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Conference Plenary

The impacts of neonicotinoid insecticides on bees: from individual behaviour to pollination services

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Abstract: Recent concern over global pollinator declines has led to considerable research on pesticide impacts. Here we report results from a series of studies examining to what extent field-realistic insecticide exposure can lead to significant sublethal impacts on individual behaviour (e.g. reduced queen colony founding success and impaired worker learning and foraging), colony function (e.g. effects on growth rates and forager recruitment), and the critical ecosystem services bumblebees provide to crops and wild plants. Taken together these effects could have widespread implications for the stability of wild pollinator populations, sustainable production of pollinator limited crops, and maintaining wild plant biodiversity.

Applying Advanced Mass Spectrometry Technology to Improve the Analysis of Neonicotinoid Pesticides

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Neonicotinoid pesticides have been heavily investigated due to their possible link to bee colony collapse disorder. The widespread and extensive use worldwide makes it critical to monitor their residual levels in the environment. Reliable analytical methods are critically needed for different environmental matrices to fully understand the distribution, fate, exposure and impacts of these pesticides. Utilizing different mass spectrometry instruments, including SCIEX QTRAP® 4000, 5500, 6500 and SCIEX X500R QTOF mass spectrometers, eight neonicotinoid pesticides, acetamiprid, clothianidin, dinotefuran, flonicamid, imidacloprid, nitempyram, thiacloprid and thiamethoxam have been studied in detail from various environmental samples. It is demonstrated that instrumentation with higher sensitivity will enable efficient and high throughput direct injection analysis of aqueous samples; The application of differential ion mobility spectrometry combined with tandem mass spectrometry was demonstrated to have great potential in reducing chemical background and/or isobaric interferences inherited in complicated sample matrices such as soil and pollen, and it is a great alternative to reduce time-consuming sample cleanup and LC method re-optimisation efforts for these complex sample matrices. The high resolution QTOF instrument can offer expanded capacity of non-target compounds screening while maintain the high selectivity for target compound analysis. The higher mass accuracy it provided can also reduce the chemical background and/or isobaric interferences from the sample matrices.

Neonicotinoid insecticides in watersheds of the Great Lakes, Ontario

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Neonicotinoid insecticides (NNIs) are widely used to control insect pests, and these compounds are used extensively in agricultural regions of Ontario. Because of their persistence and high solubility in water, there is potential for NNIs to be transported from agricultural fields into surface waters. The objective of this project was to evaluate the distribution of NNIs in Ontario surface waters that discharge into Lake Ontario, Lake Erie and Lake Huron. The Polar Organic Chemical Integrative Sampler (POCIS) was selected as the principal monitoring technique. To correct for the effect of environmental factors on the rates of uptake of NNIs into POCIS, Performance Reference Compounds (PRCs) were spiked into some of the POCIS deployed at the monitoring sites. POCIS were deployed for 2 weeks and grab water samples were collected at 13 stream sites and 5 larger watersheds in the Great Lakes basin. Laboratory experiments were conducted to estimate sampling rates of NNIs in a synthetic water using a static, renewal protocol at 15^{0}C over 14 days. Extracts were analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) using an AB Sciex QTrap 5500 instrument with electrospray ionization coupled with an Agilent 1100 HPLC. Seven NNIs were detected, but Imidacloprid was found at the highest concentrations of up to 715 ng/L. Clothianidin, thiamethoxam and thiacloprid were also detected at almost all sampling sites at levels between 1~ 271 ng/L. These data indicate that NNIs are widely distributed in surface waters in agricultural regions in Ontario within the Great Lakes basin.

Analysis of neonicotinoid pesticides in environmental samples using a Quechers based extraction to evaluate the exposure and impact of seed treatments on honey bee productivity, health and behaviour over three seasons.

