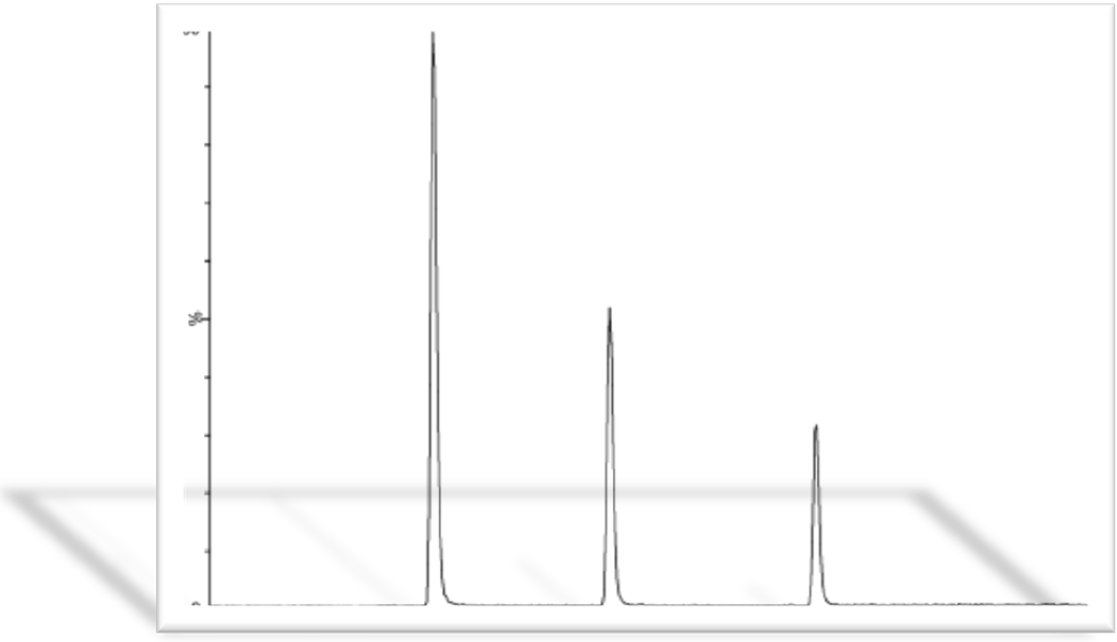
http://www.chemistry.uoguelph.ca/lcms/index.html



The 11th Annual Workshop on LC/MS/MS Applications on Environmental Analysis and Food Safety is a workshop that focuses on the application of LC/MS/MS for the analysis of environmental contaminants in a variety of matrices as well as method development and troubleshooting. Participants will have the opportunity to meet with scientists from academia, government agencies, and industry.

Invited Speakers

Dr. Diana Aga, SUNY at Buffalo
Dr. Damia Barcelo, National Research Council of Spain
Dr. James Chang, Thermo-Fisher
Dr. Marcus Kim, Agilent Technologies
Dr. Andre Schrieber, SCIEX
Dr. Vince Taguchi

ROSS NORSTROM STUDENT AWARDS

Two cash prizes will be awarded to student oral presentations that are judged to be of the highest quality. A committee will judge all presentations that are eligible to determine the winners.

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We'd like to thank all of our sponsors for their generous support. The success of the workshop is largely dependent on their financial contributions.

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Tuesday p.m.	WELLINGTON LABORATORIES Standards for Environmental Testing and Research

RECEPTION

Date: Monday September 21st, 2015
Time: 5:00 pm
Location: Emma's Back Porch
2084 Old Lakeshore Rd.
Burlington, ON L7R 1A3

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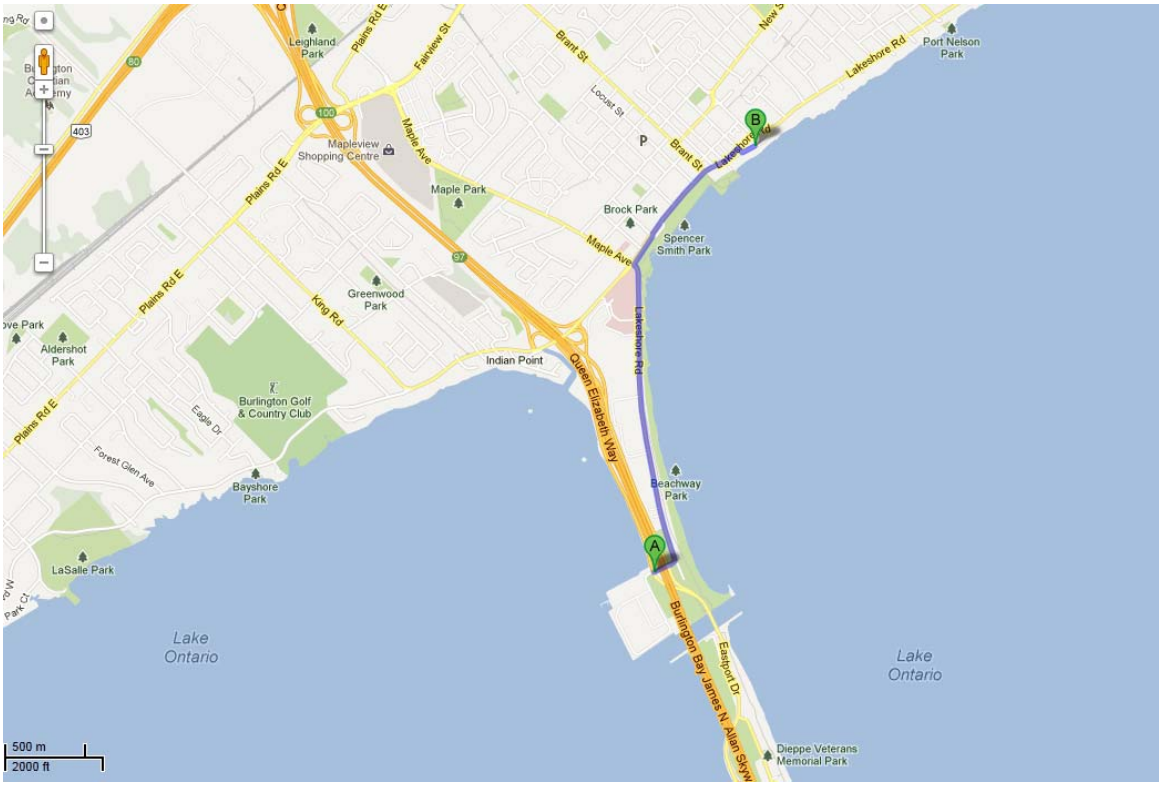
Driving Directions from CCIW to Emma's Back Porch:

Head east on Lakeshore Rd. toward Eastport Dr. (2.0 km)
Turn right to stay on Lakeshore Rd. (1.0 km)
Turn right onto Old Lakeshore Rd. Destination will be on the right (88 m)



