

AQRP Monthly Technical Report

PROJECT TITLE	Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ	PROJECT #	14-029
PROJECT PARTICIPANTS	Rebecca J. Sheesley Sascha Usenko	DATE SUBMITTED	12/8/2014
REPORTING PERIOD	From: November 1, 2014 To: November 30, 2014	REPORT #	4

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

In November 2014, we continued to progress on the chemical analysis of filter samples collected during DISCOVER-AQ. The organic tracer method was demonstrated on four filters collected at Moody Tower and three filters collected at Manvel Croix (Figures 1 and 2). The purpose of this small batch analysis was to provide preliminary ambient concentrations of organic tracers and contaminants prior to batch analysis of the four DISCOVER-AQ site filters. The manuscript-in-preparation for this method development is expected to be submitted in December 2014. A second manuscript has been started to assess carbon characterization across the four Houston sites during DISCOVER-AQ (organic, elemental and water-soluble carbon). Filters collected at Conroe have been cut and packaged for shipment to DRI for inorganic ion analysis in December 2014 (costs included in UT-A 14-024). To improve carbon capture efficiency for radiocarbon analysis of particulate matter collected during DISCOVER-AQ, method development on the Sunset Labs carbon analyzer was accomplished during November. Finally, preparation of two posters which parallel manuscripts-in-preparation (organic tracer method and carbon characterization) was accomplished.