David MacKay, University of Guelph, Environmental Sciences

The effects of neonicotinoid pesticides on pollinator health are an important agricultural issue. Neonicotinoid pesticides have been in use on North America for more than a decade and they are now detectable in soil, environmental water, non-target plants and honey bees. There have been few long term field studies on the impacts of these pesticides in Ontario. Fields studies are difficult to control when the analytes of interest are ubiquitous in the environment. This study was designed to evaluate the effects of agricultural exposure to neonicotinoid pesticides used as seed treatments for corn and soy on the colony health, honey production, overwinter survival and behaviour of honey bees. A Quechers based extraction with LC-MS/MS detection was employed to evaluate the differences in pesticide exposure between field treatments and over time in paired agriculture treatments in Southern Ontario. Pesticide levels were tested in live bees, dead bees, bee collected pollen, honey and brood. Thiamethoxam and clothianidin were the most commonly found pesticides in all matrices tested. The pesticide analysis demonstrated the colonies in the field sites were exposed to significantly different levels of neonicotinoid pesticides.

Distributions of Poly- and Perfluoroalkyl Substances (PFASs) in Surface and Subsurface Seawater of the Northeast US Pelagic Zone

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Oceans are sink of poly- and perfluoroalkyl substances (PFASs) that have been produced, used and released to the environment in large quantities since the 1950s. Pelagic zones as regions of oceans in adjacent to continents where large marine ecosystems locate are important in terms of biogeochemical cycling, ecosystem diversity and economic values. Pelagic zones are only a few hundred meters deep and all depths are inhabited by marine

wildlife, which are influenced by anthropogenic chemicals such as PFASs discharged from rivers and wastewater effluent on the coast and act as an important pathway for human exposure to the chemicals. In this study, we collected 55 surface / subsurface seawater samples and 7 plankton samples from 21 sites in the Northeast US Pelagic Zone between Rhode Island Sound and Eastern Shore of Virginia. The samples were analyzed for 21 PFASs using a method validated via inter-lab comparisons. Elevated PFASs that exceeded coastal seawater quality guidelines were found in areas close to Delaware Bay, which is heavily influenced by anthropogenic chemical sources. The data suggest PFASs were well mixed vertically and thus would influence wildlife inhabiting all depths. At depths with elevated biomass, elevated PFASs were not observed, suggesting particle sinking is not driving PFASs with less than 10 carbons to deeper ocean despite of high abundance of biomass at the pelagic zone. Concentrations of PFASs in seawater of continental shelf were negatively correlated with seawater salinities, from which we infer that PFOS are continuously discharged to the ocean from the continent even 15 years after source phase-out.

PFAS Dark Matter: Per- and polyfluorinated precursors in soil and water

Pat Benvenuto

Per- and polyfluorinated alkyl substances (PFASs) are ubiquitous, persistent, anthropogenic chemicals that bioaccumulate in both humans and biota. The toxicity of certain PFASs such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) has been observed in some rodent studies. The potential for deleterious effects in humans is suspected, and is under further study. In response to our greater understanding of the toxicological properties of these compounds, different contaminant guidelines for selected PFASs in environmental matrices have been introduced in several jurisdictions

While significant effort continues to be focused on delineating the extent of PFAS contamination, an additional difficulty that may influence remediation efforts is the potential for *in situ* transformation of PFAS precursor compounds to the current PFASs of concern. These precursor compounds are not included as part of the suite of routine PFASs currently measured, and over time may transform to these compounds, introducing potential future risk and liability. This may require remediation efforts to not only consider target compounds of interest, but to also account for these oxidizable PFAS precursors. The challenge in accounting for these precursors is that the pool of precursors can be large and generally unknown.

Maxxam Analytics has commercialized an assay, based on a previously published method[1], to measure the potential magnitude of the pool of PFAS precursor compounds (often referred to as PFAS “dark matter”) that may exist in contaminated soils and water. This presentation discusses this total oxidizable PFAS precursor assay using field sample examples and also examines its advantages and constraints.

[1] Houtz, E.F. and Sedlak, D.L. (2012). Environ. Sci. Technol., 46, 9342-9349.