PROGRAM AT-A-GLANCE

Monday September 21, 2015

8:00 am	Registration
8:40 am	Welcome Address
9:00 am	Session 1: Taguchi, Barcelo
10:20 am	Coffee Break: *Sponsored by Mandel Scientific*
11:00 am	Session 2: Chang, Kim, Vukovic
12:00 pm	Lunch: *Agilent*
1:00 pm	Session 3: Riddell, Stock, Ortiz
2:00 pm	Coffee Break: *Sponsored by Gerstel*
2:40 pm	Session 4: Jobst, De Silva, Young, Schreiber
5:00 pm	Reception: Sponsored by Wellington

Tuesday September 22, 2015

8:00 am	Registration
9:00 am	Session 5: Aga, Munaretto, Hao
10:00 am	Coffee Break: *Sponsored by SCIEX*
10:40 am	Session 6: Oviedo, Marvin, Lu, Pacepavicius
12:00 pm	Lunch: *Sponsored by Waters*
1:00 pm	Session 7: Roy, Simmons, DiLorenzo, Shoieb
2:20 pm	Coffee Break: *Sponsored by Wellington*
3:00 pm	Session 8: Rauert, Alary, Liu
4:00 pm	Presentation of Ross Nordstrom Student Awards Sponsored by Wellington
4:10 pm	Closing Remarks

OFFICIAL PROGRAM

MONDAY MORNING

8:00	Registration and Coffee
8:40	Welcome Address: Dr. Mehran Alaee, Research Scientist, Environment Canada

Talk #	Session 1	Chair: Eric Reiner	Presenter
1	9:00	A Brief History of Accurate Mass	Dr. Vincent Taguchi
2	9:40	LC-Tandem MS and LC-HRMS Strategies for the Analysis of Contaminants of Emerging Concern in Water, Soil and Biota Samples	Dr. Damià Barcelo
	10:20	**Coffee break (40 min)**	**Sponsored by Mandel**
Talk #	**Session 2**	**Chair: Ed Sverko**	**Presenter**
3	11:00	A Comprehensive Approach on Food Safety Analysis, Screening and Quantitation by Using Data Independent Acquisition (DIA) and DDMS2 on HR/AM Q Exactive system	Dr. James Chang
4	11:20	Rapid and Sensitive LC/MS/MS Direct Injection Method for the Determination of Trace Level Corexit® EC9500A Oil Dispersant in Seawater Samples	Dr. Marcus Kim
5	11:40	Selectivity of Collision Cross Section Ion Mobility Screening for the Analysis of Pesticide Residues in Food Using ionKey/MS	Mr. John Vukovic
	12:00	**Lunch (60 min)**	**Sponsored by Agilent**

MONDAY AFTERNOON

Talk #	Session 3	Chair: Mehran Alaee	Presenter
6	13:00	The Separation of 2,3,7,8-Substituted Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans using Supercritical Fluid Chromatography	Ms. Nicole Riddell
7	13:20	More than Multiple Reaction Monitoring (MRM): Alternate Liquid Chromatography-Mass Spectrometry Workflows for Environmental Analysis	Dr. Naomi Stock
8	13:40	Applications of (ultra)high resolution mass spectrometry in environmental analysis	Dr. Xavier Ortiz
	14:00	**Coffee break (40 min)**	**Sponsored by Gerstel**
Talk #	**Session 4**	**Chair: Naomi Stock**	**Presenter**
9	14:40	A Q-TOF mass spectrometer coupled to (multidimensional) gas chromatography using atmospheric pressure chemical ionization: Analysis of environmental samples by GC/MS using an LC/MS instrument	Dr. Karl Jobst
10	15:00	Spatial and Temporal Trends in Contaminants of Emerging Concern in Sediments of North America	Dr. Amila De Silva
11	15:20	New tracers for the elucidation of long-range transport pathways of perfluoroalkyl acids	Dr. Cora Young
12	15:40	Identification of Emerging Environmental Pollutants using High Resolution LC-MS/MS	Dr. Andre Schreiber
	5:00	**Reception at Emma's Back Porch (2084 Old Lakeshore Rd. Burlington, ON L7R 1A3)**	**Sponsored by Wellington Laboratories Inc.**

TUESDAY MORNING

8:00	Coffee and Registration

Talk #	Session 5	Chair: Amila De Silva	Presenter
13	9:00	Extraction and Analysis of Multiclass Veterinary Antibiotics from Solid and Liquid Fractions of Cow Manure	Dr. Diana Aga
14	9:20	Quantification of Ionophore Antimicrobials and Identification of Transformation Products in Poultry Litter Before and After Different Composting Processes	Ms. Juliana Scariot Munaretto
15	9:40	Liquid Chromatography-Tandem Mass Spectrometric Analysis of Neonicotinoids in Environmental Water	Dr. Chunyan Hao
	10:00	**Coffee break (40 min)**	**Sponsored by SCIEX**
Talk #	**Session 6**	**Chair: Xavi Ortiz**	**Presenter**
16	10:40	Stability of Endocrine Disrupting Estrogens in Dairy Manure During Pasteurization-Anaerobic Digestion Process	Ms. Katia Noguera Oviedo
17	11:00	Method Development for the Analysis of Organophosphate Flame Retardants	Dr. Chris Marvin
18	11:20	Hindered Phenol, Substituted Diphenylamine Antioxidants and Benzotriazole UV Stabilizers in the Environment	Dr. Zhe Lu
19	11:40	A Comprehensive Method for the Determination of Phthalates in Industrial and Municipal Wastewater	Ms. Grazina Pacepavicius
	12:00	**Lunch (60 min)**	**Sponsored by Waters**

TUESDAY AFTERNOON

Talk #	Session 7	Chair: Meera Shanmuganathan	Presenter
20	13:00	Measurement of Artificial Sweeteners for Tracking Groundwater Contaminants	Dr. Jim Roy
21	13:20	Trypsin versus Formic Acid digestion for shotgun proteomics using LC-MS/MS	Dr. Nina Simmons
22	13:40	Extraction and detection of amino sugar stereoisomer biomarkers in environmental matrices	Mr. Rob DiLorenzo
23	14:00	Assessing Emission of Per-Fluoroalkyl Substance to Air from WWTPs Using LC/MS/MS	Dr. Mahiba Shoeib
	14:20	**Coffee break (40 min)**	**Sponsored by Wellington**
Talk #	**Session 8**	**Chair: Nicole Riddell**	**Presenter**
24	15:00	Utilizing UPLC-MS/MS for the detection of PFAAs in passive air samples from the Global Atmospheric Passive Sampling (GAPS) Network	Dr. Cassandra Rauert
25	15:20	An Accurate LC-MS/MS Assay of Perfluorinated Compounds in Water by Laminar Flow Triple-Quadrupole Mass Spectrometry	Dr. Jean François Alary
26	15:40	Re-investigation of Aerobic Biodegradation of 6:2 and 8:2 Polyfluroalkyl Phosphate Diesters (6:2 and 8:2 diPAPs) in Soil	Ms. Chen Liu

	16:00	**Presentation of the ROSS NORDSTROM Student Awards, sponsored by Wellington Laboratories**	
	16:10	**Closing Remarks**	

ABSTRACTS

A Brief History of Accurate Mass

Vince Taguchi[1]

[1]Retired

Accurate mass is the experimental mass whereas exact mass is the theoretical mass. Accurate mass measurements facilitate empirical formulae determinations. For small molecules, the number of possible empirical formulae can be reduced to one. However, to identify a compound, the structure still needs to be determined and confirmed. In addition, sufficient resolution is necessary to ensure that no interferences are present.