Preliminary Analysis

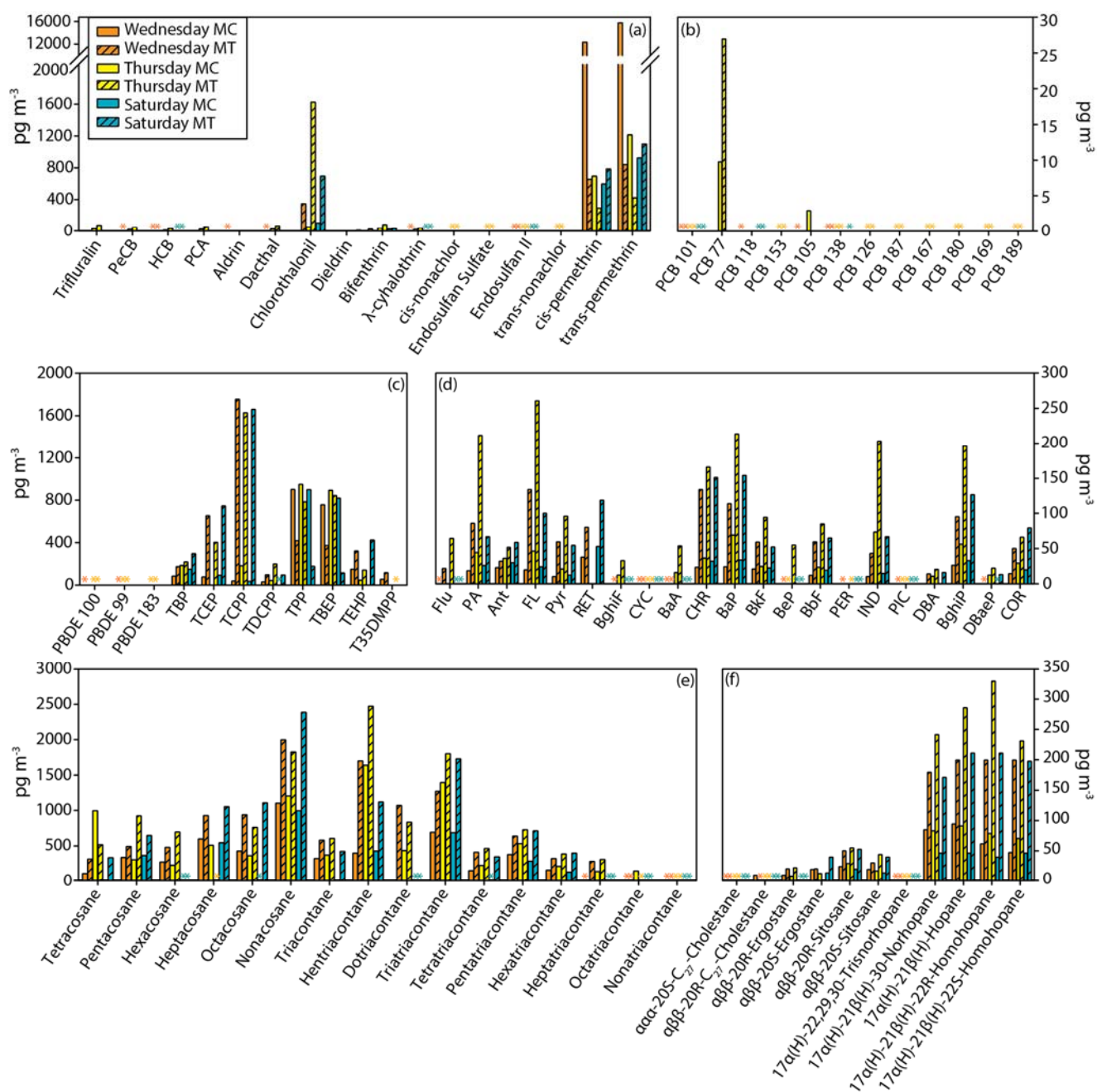


Fig 1. Organic tracers detected in the environmental samples included (a) CUPS, HUPS, (b) PCBs, (c) PAHs, (d) current and historic-use flame retardants (OPEs and PBDEs), (e) alkanes, and (f) hopanes and steranes. Orange bars indicate Wednesday samples, yellow bars indicate Thursday samples, and green bars indicate Saturday samples. The Manvel Croix (MC; suburban area south of Houston, TX) location is indicated by solid bars, while the Moody Tower (MT; downtown Houston, TX) location is indicated by striped bars. * indicate that compounds were detected below MDLs and color indicates day of the week. 85 of the 123 target analytes in Table 1 were detected.