Expansion of EPA Method 537 from 14 to 30 Per/Polyfluorinated Substances by LC/QQQ,

Ralph Hindle (*Vogon Labs*) ***Caledon Award Lecture***

Flame retardants in seals of the Antarctic: Long-range transport of organic pollutants

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Persistent organic pollutants (POPs) are compounds with negative effects on human health and the environment. The Stockholm Convention defined four criteria for POPs: persistence, bioaccumulation, potential for long-range transport and toxicity. POPs have reached remote areas like the Antarctic although human influence is limited because of their geographic isolation and extreme climate.

Polybrominated diphenyl ethers (PBDEs) are the most used flame retardants (FRs) and are included in the Stockholm Convention. Their production has been banned in Europe and North America. Hence alternative FRs are used as substitutes.

This study investigated the occurrence of PBDEs, emerging brominated FRs and dechloranes in 31 samples of two species of seals (*Mirounga leonina* and *Arctocephalus gazella*) collected in Livingston Island and Penguin Island (Antarctica). The samples include fin muscle, nervous system tissue, fat and fur.

Specific aims were to prove the long-range transport capacity of FRs and to assess the exposure of these species in the area. Furthermore, the diversity of the tissues collected allowed to evaluate the best tissue for biomonitoring and to judge the ability of these pollutants to cross the blood-brain barrier (BBB), which is relevant due to their neurological effects.

PBDEs and dechloranes were detected in some samples with the same order of magnitude (low ng/g lipid weight). BDE-28 and BDE-47 were the predominant pollutants in fat and fins with lower concentrations compared to literature. As for dechloranes, Dec 602 showed in fins, fat and nervous system tissue while *anti*-DP was only detected in fat.

Aqueous Film Forming Foam-Related Perfluoroalkyl and Polyfluoroalkyl Substances in Canadian Surface Water and Sediment

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There are limited reports of the presence of the dozens of novel perfluoroalkyl and polyfluoroalkyl substances (PFASs) that have been identified in Aqueous Film Forming Foams (AFFFs) in the environment. The detections of these compounds that have been reported are generally associated with sites that have been identified as highly AFFF impacted. Through a combination of extraction (WAX SPE for water, solvent extraction for sediments) and UPLC-MS/MS analysis with a Waters Acquity-Xevo TQ-S system AFFF-related PFASs at concentrations down to under 1 ng/L were detected and quantified according to the availability of authentic and mass-labelled standards. In a survey of rural, urban, and known AFFF-impacted surface waters, several fluorotelomer PFASs were detected at many urban sites, including 6:2 fluorotelomer sulfonic acid (FTSA, 0.05-0.1 ng/L), 6:2 fluorotelomer sulfonamide alkylbetaine (FTAB, 0.06-15.5 ng/L), 6:2 fluorotelomer mercaptoalkylamido sulfonate sulfone (FTSAS-SO_2, estimated <0.1 ng/L), and 6:2 fluorotelomer thiohydroxylammonium sulfonate sulfone (FTSHA-SO, estimated <0.2 ng/L). The relatively high concentrations of 6:2 FTAB in urban sites, as well as AFFF-impacted sites (up to 33 ng/L) are noteworthy and may indicate widespread sources of this perfluoroalkyl carboxylate (PFCA) precursor. Perfluorohexanesulfonamide (FHxSA) was the most abundant potential perfluoroalkane sulfonate (PFSA) precursor compound and was detected in all urban and AFFF-impacted surface waters (range: 0.04 to 18.5 ng/L) and may be a useful marker for the presence of C6 PFSA precursors. Comparing water and sediment extracts from an AFFF-impacted river provided preliminary insights into the role of perfluoroalkyl chain-length and polar head group in the sorption of AFFF-related PFASs.

Advances in Organic Molecule Analysis with Isotopic Fine Structure (IFS) Mass Spectrometry

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Over the last two decades, mass spectrometry has been developed for inclusion in a wide variety of new applications, including vital biomedical and proteomics workflows that have evolved around highly advanced equipment. Regardless of the migration of mass spectrometers to new arenas such as clinical applications, the major function of MS equipment worldwide continues to be the elucidation of atomic formulae for detected molecules.

Since mass spectrometry detects peaks of arbitrary charge, the recorded m/z value is of limited utility unless decoded into an analytical figure that is readily useful. More useful still is further describing a detected peak as a chemical entity which can then be used (for example) to confirm the output of a synthetic chemistry experiment.