Accurate mass measurements were initially determined on a Mattauch-Herzog double-focusing magnetic sector mass spectrometer with a forward geometry and a focal plane detector (photographic plate). Double-focusing magnetic sector mass spectrometers with point detectors (electron multipliers) utilized a peak matching unit (PMU) which was an accelerating voltage alternator (AVA). Accurate mass determinations using magnet scans and voltage scans were facilitated by the development of data systems. Recent advances in accurate mass capabilities have been made using time-of-flight (TOF), Orbitrap and Fourier transform ion cyclotron resonance (FTICR) mass spectrometers.

A brief history of the development of mass spectrometers capable of accurate mass measurements and (ultra)high resolution will be presented along with examples that illustrate the need for resolution as well as mass accuracy.

LC-Tandem MS and LC-HRMS Strategies for the Analysis of Contaminants of Emerging Concern in Water, Soil and Biota Samples

Damià Barceló[1,2], Bozo Zonja[1], Noelia Negreira[1], Marta Llorca[1,2], Josep Sanchís[1], Marinel la Farré[1], Sandra Pérez[1] and Miren Lopez de Alda[1]

[1]Water and Soil Quality Research Group, IDAEA-CSIC, c/ Jordi Girona, 18-26 / 08034 Barcelona, Spain
[2] Catalan Institute for Water Research (ICRA), Emili Grahit,101, E- 17003 Girona, Spain

Presence of emerging contaminants in the aquatic system is primarily linked to human impact on the environment. During recent years, the issue of hazardous substances in wastewater and surface water has become a major concern with respect to both human and environmental health. This has led to numerous studies published on monitoring and fate of contaminants in different aquatic environments (urban wastewaters, treated effluent, surface water, groundwater, drinkable water). In the majority of cases, the key results depended on reliable and rapid analytical techniques based on GC/LC-MS/MS and/or high resolution MS (HRMS). Depending on the class of compounds or matrix investigated there are still big challenges in the field of environmental analytical analysis with respect to screening and quantification method development. However, for a broader perspective, additional factors like biotic and/or abiotic processes that cause transformation of parent compounds to so-called transformation products (TPs) have to be taken into account. These processes can only seemingly attenuate the contaminants from the discharge site to the ground or surface water where they are typically detected when in fact some TPs can be even more persistent and more toxic.

In this talk, recent studies of our group in the field of the environmental analysis will be presented with an emphasis on HRMS approaches for detection of TPs after physico-chemical and biological processes. Likewise, advances in sample pre-treatment and application of HRMS methodologies for quantification of contaminants in real-world environment samples will be discussed and shown.

These examples will encompass the following studies:

- Presence of perfluoroalkyl substances in river and drinking waters by an on-line (Equan)-LC-MS/MS in samples from Brazil and Europe
- Transformations of human metabolite lamotrigine N2-glucuronide in the WWTPs: Unknown TPs that were detected in the environmental samples were suspected to be derived from an anticonvulsant lamotrigine. However, it was discovered that while lamotrigine is resistant to degradation, it is an indirect source of structurally-derived compounds via its principal human metabolite.

- Detection-based prioritization of Iodinated Contrast Media (ICMs) photodegradates (photoTPs) in surface water using LC-HRMS approach. 108 photoTPs were detected in lab-scale batch experiments generated from six ICMs. 11 photoTPs with frequency higher than 50 % in real surface water samples were deemed important and were identified, isolated when possible, and included in the list of target compounds for quantitative analysis.
- Degradation of anti-cancer drugs erlotinib and tamoxifen during water chlorination: Non-targeted approach for the identification of transformation products and *in-silico* toxicity assessment of their disinfection by-products.
- Application of (APPI)-Q-Eactive Orbitrap for the analysis of fullerenes and their impact (OMICS) in water, soils and mussels in samples from Brazil, Europe and Saudi Arabia.

Acknowledgements

This study has been financially supported by the EU through the FP7 project SOLUTIONS (603437), and by the Generalitat de Catalunya (Consolidated Research Groups "2014 SGR 418—Water and Soil Quality Unit" and 2014 SGR 291—ICRA).Merck is acknowledged for the gift of LC columns

A Comprehensive Approach on Food Safety Analysis, Screening and Quantitation by Using Data Independent Acquisition (DIA) and DDMS^2 on HR/AM Q Exactive system

James Chang[1]

[1]Manager, Food Safety Applications, Thermo Fisher Scientific

Multiple reaction monitoring (MRM), two stages of mass filtering are employed on a triple quadruple mass spectrometer. In the first stage the precursor ion is preselected in Q1 then into a collision chamber and collides with a neutral gas in a pressurized collision cell (Q2) which will results of induced to fragment by collisional excitation. In the second stage, instead of obtaining full scan ms/ms where all the possible fragment ions derived from the precursor are mass analyzed in Q3, only selected ions are mass analyzed in Q3. This targeted MS analysis using MRM enhances the S/N ration which results the sensitivity increase. DDMS^2 method consists of a generic chromatographic method and a full-scan data-dependent MS/MS (FS-ddMS2) mass spectrometric method which including a list of accurate mass on target compounds, the system will automatically triggered for a ms/ms scan according to the list if it find under the full scan data. Data Independent Acquisition (DIA) has been widely employed in shotgun proteomic workflow, not only has it been used in identification and characterization of proteins in a complex biological matrix, the method is also used in quantitative proteomics, particularly with the use of isobaric labeling or tagging. The system was set to sequentially isolate and fragment precursor windows of preset isolation windows by collision-activated dissociation (CAD) until a desired range was covered. Furthermore, the method provided time-consistent ion sampling and was able to confirm the results in MS1 and with the simplicity which doesn't have to know the nature of compounds need to be analyzed.

Rapid and Sensitive LC/MS/MS Direct Injection Method for the Determination of Trace Level Corexit® EC9500A Oil Dispersant in Seawater Samples

Pamela Brunswick[1], Dayue Shang[1], Graham van Aggelen[1], Craig Buday[1], Corey Dubetz[2], and Marcus Kim[3]

[1]Pacific and Yukon Laboratory for Environmental Testing Science & Technology Branch Pacific Environmental Science Centre Environment Canada, North Vancouver, British Columbia, Canada;
[2]National Contaminants Advisory Group, Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, British Columbia, Canada;
[3]Agilent Technologies, Canada

A rapid and sensitive LC/MS/MS method for the determination of trace dioctyl sulfosuccinate (DOSS) concentrations in seawater samples has been established. The method is well suited to aquatic environment impact monitoring following application of the dispersant Corexit® EC9500A. A practical and repeatable calibration range of 0.5 ng/mL (0.5 µgL1) to 25.0 ng/mL (25.0 µgL-1) DOSS is achieved. The method was shown to have excellent precision and accuracy, with a consistent ≤1.6% relative standard deviation for system suitability standards at 0.5 ng/mL (0.5 µgL1) and linear weighted (1/x) regression coefficients of determination ≥0.995. Linearity of the method was demonstrated down to 0.05 ng/mL (0.05 µgL-1) DOSS in seawater, with a 2.4% relative standard deviation precision for preparation replicates. A U.S. E.P.A. method limit of detection of <0.02 ng/mL (<0.02 µgL-1) was calculated and specificity was confirmed by monitoring of two qualifier ions at 291.1 m/z and 227.1 m/z. These transitions were confirmed by QToF analysis to be associated with the DOSS precursor ion at 421.2 m/z. The method was successfully applied to the analysis of Corexit® EC9500A in seawater samples containing crude oil and preserved with organic solvent. The surfactant nature of the analyte is discussed in relation to detection limit and loss of analyte.