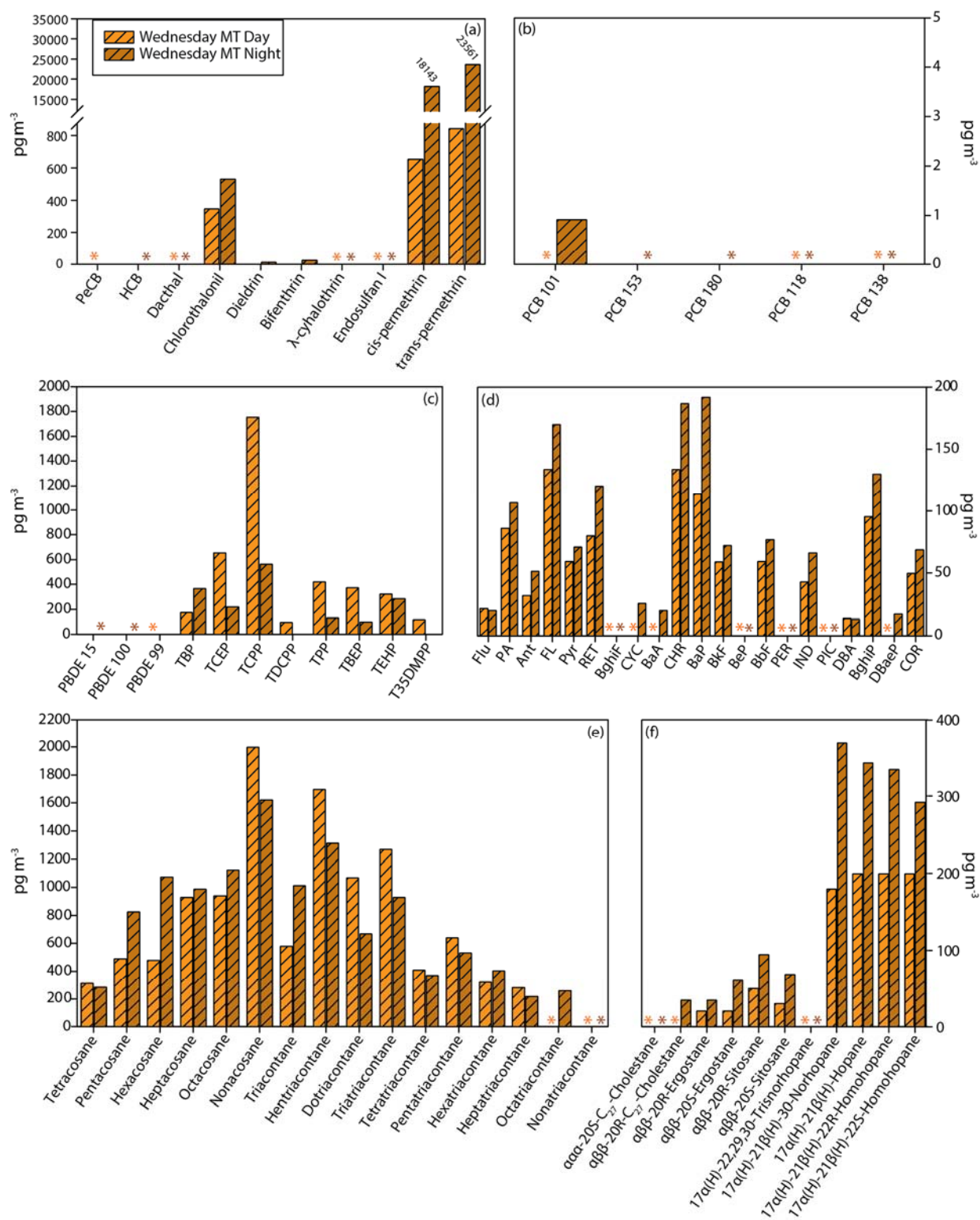


Fig 2. Organic tracers detected in the environmental samples included (a) CUPS, HUPS, (b) PCBs, (c) PAHs, (d) current and historic-use flame retardants (OPEs and PBDEs), (e) alkanes, and (f) hopanes and steranes. Light orange bars indicate Wednesday Day samples, while dark orange indicate Wednesday night samples. Both day and night samples were taken from the Moody Tower (MT; downtown Houston, TX) location, as indicated by striped bars. * indicate that compounds were detected below MDLs and color indicates day or night. OPEs were 3 – 4 times higher during the day, with the exception of TBP and TEHP while hopanes were approximately twice as high at night.

A Pressurized Liquid Extraction Technique for the Analysis of Pesticides, PCBs, PBDEs, OPEs, PAHs, Alkanes, Hopanes, and Steranes from Atmospheric Particulate Matter

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Abstract

An analytical method has been developed for the pressurized liquid extraction (PLE) of a wide range of semi-volatile organic compounds (SVOCs) from atmospheric particulate matter. Approximately 120 SVOCs from eight different compound classes were selected as molecular markers of 1) agricultural activity (30 current and historic-use pesticides), 2) industrial activity (18 polychlorinated biphenyls, PCBs), 3) consumer products and building materials (16 polycyclic aromatic hydrocarbons, PAHs), 4) incomplete combustion, specifically, motor vehicle exhaust (22 polycyclic aromatic hydrocarbons, PAHs, 16 alkanes, 4 hopanes, and 4 steranes). Currently, there is no analytical method capable of the extraction of all six compound classes in a single automated technique. Building on the work of Prims et al. (2008) and Sheesley et al. (2004), a single automated extraction using PLE and methylene chloride and acetone has been developed. The extraction efficiencies of varying solvents (methylene chloride, methanol, acetone) and solvent combinations (1:1 to 5:1) at high temperatures (100 and 120 °C) and pressures (1500 psi) were examined. Prior to extraction, quartz fiber filters (QFF) samples were spiked with known amounts of target analyte standards and/or isotopically-labeled surrogate standards. Target analytes were surrogate recovery corrected to account for analyte loss during sample preparation. Extracts were concentrated, spiked with known amounts of isotopically-labeled internal standards, and analyzed by gas chromatography coupled with mass spectrometry utilizing electron ionization and electron capture negative ionization. The optimized PLE method utilized methylene chloride:acetone (2:1) at 100 °C, three 5 min static cycles, flush volume of 80%, and a 100 x 102 cupge. Spike and recovery experiments (n=7) provided average percent recoveries for current and historical-use pesticides, PCBs, PBDEs, OPEs, PAHs, alkanes, and hopanes and steranes of 69.8 ± 4.4, 85.9 ± 2.6, 93.8 ± 2.9, 101 ± 6, 90.3 ± 6.1%, 74.4 ± 8.9%, 95.0 ± 8.4%, respectively. Method detection limits ranged from 0.5 to 66 ppb, with the exception of the alkanes which ranged from 47 to 610 ppb. The developed method was applied to atmospheric particulate matter samples from the greater Waco, TX metropolitan area, in which, 85 SVOCs were detected from eight compound classes, with ambient concentrations reported in pg m⁻³.