A new form of elemental identification named Isotopic Fine Structure Mass Spectrometry (IFS-MS) is presented here that uses high mass resolving power (>500,000) combined with high magnitude fidelity to directly detect the direct heteroatom signature by identifying discrete isotopologues. This type of measurement is vastly superior to previous methods for determining chemical formulae since the type of heteroatoms and quantity can be directly determined from measured spectra, in essence allowing chemical formulae to be "read" directly off of mass spectra. We present the mechanics and requirements behind this approach along with several applications oriented examples.

Remove the lipids from your samples but not your analyte, using EMR-Lipid for Enhanced Matrix Removal

Christopher Deckers, Agilent Technologies

Agilent Bond Elut QuEChERS Enhanced Matrix Removal—Lipid (EMR—Lipid) is the next generation of sample preparation products. This patented technologu is very easy to use and is especially effective for high-fat samples. This study demonstrates the application of this novel product for the analysis of pesticides in avocado by GC/MS/MS and by LCMSMS. EMR—Lipid provides far superior matrix removal by weight, GC/MS full scan, and matrix effect determination when compared to C18/PSA and zirconia-based sorbents. The data also demonstrate dramatically improved reproducibility for the analytes over 100 injections. This work demonstrates that EMR—Lipid dSPE fits into a QuEChERS workflow and delivers fast, robust, and effective sample preparation with the most complete matrix removal available for multiresidue analysis of pesticides in avocado. Compelling data will also be share for PAHs in salmon and vet drugs in bovine liver.

Determination of Nitro-Musks in Wastewater Using QuEChеRS Method Combined with Electron Capture Negative Ion GC/Tandem Mass Spectrometry

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Nitro musks are synthetic and semi-volatile compounds that are used as fragrance additives in personal care and household products. Nitro musks are known to be toxic and are considered to be persistent and bio-accumulative; consequently their usage has been phased out or restricted in Europe and Japan. As a result of their extensive use, synthetic musks have been ubiquitously detected in the environment.

GC/ECNI/MS has been used extensively in environmental determinations. ECNI spectra of brominated compounds are dominated by m/z =79 and 81 corresponding to the bromine ion, whereas, the spectra of organochlorine compounds are dominated by the molecular ion or M-Cl; which under CID conditions produces m/z= 35 and 37 corresponding to chlroine ion. The ECNI spectra of nitro musks are dominated by M^- or $M\text{-}CH_3$, which under CID conditions produce fragments that preserve the NO_2 moiety and maintain the charge. Over the past several years, QuEChеRS has been applied to the determination of many environmental contaminants in different matrices. The speed of extraction combined with selectivity and sensitivity of ECNI/MSMS techniques provides a robust method for detection and determination of nitro musks in wastewater. The recoveries for nitro musks spiked at 1 µg/L levels ranged between 73% and 91% and % CV ranged between 4% and 11% indicating that this is indeed a rapid and robust method. In this presentation, ECNI/MSMS mass spectra characteristics of nitro musks along with levels, trends and removal efficiencies in selected wastewater treatment plants will be presented.

Lessons Learned in Development of Liquid Chromatography – Mass Spectrometric Techniques for Analysis of Brominated Flame Retardants

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Liquid chromatography – tandem mass spectrometry (LC/MS/MS) is an effective technique for analyzing polar, higher molecular weight, or thermally-labile compounds, many of which are emerging as contaminants in the environment. Conventional methods based on gas chromatography (GC/MS) are not amenable to analysis of some of these compounds. We have developed a suite of LC/MS/MS methods to study the occurrence and fate of brominated flame retardants (BFRs) in the environment, in particular hexabromocyclododecane (HBCD). We have also investigated a variety of parameters influencing method performance, including stationary and mobile phases and ionization techniques of electrospray (ESI) and photospray (APPI) ionization sources. We also investigated sample matrix effects resulting in ion suppression, adduct formation, different response factors between native and mass-labeled compounds, and use of buffers. These tandem MS methods have proven to be useful tools for analysis of flame retardants in environmental samples; however, we encountered significant challenges during methods development, including issues of compatibility of analytes with mobile phases, achievement of adequate chromatographic resolution, matrix effects and variations in mass spectrometric response factors among isomeric compounds.