Selectivity of Collision Cross Section Ion Mobility Screening for the Analysis of Pesticide Residues in Food Using ionKey/MS

John Vukovic[1], M. McCullagh[2], D. Douce[2],V. Hanot[3], and S. Goscinny[3]

[1]Waters Limited, Mississauga, Ontario, Canada
[2] Waters Corporation, Wilmslow, UK;
[3]Wetenschappelijk Instituut Volksgezondheid/Institut Scientifique de Sante Publique, Brussels, Belgiumm

Pesticide residue analysis has become a more challenging task considering the increasing number of compounds and the complexity and ion suppressive nature of food matrices. Screening methods with full scan high resolution MS (HRMS) offer high specificity but it can still be challenging to rapidly and efficiently identify targeted compounds. To overcome these analytical hurdles, we report herein on the unique application of microflow separations technology (ionKey™) coupled with Ion Mobility Mass Spectrometry (IM-MS). This system exhibits enhanced analytical sensitivity and provides for the use of a novel physicochemical property of the analyte, Collision Cross Section (CCS), for greater confidence in pesticide residue assignment.

All data was acquired on an ionKey IM-MS system comprised of a nanoACQUITY® UPLC® system coupled to a SYNAPT® G2-S*i* High Definition Mass Spectrometer operating in the Electrospray positive mode (ES+). Full scan spectra was acquired over the range of 50 to 1200 *m/z* at a sampling rate of 5 spectra/sec. Leucine enkephalin was used as calibrating lockmass (*m/z* 556.2766) and the Travelling Wave IMS cell was calibrated with polyalanine for CCS measures. All chromatographic separations were performed on an iKey BEH C18 Separation Device (130 Å, 1.7 µm, 150 µm x 100 mm) held at 45° C.

Analysis was performed with solvent standards in addition to matrix samples: mandarin, ginger, leek, and pear extracts, plus matrix matched calibrants. Collected data was processed using Waters UNIFI Pesticide Screening software.

IonKey/MS with Ion Mobility Mass Spectrometry offers unique advantages for profiling complex matrices. IM provides for mass spectral cleanup and the concomitant CCS measurements determined, provided unique selectivity for the confident identification of analytes. Pesticides at levels as low as 200 fg on column (Pencycuron) can be detected and confidently identified using accurate mass measure and CCS assessment.

The Separation of 2,3,7,8-Substituted Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans Using Supercritical Fluid Chromatography

Nicole Riddell[1,3], Bert van Bavel[1], Ingrid Ericson Jogsten[1], Robert McCrindle[2], Alan McAlees[3], Dave Potter[3], Colleen Tashiro[3], Brock Chittim[3]

[1]Man-Technology-Environment (MTM) Research Center, Örebro University, Örebro, Sweden;
[2]Chemistry Department, University of Guelph, Guelph, Ontario, Canada;
[3]Wellington Laboratories Inc., 345 Southgate Drive, Guelph, Ontario, Canada

The analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in environmental samples is typically performed by high resolution gas chromatography (HRGC) coupled with high resolution mass spectrometry (HRMS), however the emergence of alternative separation and detection techniques for the analysis of regulated POPs could result in the modification of accepted protocols. The purpose of this project was to investigate the application of packed column supercritical fluid chromatography (pSFC) as a fast, cost effective, and green technique for the effective separation of persistent environmental contaminants, specifically PCDDs and PCDFs, and to compare the pSFC separations with those to achieved using HRGC.

All polychlorinated dibenzo-p-dioxin (PCDD), dibenzofuran (PCDF), and biphenyl (PCB) standards were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). All HRGC/HRMS analyses were conducted on an Agilent 6890N Gas Chromatograph (Agilent Technologies, Santa Clara, USA) with a direct capillary interface to an Autospec Ultima High Resolution Mass Spectrometer (Waters Corp., Milford, MA, USA) using a modified U.S. EPA Method 1613 separation method and an Agilent J&W DB5 (60 m x 0.25 mm ID, 0.25 µm film thickness) column. All SFC separations were carried out using a Waters Acquity UltraPerformance Convergence Chromatograph (UPC^2) (Waters Corp., Milford, MA, USA) system equipped with an Acquity Photodiode array (PDA) Detector. The UPC^2 was coupled to a Micromass Quattro micro atmospheric pressure ionization (API) Mass Spectrometer (MS) (Waters Corp., Milford, MA, USA) configured in positive-ion atmospheric pressure photoionization (APPI) mode. Optimal separations were achieved using gradient elution with a methanol modified carbon dioxide (CO_2) mobile phase and a Waters UPC2 Torus 1-AA column (1.7 µm, 3.0 x 100 mm).

The developed pSFC method was found to provide an elution profile very similar to that accomplished during HRGC separations using a DB-5 column with good separation of the homologue windows, TCDD resolution, and minimal congener co-elutions.

More than Multiple Reaction Monitoring (MRM): Alternate Liquid Chromatography-Mass Spectrometry Workflows for Environmental Analysis

Naomi Stock[1]

[1]Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough ON, K9J 7B8

Quantitative analysis of trace contaminants in environmental samples using liquid chromatography coupled to a triple quadrupole mass spectrometer operating in multiple reaction monitoring (MRM) mode, is often the first introduction to liquid chromatography-mass spectrometry (LC-MS) workflows for many graduate students and research scientists. There is no question this is a powerful and sensitive technique, but there are many alternate LC-MS workflows with environmental applications, that are useful for both quantitative and qualitative analysis.

Several recent research projects in our laboratory use alternate LC-MS workflows and/or instruments. Examples of such projects will be discussed and include metabolomic fingerprinting of ash trees using LC-MS in full scan mode followed by principal component analysis; identification of an unknown chemical cue, produced by tadpoles in predator prey situations, using high resolution Fourier Transform Ion Cyclonic Resonance (FTICR) mass spectrometry; quantitation of the contaminant hydroxypropyl-β-cyclodextrim using enhanced multicharge (EMC) mode with a linear quadrupole ion trap instrument; and characterization of dissolved organic matter using a high resolution Orbitrap mass spectrometer operating in full scan mode.

There is more to LC-MS than MRM!