Introduction

- In 1996, with the introduction of pressurized liquid extraction (PLE), extractions became faster (~20 minutes/sample) and more environmentally friendly (95% less solvent).^{1,3}
 - PLE efficiency can be manipulated using parameters, such as solvent(s), temperature and static cycle length/number⁴.
- Atmospheric particulate matter (PM) concentrations of semi-volatile organic compounds (SVOCs), including current and historic-use pesticides (CUPs and HUPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), hopanes and polybrominated diphenyl ethers (PBDEs), are often determined by measuring the mass of contaminants on quartz fiber filters (QFF).⁵
- Due to the valuable, irreplaceable nature of air samples, it is important to maximize the information obtained per analysis while minimizing the amount of sample used, allowing greater opportunities for future studies.
- Several methodologies exist for the extraction of CUPs, HUPs, PCBs, PAHs, alkanes, hopanes and steranes, and PBDEs from PM on QFF utilizing both Soxhlet and PLE techniques.
 - Sheesley et al. (2004) uses a Soxhlet extraction of dichloromethane (DCM) and methanol (MeOH) for the extraction of PAHs, alkanes, hopanes, and steranes from QFF.⁶
 - Prims et al. (2008) utilizes hexane (HEX) and acetone (ACE) in a PLE to extract PCBs, HUPs and PAHs from quartz fiber filters.⁷
- Currently, there is no PLE methodology capable of extracting of PBDEs, PCBs, PAHs, CUPs, HUPs, OPEs, alkanes, and hopanes and steranes from PM.

Objectives

- Utilize the high-throughput capabilities of the PLE system to develop a method capable of measuring 16 PBDEs, 11 OPEs, 18 PCBs, 22 PAHs, 30 CUPs and HUPs, 16 alkanes, and 4 hopanes and steranes, from atmospheric PM collected on QFF.
- Utilize existing methods as the foundation and starting point for this line of research.
- Examine different combinations of solvents and temperatures using spike and recovery experiments.
- Reduce extraction solvent volumes by reducing extraction cell flush volumes.
- Validate the method using reproducibility studies, SRMs, and environmental samples.

Target Analytes

Pesticides and degradation products	PAHs, alkanes, hopanes, and steranes
• a, b, γ, and o'-HCH	• cis-Permethrin
• Heptachlor	• trans-Permethrin*
• Aldrin	• Bifenthrin
• Heptachlor Epoxide	• Deltamethrin
• Trans-chlorfene	• Cyfluthrin
• cis-chlordane	• Chlorfenthrin
• Endosulfan I and II*	• Dacthal
• Endosulfan Sulfate	• HCB
• Trans-nonachlor	• PCB
• cis-nonachlor	• PCB
• Dieldrin	• PCA
• Endrin	• Trifluralin
• Endrin Aldehyde	• Mirex
• Endrin Ketone	

PCBs

• PCB 77*	• PCB 118	• PCB 157	• PCB 158
• PCB 81	• PCB 123	• PCB 167	• PCB 187
• PCB 101	• PCB 129*	• PCB 169*	• PCB 189
• PCB 105	• PCB 138	• PCB 180	• PCB 190
• PCB 110	• PCB 153	• PCB 187	• PCB 195
• PCB 114	• PCB 156	• PCB 193	

Flame Retardants (PBDEs & OPEs)