Liquid Chromatography-High Resolution Mass Spectrometric Analysis of Pesticides in Environmental Samples

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Pesticides are chemicals that have been used to control undesired insects, weeds, rodents, fungi, bacteria or other organisms in order to protect agricultural crops and animals. However, the detection of pesticides does lead to concerns over their impacts to the environment and human health, especially for newly developed pesticides that have more potent with specific modes of action allowing them to be used at lower levels. Consistent sampling methods coupled with sensitive, selective and reliable analytical methods are required to monitor these chemicals in the environment to develop appropriate mitigation strategies. Using liquid chromatography for separation and full-scan high-resolution mass spectrometry (LC-HRMS) detection in the data independent acquisition (DIA) mode, an analytical workflow for the quantitative determination of 174 pesticides, qualitative screening of non-targeted pesticides and their metabolites is described. Polar organic chemicals collected from surface water and waste water treatment plant effluents were ultrasonically extracted and analysed using LC-HRMS. The full-scan HRMS data provide not only quantitative results for targeted compounds but also information on the non-targeted pesticides that would otherwise not be available in a targeted analysis. Applications of retrospective analysis of existing data set allowed confirmation of the occurrence of "new" pesticides, e.g., metabolites, using newly available standards, without requiring re-sampling and re-analysis of the samples. From an environmental protection perspective, employing analytical methods described here, combined with broad surveillance area, provides key information for pesticide management.

GC-MS/MS Pesticide Analyzer for Complex Pesticide Residues

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Maximum residue limits required by regulatory agencies such as the European commission[1] and the FDA[2] is often lowered in response to new toxicity data on thousands of pesticides currently used worldwide. Consequently, setting up a triple quadrupole GC/MS/MS method for pesticide analysis has become one of the most challenging and daunting tasks in laboratory practice. From the hardware standpoint, a fast scanning analyzer is required to enable analysis of large number of analytes in short time periods. As a solution, Improvements in collision cell technologies and new Timed-SRM methodology are now available for high-analyte-capacity methodology for such complicated pesticide analysis tasks. While MRM transitions and collision energy data are often known before hand for the vast majority of currently used pesticides, software tools are required to help develop this aspect of methodology for newly regulated pesticides. Even for some those pesticides for which the MRM transitions are known, alternate transitions need to be explored based on matrix interferences. Quick

and easy method MRM transitions and collision energy determination and modifications enabled y software tools are therefore crucial to save on money and time. In this talk, various aspects of the currently available hardware and software tools for pesticides analysis will be discussed along with comparison of data with high resolution GC/MS data.

Keywords: Triple quadrupole mass spectrometry, pesticide analysis.

References:
[1]. European Regulation 396/2005 and Commission Directive 2006/125/EC)
[2]. CPG Sec. 575.100 Pesticide Residues in Food and Feed

Fast and Extended Analysis of Over 200 FDA Regulated Pesticides in Organic and Non-organic Grapes by LC-MS/MS using Time-Managed-MRM

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Triple quadrupole mass spectrometers are routinely used for fast and accurate quantitation of hundreds of analytes simultaneously in many laboratories around the world. However, better quality data is continually being sought for the target monitoring of hundreds of analytes in one LC-MS/MS injection. The time-managed-MRM^{TM} offered in the QSight^{TM} triple quadrupole automates the calculation of optimum dwell time for MRM transitions based on the number of co-eluting transitions, expected cycle time, retention time and acquisition time window centered on retention time of the targeted analytes. Such method automation results in improved sensitivity, accuracy, and reproducibility of analysis as compared to those from traditionally developed MRM methods. In the present study, time-managed-MRM with LC-MS/MS is demonstrated for analyzing over 200 pesticide residues in grapes.

