

DIVISION OF ENVIRONMENTAL CHEMISTRY

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SUNDAY MORNING

Advances in Analytical Chemistry for Environmental Applications

T. Jones-Lepp, *Organizer*

D. Alvarez, *Organizer, Presiding*

8:30 — Introductory Remarks.

8:45 —1. Analytical methods for contaminants of emerging concern. **B. C. Englert**

9:20 —2. Innovative sampling techniques to determine contaminant flux in Las Vegas Bay. **D. Alvarez**, M. Rosen

9:40 —3. Chromatographic considerations for analysis of glucuronide and sulfate metabolites of pharmaceuticals in environmental samples. **M. J. M. Wells**, M. Sunkara

10:00 — Intermission.

10:20 —4. Development of a comprehensive LC/MS/MS method for the detection of cocaine and other illicit drugs in municipal wastewater. **K. J. Bisceglia**, A. L. Roberts, K. A. Lippa

10:40 —5. Exploring the non-target analyte screening capabilities of high resolution mass spectrometry for natural water samples. **H. P. Singer**, P. Longree, S. Kern, K. Fenner, J. Hollender

11:00 —6. API and ESI LC-MS: The enabling technology for determination of emerging contaminants in environmental samples. **M. S. Young**, J. C. Shia, D. M. Diehl

11:20 —7. Characterizing the influence of environmental variables on the use of passive polar organic chemical integrative samplers (POCIS) for monitoring applications in the Great Lakes. H. Li, **P. Helm**, C. D. Metcalfe

ABSTRACTS

ENVR 1

Analytical methods for contaminants of emerging concern

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Contaminants of emerging concern (CECs), have been the subject of many recently published insightful literature reviews and publications covering general topic knowledge, environmental data and analytical methods. Since some of the earliest initial literature reports, occurrences of a variety of CECs have been reported in various types of water samples. The focus of this talk is to discuss some of the current gaps in the analysis of emerging contaminants. Most importantly, what are desired detection limits? What are the most effective extraction and cleanup techniques? What are most important compounds and reliable analytical techniques that can be used to accurately identify and measure these compounds at environmentally relevant concentrations in surface waters and challenging matrices, such as sewage? In addition to discussing the above gaps, there will also be brief discussion of some of EPA's current activities in regards to holding-time studies. These compounds also have a wide range of different chemical properties. What are effective holding times and preservation techniques? How extensively are these properties being studied and what approaches should be used to collect and preserve samples? This talk will also briefly discuss some of the difficulties encountered in this type of analysis. In some cases, these compounds are very different from the organic pollutants traditionally monitored in water, and present new analytical challenges. Some compounds are very polar while others are hydrophobic. They have many different properties due to the multiple types of functional groups they contain when compared to some conventional pollutants containing only halogens or other hetero-atoms. There is a constant need for new analytical methods that accurately measure the multitude of new contaminants of emerging concern.

ENVR 2

Innovative sampling techniques to determine contaminant flux in Las Vegas Bay

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Treated wastewater effluent from Las Vegas, Nevada and surrounding communities flows through Las Vegas Wash into Lake Mead at Las Vegas Bay (LVB). Lake sediment is a likely sink for many organic wastewater contaminants (OWCs); however, partitioning between the sediment and the overlying water could result in the sediment acting as a secondary contaminant source. Passive sampling devices (semipermeable

membrane devices-SPMDs and polar organic chemical integrative samplers-POCIS) were placed in LVB between June and July of 2008 to determine the vertical gradient of OWCs in the water column and potential contribution of OWCs from the sediment. A custom deployment housing was used to bury the SPMDs and POCIS in the sediment at depths of 0-10, 10-20, and 20-30 cm. SPMDs and POCIS were also suspended in the water column at depths of 3.0, 4.9, and 6.7 (lake bottom) meters.

ENVR 3

Chromatographic considerations for analysis of glucuronide and sulfate metabolites of pharmaceuticals in environmental samples

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The pharmaceutical agent, acetaminophen (paracetamol, Tylenol®), and its glucuronide and sulfate, were used as a model system for analytical method development for Phase II metabolites. Wastewater (influent and effluent) was extracted by solid-phase extraction (SPE) and analyzed using high-performance liquid chromatography with tandem mass spectrometry (LC/MS/MS). This presentation focuses on optimization of the chromatographic extraction and separation processes. Fundamental physical/chemical properties of the analytes are discussed relative to their chromatography. The applicability of hydrophobicity/ionogenicity (D_{OW}) to understanding reversed-phase chromatographic retention of ionizable compounds and the Donnan salt-exclusion effect as applied to reversed-phase chromatographic retention will be presented.