Applications of (ultra)high resolution mass spectrometry in environmental analysis

Xavier Ortiz Almirall[1*], Karl Jobst[1], Eric Reiner[1], Vince Taguchi[1] and Paul Helm[1]

[1] Ministry of the Environment and Climate Change of Ontario

Analysis of contaminants in the environment is a challenging task due to the complexity of the samples and low concentration of the analytes. Targeted analysis methods do not take into account the presence of other unknown compounds that could potentially have a negative impact in the environment. Compounding this problem, some contaminants such as naphthenic acids, PAH and other hydrocarbon based compounds derived from crude oil require ultrahigh mass resolution in order to distinguish their exact masses. These limitations can be overcomed by Fourier transform ion cyclotron resonance mass spectrometry, which offers unparalleled mass resolution (over 1,000,000 resolving power at FWHM) and mass accuracy (sub ppm) working in full scan mode.[1]

The present study showcases two different applications of this techniques in environmental analysis: a) fingerprinting of PAH and other hydrocarbons in crude oil derived compounds (coal tar sealants) as a source of environmental contamination, and b) identification of halogenated contaminants in electronics waste dust using mass defect plots.

When the mass defect plots of the extracts obtained from coal tar sealant and a road suspected to have been treated with that particular sealant were compared, it could be easily concluded that, efectively, the pavement had been treated with the coal tar sealant. If results are plotted in a mass scale were the exact mass of the substitution of a hydrogen by a chlorine atom has an exact mass of 34.0000 Da, chlorinated and brominated compounds are easlily identified in the plot due to their disctinctive mass defect, horizontally aligning pollutant families with different degree of halogenation.[2]

Ultrahigh resolution MS is a powerful tool to fingerprint complex environmental samples. Kendrick and H/Cl mass defect plots facilitate the interpretation of the mass spectrum, sorting out the hydrocarbon series and isolating in the plot halogenated compounds thanks to their distinctive mass defect.

References:

[1] Ortiz, X.; Jobst, K.; Reiner, E.; Backus, S.; Peru, K.; McMartin, D.; O'Sullivan, G.; Taguchi, V.; Headley, J. Characterization of Naphthenic Acids by Gas Chromatography- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Anal. Chem., 2014, 86 (15), 7666–7673.

[2] Jobst, K.; Shen, L.; Reiner, E.; Taguchi, V.; Helm, P.; McCrindle, R.; Backus, S. The use of mass defect plots for the identification of (novel) halogenated contaminants in the environment. Anal. Bioanal. Chem., 2013, 405, 3289-3297.

A Q-TOF mass spectrometer coupled to (multidimensional) gas chromatography using atmospheric pressure chemical ionization: Analysis of environmental samples by GC/MS using an LC/MS instrument

Karl J. Jobst[1,2], Liad Haimovici[2], Sujan Fernando[1], David Megson[3], Matthew Robson[2], Xavier Ortiz[2], Paul A. Helm[2] and Eric J. Reiner[2,4]

[1]Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON
[2]Ministry of the Environment and Climate Change, Laboratory Services Branch, Etobicoke, ON
[3]Department of Chemistry and Biology, Ryerson University, Toronto, ON
[4]Department of Chemistry, University of Toronto, Toronto, ON

Comprehensive two-dimensional gas chromatography (GC×GC) and high resolution mass spectrometry (MS) are powerful, complementary techniques for the analysis of complex environmental samples. Currently, the majority of GC- and GC×GC-MS instruments rely upon conventional electron ionization. However, the past two decades have witnessed the advent of a wide range of (atmospheric pressure) ionization techniques and (hybrid) mass analyzers, whose development was primarily driven by the need for liquid chromatography (LC) and direct analysis applications. Recently, the concept of performing "GC-MS on an LC-MS instrument" [1] has attracted renewed interest [2] and its benefits for environmental analysis are now being explored [3].

Here, we report on the hyphenation of GC×GC with a hybrid quadrupole-time-of-flight (Q-TOF) mass spectrometer using atmospheric pressure chemical ionization (APCI). This universal platform enables high resolution (R>20,000 FWHM), accurate mass (< 2 mDa) measurements as well as tandem mass spectrometry experiments in a timeframe compatible with GC×GC. The generation of intense molecular ions under APCI conditions is an attractive feature for target compound analysis, while structure diagnostic fragmentation and ion-molecule reactions are still accessible using (mass selected) collision experiments. In combination with GC×GC separation, the Q-TOF can perform both target and non-target analyses with a single injection.

This presentation will highlight the capabilities of the GC×GC-QTOF instrument for the analysis of (mixed) halogenated dibenzo-p-dioxins, furans, and flame retardants. The combined target/non-target approach will be demonstrated using samples obtained from industrial fires, waste electronics and electrical equipment as well as other real-world environmental samples.

[1]E.C. Horning, DI Carroll, I Dzidic, KD Haegele, S-N Lin, CV Oertil, RN Stillwell, Clin. Chem., 23 (1977) 13.
[2]CN McEwen, RG McKay, J. Am. Soc.Mass Spectrom., 16 (2005) 1730.
[3]A. Ballesteros-Gomez, J de Boer, PE Leonards, Anal. Chem., 85 (2013) 9572.

New tracers for the elucidation of long-range transport pathways of perfluoroalkyl acids

Cora J. Young[1], John J. MacInnis[1]

[1]Department of Chemistry, Memorial University, St. John's, NL

Perfluoroalkyl acids (PFAAs) are found ubiquitously in the environment, including in remote regions without local sources. This indicates that PFAAs are undergoing long-range transport (LRT). Since PFAAs are ionized under environmental conditions, the obvious LRT pathway is through ocean currents. However, many PFAAs can also be formed indirectly through atmospheric oxidation or biotransformation of volatile recursors indicating that atmospheric transport could also play a role in the LRT of PFAAs. Furthermore, marine aerosols can loft oceanic PFAAs into the atmosphere, leading to mixed atmosphere-ocean LRT. Over the past decade, there have been attempts to elucidate mechanisms of LRT, but it has proved challenging. Original studies sampled for PFAAs in precipitation or water/ice bodies that were derived exclusively from atmospheric deposition. Although this provided some evidence for the role of the atmosphere in PFAA LRT, it was not definitive. With recent improvements in LC-MS-MS analytical capability, chemical tracers can be used to examine the relative roles of oceanic and atmospheric transport of PFAAs. Isomers of perfluorooctanoate (PFOA) have been used to trace sources of this compound, which can inform LRT mechanisms. In this talk, the case for PFAA congener tracers for LRT processes will be made. Only in the last few years have LC-MS-MS capabilities allowed detection of long-chain PFAAs and the role of these congeners in tracing LRT processes will be discussed.

Identification of Emerging Environmental Pollutants using High Resolution LC-MS/MS

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The use of Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS) for targeted quantitation of PPCP has been well established. More recently there is a growing interest from environmental researchers to also screen for and identify non-targeted compounds in environmental samples, including metabolites and degradates, but also completely unexpected pollutants. High resolution and accurate mass LC/MS/MS system is capable of performing highly sensitive and fast MS scanning experiments to search for unknown molecular ions while also performing selective and characteristic MS/MS scanning for further compound identification and, therefore, is the instrument of choice for this challenging task. General unknown screening workflows do not use a target analyte list and compound detection is not based on any a priori knowledge, including retention times and information on possible molecular and fragment ions. Therefore, acquired chromatograms are very rich in information and can easily contain thousands of ions from both any compounds present in the sample as well as from the sample matrix itself. Thus, powerful software tools are needed to explore such data to identify the unexpected compound.