Methods

Organic and non-organic grape samples were obtained from a local grocery store in Ontario, Canada. The mixed pesticide standards were obtained from ULTRA Scientific (North Kingstown, RI). The samples were prepared using Supra-d QuEChERS kits (AOAC 2007.01 method). 10 µL of each supernatant was diluted and subsequently injected on column. LC separation of analyte was performed using a PerkinElmer Brownlee^{TM} phenyl-hexyl (100x2.1mm, 2.7um) column. The mobile phases were A) water and B) methanol, both containing 5mM ammonium formate, at a flow rate of 0.3 mL/min. Detection was via the QSight^{TM} triple quadrupole with-managed-MRM. The signal-to-noise, accuracy, and reproducibility results for selected analytes were compared to those acquired by a traditional MRM method.

Preliminary data

The calibration standards were prepared with different levels of pesticides to determine instrument detection limits and set up calibration curves. Detection limits for all pesticides were less than 5 µg/kg. The calibration curves for all analytes were linear over three orders of magnitude with a R^2 value higher than 0.995. Five non-organic grape samples were screened for pesticides with the method developed in this work. Based on retention time, ion ratio of qualifier to quantifier, and quantifier ion response, three pesticides (thiabendazole, pyrimethanil and propiconazole) were detected at concentration higher than 500 ppb in non-organic grape sample. A reproducibility study was also performed with 5 replicate injections at low levels near the detection limits, using both the time-managed-MRM method and the traditional MRM method. The data demonstrated that the average reproducibility at low levels and detection limits for all pesticides improved roughly by a factor of 3 using time-managed-MRM method in comparison to the traditional MRM method.

Future work would include the analysis of pesticides in other brands of non-organic grape and organic grape, using time-managed-MRM method developed in this study.

Automated analysis of 1,4-dioxane in water by large volume injection GC/HRMS

Eva Korenková, Jerry Chao, Karl Jobst, Michelle Burlak, Karen MacPherson

A sensitive, accurate, and rugged method for the analysis of 1,4-dioxane in water was developed. Sample preparation process was performed by automated Multi-Purpose Sampler (MPS). A 10 mL aliquot of the sample was extracted using ITSP cartridge containing 20 mg coconut charcoal with 30 µm polyethylene (PE) pre-filter frit. Sample loading speed and cartridge elution volume with dichloromethane were optimized at 50 µL/s and 500 µL, respectively. 10 µL of the final extract was analyzed by large volume splitless injection with Concurrent Solvent Recondensation gas chromatography - high resolution mass spectrometry. Aimed to meet the potential regulatory requirements in Ontario, the method was able to analyze low level concentration of 1,4-dioxane in drinking and ground water in the calibration range 0.02 – 3.0 µg/L. The method detection limit was 0.009 µg/L. At 0.1 µg/L, method repeatability and reproducibility was 3.2% and 4.7% RSD, respectively and expanded uncertainty was 11%. In an inter-laboratory study (Sigma-Aldrich RTC) the method achieved z-score of -0.06 and 0.15 on two separate test samples; where z-score < |2| is considered to be in control. Pilot study with fifty ground water samples collected from various Southern Ontario sites was also performed.

SPE in US EPA Method 625, the Performance of Smaller Samples

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US EPA method 625 is a general semivolatile method for wastewater analysis applied to a large suite of target analytes. Although method 625 was developed a number of years ago, through the EPA Office of Water, Office of Science and Technology, the method has been updated several times and a new revision has been released with the Method Update Rule, proposed in February 2015. As new technology is developed either for the determinative measurement or, earlier in the analysis process, for the sample preparation, data must be collected to demonstrate that the new technology is compliant and reproducible.

This study focusses on the use of 100-mL water samples, rather than larger samples often used to achieve the sensitivity needed for compliance results. The smaller samples may be faster to prepare and easier to handle, providing a number of benefits to the laboratory and client.

This paper will discuss the performance of SPE in general for method 625 and the specific performance of a disk used with a single pass of acidified water through it rather than a pass with basified water and a second pass with the same water, now acidified, which is typical for liquid-liquid extraction. Recoveries of a large suite of compounds from a variety of matrices and laboratories will be examined and the effect of surrogates will be considered. The implications of larger and smaller sample volumes for overall costs, analytical performance and handling will be discussed.