ENVR 4

Development of a comprehensive LC/MS/MS method for the detection of cocaine and other illicit drugs in municipal wastewater

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We have developed an isotopic dilution SPE-RPLC/MS/MS method for the analysis of 23 illicit drugs, drug metabolites, and human use markers in municipal wastewater. We placed particular emphasis on cocaine, and include eleven of its principal metabolites to maximize our ability to accurately quantify cocaine consumption, and to determine routes of ingestion. This method, which includes a confirmatory LC separation, displays good reproducibility in the analysis of untreated municipal sewage, and is sufficiently sensitive to directly quantify several analytes without pre-concentration. We have also developed a streamlined analysis procedure that collapses cocaine and its metabolites into two hydrolysis products. These products can be directly quantified using NPLC(HILIC)/MS/MS without SPE. This enables shorter chromatographic run times, and reduces uncertainty in sewage-derived estimates of cocaine usage by eliminating the need for assumptions regarding the influence of human metabolism and sewer conditions on metabolite distribution – a principal weakness in current monitoring techniques.

ENVR 5

Exploring the non-target analyte screening capabilities of high resolution mass spectrometry for natural water samples

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As the discovery of new emerging contaminants in the aquatic environment based on consumption data and fate assessment is often very time consuming, we tested the possibility to obtain data about relevant water contaminants directly from high resolution mass spectrometric measurements of natural water samples. For this non-target analyte screening we performed measurements with an LTQ-Orbitrap running in full scan acquisition mode at a resolving power of 60000 supplemented with data-dependent MSMS experiments. Before MS detection, enriched water samples were separated with liquid chromatography. For the identification of non-target analytes a multi-stage filtering procedure for the MS data was tested. The procedure consists of a compound detection by accurate mass screening followed by an elemental formula fit and a data bank search for the proposition of potential chemical structures. We will show the opportunities and limitations of such an approach, based on three illustrative examples of newly detected compounds.

ENVR 6

API and ESI LC-MS: The enabling technology for determination of emerging contaminants in environmental samples

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With the development of modern GC-MS in the 1970's, many pollutant analytes could be determined at heretofore unheard of sensitivity and specificity. Perhaps as significant as this enabling development was the development of atmospheric ionization and electrospray ionization mass spectrometry coupled with liquid chromatography. Since the introduction of these techniques in the early 90's, analysis of pharmaceutical and other non-volatile compounds has routinely been performed without tedious and hazardous derivatization. The preponderance of emerging contaminants are polar, non-volatile compounds well suited to LC-MS techniques. In this presentation we will present examples of emerging analytes that illustrate the powerful ability of modern LC-MS (particularly UHPLC) for determination of compounds that are difficult at best to analyze using GC-MS. Among the compounds discussed are veterinary drugs, perfluorinated compounds (such as PFOS) and quaternary ammonium compounds (such as paraquat). Also, sample preparation techniques suitable for LC-MS determination of these compounds will be discussed.

ENVR 7

Characterizing the influence of environmental variables on the use of passive polar organic chemical integrative samplers (POCIS) for monitoring applications in the Great Lakes

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Passive sampling of environmental contaminants has become an accepted monitoring approach. The use of the POCIS, developed by the USGS, is gaining in popularity. To support monitoring programs, laboratory and field studies were undertaken to evaluate environmental variables such as temperature and flow on the uptake of selected pharmaceuticals and personal care products into the POCIS. Sampling rates (Rs) of selected analytes at water temperatures of 5, 15, and 25°C were determined in static tests with results varying from 0.07 to 2.5 L/day. Field studies under controlled flow conditions were also used to evaluate impacts of flowrates past the samplers. Water temperature and flow did impact accumulation rates in the samplers, but these effects were relatively small, consistent with theoretical considerations. These sampling rate values were applied to Great Lakes monitoring studies in nearshore areas. Further work includes the exploration of sampling rates with physical chemical properties of analytes.