Here we describe the use of the SCIEX TripleTOF® system for the screening for unexpected environmental pollutants. Data was processed using automated sample-control-comparison followed by MS/MS library searching, empirical formula finding, and ChemSpider searching in MasterView™ software.

Extraction and Analysis of Multiclass Veterinary Antibiotics from Solid and Liquid Fractions of Cow Manure

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Analysis of veterinary antibiotics in separated liquid and solid fractions of animal manures is vital due to the wide variation in the water content of agriculturally applied manure. In addition, because sorption of antibiotics on the solid fraction of manure depends on the physico-chemical properties of each antibiotic and the composition of manure (e.g. organic matter content, pH) it is important to distinguish the antibiotic concentrations between liquid and solid fractions of manure since each fraction may be treated and re-used differently. A robust and sensitive analytical method for the quantitative determination of 22 common veterinary antibiotics in both liquid and solid manure matrices was developed based on liquid chromatography with tandem mass spectrometry (LC/MS/MS) under multiple reaction monitoring mode. Antibiotics belonging to the tetracycline, macrolide and sulfonamide classes were extracted from liquid manure by liquid-liquid extraction. Extraction of antibiotics from the solid fraction was performed with ultrasonic assisted extraction. Clean-up of water extracts was achieved by solid phase extraction with hydrophilic-lipophilic balance cartridges, while solid extracts used amino (NH2) and HLB cartridges in tandem. Recoveries ranging from 58%-115% were obtained in liquid manure, and 62%-114% in manure solids. Method detection limits range from 1.2 to 12 ng/L and 0.5 to 7.9 µg/Kg in liquids and solids, respectively. The reported method allows for the simultaneous extraction and analysis of the highly mobile antibiotics in the liquid phase, and the more hydrophobic antibiotics adsorbed on the solid fraction. Without separate analysis, the solid concentrations are typically either underestimated or overestimated, depending on the nature of the antibiotics, if the manure slurry is analyzed instead of the separated solid and liquid. The importance of mobile phase selection on the type of adducts formed, and the advantage of wrong-way round ionization in obtaining high signal-to-noise ratios in LC/MS/MS will be discussed.

Quantification of Ionophore Antimicrobials and Identification of Transformation Products in Poultry Litter Before and After Different Composting Processes

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Ionophore antimicrobials (IPAs) are widely used in chicken production to treat coccidiosis, and they are exclusively used as feed additives. These compounds are the second top-selling antimicrobials in the USA. IPAs are poorly absorbed and not metabolized completely in the animal's intestine; therefore more than 80% of the IPAs are excreted and found in poultry litter (PL). The land application of poultry litter as fertilizer in agricultural croplands is the main source of contamination by IPAs in the environment. Different composting processes can be applied to treat poultry litter before they are applied in the field, but very little information is known on the fate and behavior of IPAs during composting and land application. The goal of this study was to develop and validate a sensitive method for the determination of IPAs (lasalosid, monensin, salinomycin, narasin and maduramicin) in poultry litter, as well as to investigate the transformation products formed during different compost processes.

Sample preparation was performed based on original QuEChERS method. Analyses were performed using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) and with high-accurate mass measurements based on quadrupole time of flight mass spectrometry (QToF/MS). The samples were analyzed before and after composting (turned, aerated and turned/aerated). Three of the IPAs studied (monensin, salinomycin and narasin) were detected in all samples. The recovery results with values between 71-120% showed that the proposed method was efficient for the extraction and quantification of IPAs in poultry litter. The method LOD for all IPAs was 10 μg/kg. Four transformation products were identified before and after composting. High concentrations of IPAs remained after 5 months of composting, with 13-67% decrease in concentrations observed.

Liquid Chromatography-Tandem Mass Spectrometric Analysis of Neonicotinoids in Environmental Water

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Neonicotinoids are a relatively new but the fastest growing group of pesticides in the last two decades, and may be a significant contribution factor in bee mortality. Their widespread and extensive use worldwide makes it critical to monitor neonicotinoid residual levels in the environment. Published methods for neonicotinoid analysis were mainly focused on food and agricultural products, and many of them only measured a subset of the neonicotinoid pesticides. Utilizing the novel biphenyl column, we developed a sensitive liquid chromatography -tandem mass spectrometry (LC-MS/MS) approach to determine all eight commercially available neonicotinoids, including acetamiprid, clothianidin, dinotefuran, flonicamid, imidacloprid, nitempyram, thiacloprid and thiamethoxam.

Two multiple reaction monitoring (MRM) transitions were measured to achieve true positive identification. Isotope labelled surrogates d_3-acetamiprid, d_3-clothianidin, d_4-imidaclopride and d_3-thiamethoxam were used to compensate for instrument variability and matrix effects while monitoring real time method performance. Stability of target compounds in environmental water samples was investigated for a four-week time period. Results obtained on Qtrap 4000 and Qtrap 5500 were compared in details.

Target compounds in aqueous samples were analyzed without concentration by direct aqueous injection (DAI) with method detection limits (MDLs) in the range of 2.5-10 ng/L on 5500 Qtrap. The method was successfully applied for the determination of neonicotinoids in drinking water, surface water and ground water. This accredited method has been employed for an extensive study to determine the distribution of neonicotinoids in Ontario's water.

Stability of Endocrine Disrupting Estrogens in Dairy Manure During Pasteurization-Anaerobic Digestion Process

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Manure generated by dairy farms contains excreted natural estrogens, which are known potent endocrine disruptor compounds. Natural estrogens from livestock origin may be released into the environment by land application of the manure, storage lagoon overflow, or leakage from storage structures, all of which can potentially contaminate surface and ground waters. Livestock farms implement manure storage and treatment systems to decrease nutrient loading to the environment. Therefore it is important to evaluate the extent at which estrogens are removed during storage or treatment of manure. In this study, the concentrations of estrogens and their conjugates in dairy manure were measured in the different stages of a full-scale anaerobic digestion system that incorporates pasteurization pretreatment.

Estrogen concentrations were assessed by gas chromatography with mass spectrometry (GC/MS), and their polar metabolites were determined by liquid chromatography tandem mass spectrometry (LC/MS/MS). In addition, yeast estrogen screen (YES) assay was used to determine the effect of pasteurization and anaerobic digestion on the estrogenic potential of the manure. In the liquid fraction, total hormone concentrations (mainly estrone, α and β estradiol, and sulfated estrogens) were observed up to 7097 ng/L in the untreated manure. After anaerobic digestion, the total concentration in the treated manure was reduced by 23-42%, with estrone as the main estrogen detected at concentrations ranging from 281 to 3557 ng/L.

Despite the significant decrease in α and β estradiol, the estrogenicity of dairy manure based on YES assay increased after treatment, consistent to what has been reported in other biodegradation studies on estrogens. For an overall assessment of the process, solid fraction of the manure will be also evaluated for estrogens and estrogenic potential.