Determination of Haloacetic Acids in Drinking Water by Ion Chromatography

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Disinfection byproducts (DBPs) are a class of compounds formed through reaction of organic matter with disinfectants in the treatment process for municipal drinking water. These compounds include haloacetic acids (HAAs) that are produced during chlorination of water containing natural organic matter. Haloacetic acids are known carcinogens that have been regulated for many years. Of the nine HAAs commonly found, only the most prevalent five haloacetic acids (HAA5) are monitored. US EPA Methods 552.1, 552.2 and 552.3 used to determine HAAs require derivatization and multiple extraction steps followed by gas chromatography (GC) with electron capture detection (ECD) and mass spectrometry (MS). This presentation will describe the use of ion chromatography coupled to mass spectrometry to quantitate HAAs at low µg/L concentrations, which offers a sensitive and selective alternative that does not require sample pretreatment. Water samples are directly injected into an ion chromatograph coupled to a triple quadrupole mass spectrometer. The separation of all nine HAAs addressed in EPA methods is achieved on the IonPac AS24 anion-exchange column using a hydroxide eluent under gradient conditions. The unique selectivity of this column allows separation of these analytes from common inorganic matrix ions, so that chloride, sulfate, nitrate and bicarbonate can be diverted to waste during the analytical run and thus avoiding contamination of the ESI–MS/MS instrument. Excellent peak resolution and linearity are achieved between 0.4 µg/L and at least 20 µg/L in a high electrolyte matrix. Four isotope-labelled internal standards have been studied and the current regulatory levels (MRLs) of 1 and 2 µg/L for HAA5 are easily achieved. Similar sensitivity is observed for HAA9 targets. Recoveries of all nine HAAs are greater than 90% in a simulated matrix.

As an alternative, the use of a heart cutting technique is described to quantitate HAAs at low µg/L concentrations. In the first channel, a standard bore column is used to separate matrix components from HAAs, which are then transferred to a concentrator column. The captured HAAs are then separated on a capillary column with different selectivity in the second channel. The use of columns with different internal diameters yields enhanced sensitivity and the different selectivity of the columns reduces the potential for inaccurate reporting due to coelution. Both methods requires low temperature separation (15 °C), necessitating the use of an IC system capable of maintaining subambient temperature within narrow limits. With this direct injection method, recoveries for HAAs ranged from 80–120% and the lowest concentration minimum reporting levels (LCMRL) were sub-µg/L, levels that are comparable to those obtained using IC coupled to tandem mass spectrometry mentioned above.

The use of plasma and integrated OMICs approaches for Environmental Toxicology

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Introduction:

OMICs methods can be used to assess the health of animals, to determine protein biomarkers that are specific to environmental exposures, and also to characterize unique mechanisms of action by contaminants. Plasma offers many unique advantages: it provides a snapshot of whole organism health, sample preparation is easy, and there is potential for non-lethal sampling methods.

Methods:

A highly cost effective and efficient method for analyzing the plasma proteome using formic acid protein digestion and liquid chromatography mass spectrometry was developed. Non-targeted proteomic and targeted metabolomics analyses were performed on plasma sampled from fish in 2 studies: (1) rainbow trout exposed to a flame retardant in the laboratory and (2) goldfish exposed to pharmaceutical drugs in the field.

Results:

There was a dose-response relationship for proteins and metabolites in rainbow trout exposed to the flame retardant. The expression of several proteins and metabolites were significantly altered in the plasma of goldfish which corresponded to site-specific alterations in behavior and levels of plasma contaminants.

Novel Aspect:

Together these integrated OMICs approaches provide powerful insight into the molecular effects of environmental contaminant exposures.

