The predictor, based on eight software-chosen molecular descriptors, was optimized using CCS values of 205 small molecules and validated using a set of 131 pesticides. The relative error was within 6% for 95% of all CCS values for protonated molecules, resulting in a median relative error less than 2%. In order to demonstrate the potential of CCS prediction, the strategy was applied to spinach samples. It notably improved the confidence in the tentative identification of suspect and nontarget pesticides.





Acknowledgements and Thank You!

- References:
 - Ouyang X. et al. *Chemosphere* 166 (2017) 431-437
 - Bjorklund JA, Thuresson K, deWit CA (2009) *Env. Sci. and Tech.* 43 (2009) 2276-2281
 - Abdallah M. et al. *Env. Int.* 94 (2016) 235-250
 - Bijlsma A. et al. *Anal. Chem.* 89 (2017) 6583-6589
- Acknowledgements: Dimple Shah and Gareth Cleland (Waters), Linh Ngyugen (Dept. of Physical and Environmental Sciences, University of Toronto at Scarborough), Victoria Arrandale (Dalla Lana School of Public Health, University of Toronto), Marta Venier and William Stubbins (Indiana University), Liisa Jantunen (Environment and Climate Change Canada), Lisa Melymuk (RECETOX, Masaryk University, Czech Republic)



Thank you for your attention

Any questions



www.waters.com