• PBDE 15	• PBDE 75	• PBDE 155	• TDCPP
• PBDE 17	• PBDE 85	• PBDE 183	• TBP
• PBDE 28	• PBDE 99	• PBDE 207	• TCEP
• PBDE 33	• PBDE 100	• PBDE 226	• TCEP
• PBDE 47	• PBDE 119	• PBDE 232	• TCEP
• PBDE 49	• PBDE 133	• PBDE 246	• TCEP
• PBDE 66	• PBDE 154	• PBDE 260	• TCEP
• PBDE 75	• PBDE 155	• PBDE 274	• TCEP

*Isotopically-labeled version was used as a surrogate. *Analyte was detected through non-target analysis

Extraction & Analysis

Aliquots of quartz fiber filters (QFF; 125 cm²) were spiked with known amounts of target analyte and isotopically-labeled surrogate solutions in the 34 mL ASE cell prior to extractions. Spiked filters were allowed to sit for 60 minutes. Spiked filters were extracted using a Thermo Scientific™ Dionex™ Accelerated Solvent Extractor (ASE) 350 (Fig. 1), which is common instrumentation for PLE, under the conditions outlined in Table 1. Extracts were concentrated to <200 µL under a gentle stream of nitrogen using a 35 °C water bath and then spiked with 10 µL of isotopically-labeled internal standards (IC₁₇, PCB-138 & d₁₂-benzo(e)pyrene). Extracts were analyzed using GC-ECNI-MS and GC-EI-MS. Average surrogate recoveries for the experiments in Table 1 are reported in Fig. 2. Target analyte recoveries are surrogate corrected and, therefore, not shown.

Fig. 1. Dionex ASE 350

Method Development Experiments & Results

Table 1. Summary of method development. Static Cycles (3), Static Time (5 min) and N₂ Purge (100 s).

Exp	Solvent Composition	Temp (°C)	Flush Vol	Exp	Solvent Composition	Temp (°C)	Flush Vol	Exp	Solvent Composition	Temp (°C)	Flush Vol
1	2:1 DCM:MeOH	100	120%	6	3:1 DCM:MeOH	120	120%	11	4:1 DCM:ACE	120	80%
2	3:1 DCM:MeOH	100	120%	7	4:1 DCM:MeOH	120	120%	12	2:1 DCM:ACE	120	80%
3	4:1 DCM:MeOH	100	120%	8	5:1 DCM:MeOH	120	120%	13	1:1 DCM:ACE	120	80%
4	5:1 DCM:MeOH	100	120%	9	3:1 DCM:MeOH	120	80%	14	4:1 DCM:ACE	100	80%
5	2:1 DCM:MeOH	120	120%	10	4:1 DCM:MeOH	120	80%	15	2:1 DCM:ACE	100	80%

A total of 15 experiments were conducted to find suitable methodology for the extraction of CUPs, HUPs, PCBs, PBDEs, OPEs, PAHs, alkanes, hopanes, and steranes from a single filter aliquot (Table 1). The average surrogate recoveries for each of these experiments are shown in Fig. 2.

- The final method is 2:1 DCM:ACE at 120 °C with 3 static cycles, each 5 min long, and 80% flush volume.
- Experiments 12 and 15 produced the only results that were statistically significant from all the remaining experiments, but were not statistically different from each other.
 - 100 °C was chosen to preserve the lifetime of consumables
- Markers represent the overall average surrogate recovery with the error bars representing standard deviation of all surrogate recoveries for triplicate (n=3) method development experiments.
 - Black markers represent experiments 1-8, which were varying ratios of DCM:MeOH with 120% flush volumes.
 - Red markers represent experiments 9 and 10, which were repeats of experiments 6 and 7 with a reduction in flush volume to attempt to alleviate volatility issues outlined below.
 - Blue markers represent experiments 11-15, where MeOH was replaced with ACE to attempt to alleviate solubility issues outlined below.
- Due to volatility and solubility issues with Trifluralin and HCB surrogates (and their corresponding target analytes), MeOH was replaced with ACE (Experiments 11-15) reducing overall blowdown time from 4 h to less than 1 h and improving overall analyte recoveries.
 - Statistically significant surrogate recovery averages occur in both experiments 12 and 15, and ultimately experiment 15 was chosen as the final methodology.