Risk Assessment of Smoke Exposure of Firefighters in the 2016 Fort McMurray Wildfire using GC-MS

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The Fort McMurray Wildfire made international headlines last May 2016, after spreading across 590,000 ha of forested, oil sand, and residential areas in northeastern Alberta. This expansive fire resulted in wide spread release of smoke, exposing firefighters, residents and rescue volunteers to high levels of toxic compounds, including polycyclic aromatic hydrocarbons (PAHs). Herein, a risk assessment study of a cohort of wildland firefighters involved in the Fort McMurray Wildfire was performed based on measurements from random single-spot urine samples collected following deployment. A urinary metabolite of pyrene, 1-hydroxypyrene, was measured in human urine, using on an optimized protocol involving enzyme deconjugation, solid-phase extraction and

chemical derivatization. Analysis of the extracts was performed using a gas chromatography-quadrupole-time of flight (GC-Q-TOF) mass spectrometry, equipped with an atmospheric pressure chemical ionization (APCI) source. Precision and accuracy for reliable measurements of trace levels of deconjugated 1-hydroxypyrene were evaluated in human urine samples when using a stable isotope-recovery standard and an inter-method comparison study. The method outlined here was shown to have a limit of detection of (LOD) of 1-hydroxypyrene equal to 16 ng/L and a limit of quantification (LOQ) of 54 ng/L. Due to the potential adverse health impacts of chronic exposure to toxic chemicals in smoke, this study will enable a risk assessment of deployed firefighters in the Fort McMurray Wildfire as compared to occupational health guidelines.

A (non)targeted method for analysis of the serum exposome using atmospheric pressure gas chromatography-mass spectrometry

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Abstract

Environmental risk factors, such as diet, obesity, smoking and exposure to environmental toxicants, may contribute more than genetic factors to the risks of cancer and other non-communicable diseases.[1,2] The *exposome*[3] represents all environmental exposures during the course of a lifetime. Persistent organic pollutants (POPs) represent an important subset of environmental toxicants that exhibit common characteristics, such as persistence, toxicity and a tendency to (bio)accumulate in wildlife and humans. This contribution reports on a sensitive, quantitative and high-throughput method for the analysis of a signature list of legacy and emerging halogenated POPs in 0.5 mL of serum. The method employs stir-bar sorptive extraction (SBSE), which enables preparation of >20 samples in four hours. Detection is achieved using thermal desorption gas chromatography (GC) coupled to a quadrupole time-of-flight mass spectrometer (qTOF-MS). Sensitivity is enhanced by atmospheric pressure chemical ionization (APCI), a soft ionization technique that minimizes fragmentation and maximizes the yield of target molecular ions. Experiments performed with standard reference materials (SRM 1957, non-fortified serum) showed good agreement with certified values. Method detection limits were constrained by background levels, in line with traditional methods.

The identities of most environmental toxicants and their roles in causing chronic diseases are not known. The full scan data acquired using the qTOF represents a trove of data that can be retrospectively searched for as yet unidentified toxicants. A semi-automated approach will be described that highlights unknown POPs on the basis of their position in *compositional space*, as defined by accurate mass and isotope ratio measurements.

References

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Orthogonal Gas Phase Separation and Identification of Protomers

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:Direct Analysis of Naphthenic Acids and Microcystins in Complex Samples using Membrane Introduction Mass Spectrometry

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Recent work in our group has employed the use of semi-permeable membranes to directly measure trace organic compounds of emerging concern in complex heterogeneous samples. The approach uses a hollow capillary polydimethylsiloxane membrane probe, which can be immersed directly into an aqueous sample. A solvent (methanol) flowing through the core of the immersion probe acts as an acceptor phase transporting permeating molecules to an atmospheric pressure ionization source (typically electrospray), where they are resolved by a triple quadrupole mass spectrometer without sample work up or chromatography. This presentation will report on the direct analysis of naphthenic acids in natural waters in negative ion mode as $[M-H]^-$ using an internal standard in the acceptor phase to monitor ionization efficiency and standard addition to the sample for quantitation. We also include a recent application to rapidly screen for microcystins associated with harmful algal blooms by directly measuring 2-methyl-3-methoxy-4-phenyl butanoic acid (MMPB) in post-oxidation mixtures, by tandem mass spectrometry (*m/z* 207 → 131).

A high throughput targeted and non-targeted method for the analysis of microcystins and anatoxin-A using on-line SPE coupled to LC-QToF MS

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