Method Development for the Analysis of Organophosphate Flame Retardants

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Abstract not provided

Hindered Phenol, Substituted Diphenylamine Antioxidants and Benzotriazole UV Stabilizers in the Environment

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Hindered phenols (HPs) and substituted diphenylamines (SDPAs) are antioxidants that used in rubber, lubricants, plastic, fuel, polymers, cosmetic formulations, and food applications. Benzotriazole UV stabilizers (BZT-UVs) are used in a range of applications to protect materials from UV degradation. Once released into the aquatic environment, these contaminants are hypothesized to be persistent and bioaccumulative. In addition, they may be potentially toxic to aquatic organisms. Therefore, these compounds are prioritized for risk assessment in Canadian government's Chemicals Management Plan (CMP). However, the occurrence and distribution of HPs and SDPAs in aquatic environment are still poorly understood, while BZT-UV data has only emerged in the last 5 years. To this end, ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS–MS) based methods have been developed for the determination of 6 HPs, 9 SDPAs and 6 BZT-UVs in environmental samples.

Sample preparation was based on liquid-liquid extraction or solid phase extraction, depending on the specific environmental matrix. A Waters ACQUITYXEVO-TQS LC-MS/MS system with negative atmospheric chemical ionization was used for the determination of HPs. The method used a Waters ACQUITY LC coupled to an SCIEX 4000 MS/MS with positive electrospray ionization for the detection of SDPAs and BZT-UVs. All compounds are monitored using multiple reaction monitoring transitions.

The preliminary data showed that the total concentrations of HPs in wastewater samples collected from Canada were up to 1300 ng/L, with the highest concentration found for 2,6-di-tert-butyl-4-methylphenol in influent. The total concentrations of SDPAs and BZT-UVs in wastewater samples were 7-2720 ng/L and <method detection limit-200 ng/L, respectively. Some SDPAs were also determined in the blood plasma of bottlenose dolphin and white sucker, with concentrations up to 2600 pg/mL. These results suggest that there is a potential exposure/health risk of these contaminants to aquatic organisms in the sampling area and may warrant further investigation.

A Comprehensive Method for the Determination of Phthalates in Industrial and Municipal Wastewater

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Abstract not provided

Measurement of Artificial Sweeteners for Tracking Groundwater Contaminants

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Artificial sweeteners are found in many foods, drugs and other domestic products, and thus can be found in various domestic waste streams. Many artificial sweeteners persist in the environment and anionic forms are not substantially retarded in the subsurface, making them potentially useful tracers of groundwater affected by these human wastes. In this work, we investigate the use of AS for assessing groundwater contamination and its potential influence on surface water bodies.

The artificial sweeteners acesulfame, cyclamate, saccharin and suscrolose were analyzed using a Dionex (Sunnyvale, CA, USA) 2500 ion chromatography (IC) system coupled to a QTRAP 5500 (AB Sciex, Concord, ON, CAN) triple-quadrupole tandem mass-spectrometer, operated in negative electrospray ionization (ESI) mode. Isotope-labeled internal standards were used. These four artificial sweeteners were assessed in septic systems, waste lagoons, and landfill leachates, with effects on groundwater or its subsequent influence on surface waters assessed from the scale of a single site (plume) to more-regional effects. Sweeteners were found to be wide-spread in urban environments and at still-notable concentrations in more rural settings (cottage areas of Georgian Bay). The relative abundance of these four artificial sweeteners may allow for age-dating contamination or distinguishing different sources.

Trypsin versus Formic Acid digestion for shotgun proteomics using LC-MS/MS

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The proteome is the entire complement of proteins synthesized by a genome, cell, tissue, or organism at a particular time under a given set of conditions. Shotgun proteomics describes a bottom-up methodology where complex mixtures of large protein molecules are digested into smaller peptide molecules for characterization using high performance liquid chromatography tandem mass spectrometry. The proteins originally present in the complex mixture are then inferred when the peptide amino acid sequences characterized by the mass spectrometer are matched to larger protein sequences using database search software. Trypsin is a proteolytic enzyme produced in the pancreas and is the protein digestion enzyme of choice because its cleavage is well understood, specific and established digestion methods using trypsin are readily available and relatively easy to perform. Formic acid protein digestion offers an attractive alternative by saving time and lowering cost, however little information is available in the literature about. This presentation will present a formic acid protein digestion method, the empirically determined cleavage specificity of formic acid versus what is known in the literature, and present results that compare the digestion efficiency of formic acid with trypsin using protein standards and fish plasma as a biological matrix.

Extraction and detection of amino sugar stereoisomer biomarkers in environmental matrices

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Muramic acid and stereoisomers glucosamine, galactosamine and mannosamine are amino sugars utilized as biomarkers for tracking microbial (e.g. bacterial and fungal) contributions to organic matter in sea water, sediments, and soils. In particular, the quantification of these components of cell walls enables tracking biological transformations of organic matter and can provide further insight through stable isotope analysis. Analytical methods yielding acid hydrolysates of the amino sugar precursors (e.g. chitin, peptidoglycan) in sample matrices previously required multiple cleanup steps, often including chemical derivatization, and sometimes separate instrumental analyses for the quantitation of the amino sugar stereoisomers and muramic acid. In this work, we aim to develop a simple and rapid extraction and analysis technique to quantify individual amino sugar stereoisomers with using common analytical techniques and readily available instrumentation.

We have optimized a selective recovery of these compounds from acid hydrolysates via an ion retardation and solid phase extraction cleanup, utilizing an internal standard approach, followed by ultrahigh performance liquid chromatography and tandem mass spectrometry. Separation of all compounds, including the stereoisomers, was achieved and optimized on a Waters X-Bridge amide hydrophilic interaction column. An injection standard, and the parent and transition ions were used for selective and specific quantitative detection of the target compounds, yielding instrument detection limits on the order of 5 ppb for glucosamine, mannosamine and muramic acid, and 20 ppb for galactosamine.

The utility of this method in the detection of amino sugars and muramic acid in real soil depth profiles from a latitudinal transect of boreal forest sites is discussed. The potential application of this method to source apportionment of atmospheric aerosols is also considered.

Assessing Emission of Per-Fluoroalkyl Substance to Air from WWTPs Using LC/MS/MS

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Emissions to air of poly- and perfluoroalkyl substances (PFASs) were determined for different wastewater treatment plants (WWTP) by measuring concentrations in air upwind and on-site (above the active tank). The WWTPs included secondary activated sludge (AS), secondary extended aeration (EA) and facultative lagoons (LG), that were characteristic of wastewater treatment in urban areas (UR-AS), towns (TW-EA), and rural areas (RU-LG), respectively. Air sampling was time-integrated using sorbent-impregnated polyurethane foam (SIP) disk passive air samplers (PAS) during summer 2013 and winter 2014. The samples were analyzed for five groups of PFASs including: neutral PFASs; fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs) perfluorooctane sulfonamidoethanols (FOSEs) using GC/MS and perfluoroalkyl acids (PFAAs); perfluoroalkyl sulfonic acids (PFSAs), and perfluoroalkyl carboxylic acids (PFCAs) using LC/MS/MS. The ΣPFASs concentrations in air were 2.3-4.5 times higher on-site (350-3380 pg/m^3 in summer and 170-1700 pg/m^3 in winter) compared to the upwind locations (150-760 pg/m^3 in summer and 70-610 pg/m^3 in winter) indicating an important contribution of emissions from the wastewater to air. The concentrations in air determined on-site were ~2 times higher in summer compared to winter, possibly reflecting enhanced volatilization due to higher wastewater temperatures. Different relative distributions (%) of PFAAs calculated as Σ(PFSAs and PFCAs)/ ΣPFASs, were observed at the WWTPs sites. PFAAs in air at UR-AS sites comprised 16% of total PFASs, while this percentage was on average 45% and 70% at the TW-EA sites and RU-LG sites, respectively. The high contribution of PFAAs at the TW-EA and RU-LG sites could be attributed to longer hydraulic retention time that enhances transformation to PFAAs from neutral PFASs precursors, particularly FTOHs. A positive significant correlation (excluding lagoons) was observed between ΣPFASs concentrations in air and wastewater operation parameters (tank surface area and influent flow rate) at UR-AS and TW-EA sites, while a negative correlation was obtained with hydraulic retention time. Emissions to air were estimated for winter and summer periods using a simplified dispersion model.