Fig. 2. Average surrogate recoveries for method optimization experiments. Experiment parameters (1-15) have been summarized in Table 1.

Reproducibility Studies (n=7)

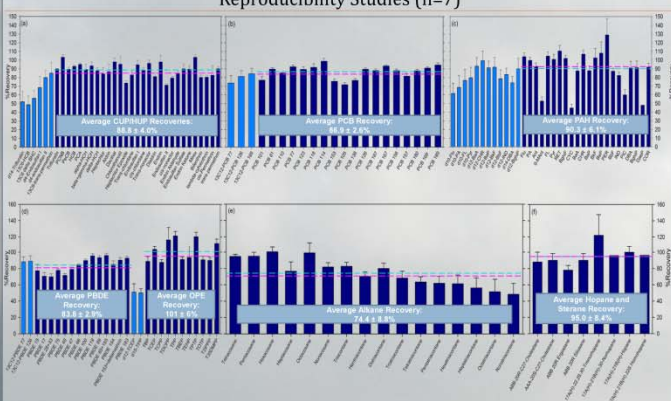


Fig. 3. The bars represent surrogate (light blue) and surrogate corrected target analyte (dark blue) recoveries of an n=7 reproducibility study for (a) CUPs and HUPs, (b) PCBs, (c) PAHs, (d) flame retardants (PBDEs and OPEs), (e) alkanes, and (f) hopanes and steranes. The lead dashed line represents the average target analyte recoveries of that study. The pink dashed line represents the average target analyte recovery for the secondary triplicate study. The differences between these averages were not statistically different.

Standard Reference Materials & Method Detection Limits

- ### Standard Reference Materials (SRMs)
- SRMs 1649b and 2585 were analyzed as part of method validation. Two separate masses of SRM 1649b were used to analyze for PCBs and CUPs, HUPs (50 mg), and PAHs, alkanes, and hopanes (10 mg). A mass of 75 mg of SRM 2585 were used to analyze for PBDEs.
 - Detected values were compared to reported certified, reference and informational values give in the certificates of analyze from NIST and were calculated as a percent error.
 - For PBDEs, average percent error was 26%.
 - For CUPs and HUPs, average percent error was 24%, while average percent error for PCBs was 19%.
 - For PAHs, average percent errors was 35%.
 - For alkanes, average percent error was 15%, while average percent error for hopanes was 64%.
 - Alkanes and hopanes values given in certificate of analyze were informational values.
- ### Method Detection Limit (MDLs)
- MDLs were determined using USEPA methods⁸ and ranged from 0.93 to 26.5 ppb for CUPs, HUPs, PCBs, PBDEs, OPEs, PAHs, 0.036 to 0.88 ppm for alkanes, and 11.9 to 54.0 ppb for hopanes and steranes.

Environmental Samples

The method was further validated using seven environmental samples, which represent the matrix of interest (atmospheric particulate matter), collected from two different sites during DISCOVER-AQ Houston in September 2013 (Fig. 4 and 6).

- Detects occurred in each compound class of interest, for a total of 88 of 123 target analytes detected.
 - Non-target analytes (αβ-205-Ergostane, αβ-205-Sitostane, and 17α(H)-21β(H)-22R-Homohopane) were also quantified.
 - 17α(H)-21β(H)-22S-Bishomohopane, 17α(H)-21β(H)-22R-Bishomohopane, and 17α(H)-21β(H)-22S-Trishomohopane, 17α(H)-21β(H)-22R-Trishomohopane were positively identified.