Utilizing UPLC-MS/MS for the detection of PFAAs in passive air samples from the Global Atmospheric Passive Sampling (GAPS) Network

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Perfluoroalkyl acids (PFAAs) are globally used surfactants with applications as coatings for cookware, textiles, food contact papers and aqueous film-forming foams used to extinguish fires[1]. The longer chain PFAAs are commonly detected in the environment and in human serum which has led to the voluntary phase out of production of Perfluorooctane sulfonate (PFOS) and Perfluooctanoic acid (PFOA) by their major global manufacturer in 2002. Subsequently, PFOS was added to the Stockholm Convention on Persistent Organic Compounds in 2009 for restriction of use and PFOA has been targeted for elimination of use by 2015 in a USEPA stewardship with 8 global companies[1]. As such, PFAAs (in particular PFOS and PFOA) are priority chemicals for monitoring under the Chemicals Management Plan (CMP). The Global Atmospheric Passive Sampling (GAPS) network monitors priority chemicals at over 50 global sites, to contribute to the CMP. Previously, passive samples from 20 sites in the 2009 GAPS sampling campaign were analysed for PFAAs using HPLC-MS/MS with detection of 7 PFAAs in concentrations above method detection limits (MDLs) [2]. Recent acquisition of a UPLC-MS/MS has allowed increased detection frequency of PFAAs in samples, due to a 5 fold reduction in MDLs, as well as allowing an increase in the number of PFAAs analysed.

A Waters Acquity I-class Ultra Performance Liquid Chromatograph (UPLC) coupled with a Xevo TQ-S triple quadrupole Mass Spectrometer (MS/MS) was optimized for the analysis of 17 PFAAs. The previously analysed 2009 GAPS samples were rerun with the new high performance method, with increased detection of PFAAs. Passive samples from the 2011 and 2013 sampling campaigns were also analysed, providing information on spatial and temporal trends of these chemicals in air. Perfluorobutanoic acid (PFBA) was present in the highest concentrations of all PFAAs, with the highest detection frequency, and a few sites displayed increasing concentrations from 2009-2013. PFBA is currently employed as a replacement chemical for PFOA.

The new UPLC-MS/MS PFAAs method allowed detection of a wider range of analytes in passive air samples, providing information on global trends of these compounds.

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An Accurate LC-MS/MS Assay of Perfluorinated Compounds in Water by Laminar Flow Triple-Quadrupole Mass Spectrometry

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Perfluorinated compounds (PFCs) are widely used in diverse industrial applications and consumer products due to their stability and surfactant properties. However, PFCs such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) do not decompose easily in the natural environment and can bio-accumulate in certain living organisms. PFCs are now recognized as emerging pollutants of global relevance which has led to efforts to regulate them and prompted the need for PFCs monitoring and risk assessment in humans [1].

Using an IONICS 3Q 120 triple quadrupole mass spectrometer coupled to a Shimadzu Nexera LC system, an MRM-based LC-MS/MS method has been developed for a panel of 17 PFCs comprised of 13 perfluorinated carboxylates (PFCAs) and 4 perfluorinated sulfonates (PFSAs). The analytical column is a Luna C-18(2) (3 µm) 50 x 2.0 mm column. Solutions of PFCs are prepared in 50% aqueous methanol and 2 mM ammonium acetate and analytes eluted with a water/methanol gradient with 2 mM ammonium acetate. The 3Q 120 mass spectrometer is based on laminar flow and equipped with a heated coaxial ESI flow ion source and a hot "source-induced desolvation" interface which greatly lowers chemical background noise and improves sensitivity. Because of the laminar flow sampling they use, the 3Q systems support an efficient MS^3 mode that is used in this work for compound confirmation.

The LLODs of the 17 analytes were all lower than 0.01 ng/mL with RSD values lower than 10%. Good linearity was achieved for all 17 PFCs over a concentration range up to 500 ng/mL with correlation coefficient R2 >0.99. The accuracy for all the analytes ranged from 90-105%, with CVs of less than 15% over the entire concentration range.

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Re-investigation of Aerobic Biodegradation of 6:2 and 8:2 Polyfluroalkyl Phosphate Diesters (6:2 and 8:2 diPAPs) in Soil

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Polyfluoroalkyl phosphate esters (PAPs) have been widely detected in the environment and proposed as precursors to persistent perfluoroalkyl carboxylic acids (PFCAs). During an investigation of the environmental fate of 6:2 diPAP and 8:2 diPAP in soils, it was found that soil extraction methods have a great impact on study outcome. Some commonly used extraction methods either cannot efficiently recover the PAPs, or caused substantial solvent-enhanced hydrolysis to bias study results. The objective of this study was to develop a proper extraction method for PAPs and re-estimate the degradation rates, metabolites trends, yields of PFCAs using the improved method. The implications of solvent-enhanced hydrolysis in assessing the environmental fate of these chemicals were discussed.

Prior to biodegradation tests, six different solvents were tested for recovering 6:2 and 8:2 monoPAPs and diPAPs from soil. All the chemicals of interests were analyzed using ultra-high performance liquid chromatography tandem mass spectrometry. Extraction using MTBE (methyl tert-butyl ether)/acetic acid or acetonitrile/acetic acid was found satisfactory for quantitative recovery of the diPAPs, while methanol/ammonium hydroxide, acetonitrile/sodium hydroxide, ethyl acetate, or MTBE were unsuitable. 6:2 and 8:2 monoPAPs exhibited rapid solvent-enhanced hydrolysis in all the solvents, and, therefore, quantitative recoveries were not possible. Simultaneously, quantitative measurement of fluorotelomer alcohols was negatively impacted by the hydrolysis.

With the improved extraction methods, aerobic soil biodegradation of 6:2 diPAP and 8:2 diPAP were re-investigated in semi-dynamic soil microcosms over 112 days. The major degradation products of 6:2 diPAP were 5:3 fluorotelomer carboxylic acid, perfluoropentanoic and perfluorohexanoic acids, and the major product of 8:2 diPAP was perfluorooctanoic acid. Soil half-lives of 6:2 and 8:2 diPAPs were 11.5 and 120.8 days, respectively.