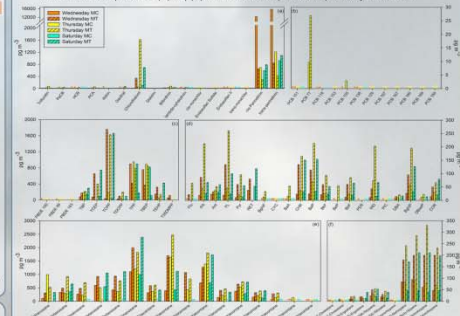


Fig. 4. Day Samples: Preliminary data from downtown Houston (MT) and ~20 km south (MC) showing detectable levels of (a) CUPs/HUPs, (b) PCBs, (c) PAHs, (d) flame retardants (PBDEs and OPEs), (e) alkanes, and (f) hopanes and steranes for Wednesday, Thursday, and Saturday. Stars (*) represent detects below MDLs.

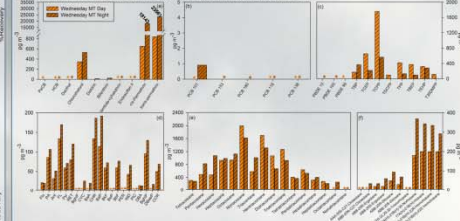


Fig. 5. Day and Night Samples: Preliminary data from downtown Houston (MT) showing detectable levels of (a) CUPs/HUPs, (b) PCBs, (c) PAHs, (d) flame retardants (PBDEs and OPEs), (e) alkanes, and (f) hopanes and steranes. Stars (*) represent detects below MDLs.

Conclusions

- Using PLE, DCM and ACE are capable of extracting CUPs, HUPs, PCBs, PAHs, PBDEs, OPEs, alkanes, hopanes and steranes.
- Final methodology: 2:1 DCM:ACE at 120 °C with 3 static cycles, each 5 minutes long and 80% flush volume, yielding overall average recoveries ranging from 74.4 – 101%.
- Increasing temperature (100 °C to 120 °C) did not significantly improve recoveries for most analytes.
- Reducing the flush volume from 120% to 80% reduced total concentration step time while providing comparable recoveries.
- The method was validated using two reproducibility studies (intraday), SRMs and environmental atmospheric PM samples.
- This method expands the number of classes examined (including emergent classes of concern; OPEs) in a single aliquot in order to more fully characterize atmospheric PM.

Acknowledgments

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References

- Schantz, M. M. Pressurized liquid extraction in environmental analysis. *Anal Bioanal Chem* 2006, 386 (6), 1043-7.
- Prims, T. et al. Solvent Selection for Pressurized Liquid Extraction of Polychlorinated Biphenyls and Organochlorine Pesticides. *Environ Sci and Chem* 2008, 27, 1267-1272.
- Mahe, L. M. L. Chromatographic analysis of the environment 3rd ed. CRC/Taylor & Francis Boca Raton, 2006, xiv, 1297 p.
- U.S. EPA. Office of Water. U.S. Environmental Protection Agency. <http://water.epa.gov/qa/qa303/303m.cfm>
- US EPA. Office of Water. U.S. Environmental Protection Agency. <http://water.epa.gov/qa/qa303/303m.cfm>
- US EPA. Office of Water. U.S. Environmental Protection Agency. <http://water.epa.gov/qa/qa303/303m.cfm>

Data Collected

- Preliminary data for 7 Houston PM samples from DISCOVER-AQ.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

NA

Goals and Anticipated Issues for the Succeeding Reporting Period

First organic tracer method manuscript will be submitted in December 2014. Manuscript preparation will continue on spatial and temporal characterization of bulk carbon.

Detailed Analysis of the Progress of the Task Order to Date

- Shared WSOC data for Conroe.
- Completed WSOC analysis for Conroe, Moody Tower, Manvel Croix and La Porte.
- Purchased and prepared standards for organic tracer analysis
- Began preliminary sample analysis for organic tracers and contaminants at Moody Tower and Manvel Croix.
- Validated method for organic tracers and contaminants using NIST SRMs 1649b and 2585.
- Preparation of posters for AGU
- Demonstrated organic tracer method using multiple days of Moody Tower and Manvel Croix particulate matter samples
- Method development to improve carbon capture efficiency on Sunset for radiocarbon sample preparation
- Near-final draft of organic tracer method paper completed
- Prepared filters for shipment to DRI for inorganic ion analysis
- Began manuscript preparation of carbon characterization across the four Houston sites during DISCOVER-AQ

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